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Real-time analysis of peak shape: a theoretical approach to sample controlled thermal analysis

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Abstract

This paper describes a theoretical framework, based on real-time analysis of the shape of thermoanalytical peaks, for two new approaches to sample controlled thermal analysis (SCTA). These new methods have the common aim of effecting changes in the heating rate at a given point in a process (i.e. at a set value of α) irrespective of the absolute magnitude of the peaks produced by that process. This permits the automatic on-line optimisation of the resolution/experiment time ratio without the need for preliminary experiments. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

In conventional thermal analysis the sample is heated using a pre-determined temperature programme typically comprising a linear heating ramp of between 1 and 20°C min^{-1}. Although simple to implement, this approach leads to temperature and pressure gradients within the sample which decrease resolution between adjacent thermal processes and produces uncertainty in kinetic measurements. A series of related methods, now given the generic name of sample controlled thermal analysis (SCTA),[1] has been developed to address the problems produced by linear heating. The unifying concept underlying all SCTA techniques is that the heating rate is altered as some function of the measured reaction rate to maximise resolution in terms of either the time, or the temperature, between adjacent events whilst minimising the experiment time [1].

Rouquerol [2,3] and the Pauliks [4,5] developed SCTA techniques based on evolved gas analysis and thermogravimetry, respectively, which are now widely referred to as constant rate thermal analysis (CRTA). In CRTA the aim, as the name of the technique suggests, is to maintain a thermally induced physiochemical process (e.g. mass loss, gas evolution, physical expansion, etc.) at a constant, pre-determined,

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[1] The proposal for the term 'SCTA' first arose in discussions between the authors and Dr. J. Rouquerol at the ESTAC 6 (Grado, 1994) and TAC96 (Leeds, 1996) conferences and was endorsed at the workshop on SCTA methods held at the 11th ICTAC, Philadelphia 1996.

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reaction rate. To achieve this the sample temperature is either increased or decreased as necessary with the result that the heating rate is generally low *through* a process and fast between processes. The CRTA has been demonstrated to achieve high resolution [6,7] and provide suitable conditions for kinetic measurements [8,9], especially when combined with the 'rate jump' method [10–12].

A more recently developed SCTA technique is the stepwise isothermal analysis (SIA) approach of Sorensen [13]. Here the heating rate is switched from a positive value to zero when the reaction rate exceeds a pre-set upper threshold and back to heating again when the rate falls below a pre-set lower threshold. Other SCTA approaches, which have been described in the literature, include 'Constrained Rate' (Reading [14]), 'Proportional Heating' (Parkes et al. [1]) and the 'Hi-Res' method of TA Instruments [15].

2. Pre-selected 'target' rates in current SCTA methods

A key feature of the above-mentioned techniques is that they utilise a pre-selected 'target' reaction rate and some simple relationship between the heating rate and the measured reaction rate (e.g. the sigmoidal relationship used in TA Instruments 'Hi-Res' method [16]). The difference between these target values and the *measured* rate of the process governs the changes in the heating rate. The choice for the value of the 'target' rate in CRTA is usually determined by the degree of resolution/accuracy of information required. Low 'target' rates produce the highest resolution and the most accurate kinetic information but at the expense of very long experiments. The major drawback of this approach is the difficulty in determining a *single* suitable target rate for complex processes having reactions rates that vary greatly in magnitude.

This can be explained by reference to schematic diagrams for two decomposition processes, A and B, each giving a peak, where it is planned to use the SCTA technique of CRTA to improve the resolution and obtain mechanistic information. It is assumed that the processes are being monitored using a techniques such as evolved gas analysis (EGA) or derivative thermogravimetry (DTG) which produce peaks, the magnitude of which is directly proportional to the reaction rate (i.e. dα/dt, where α is the extent of reaction, usually expressed on a scale of 0–1).

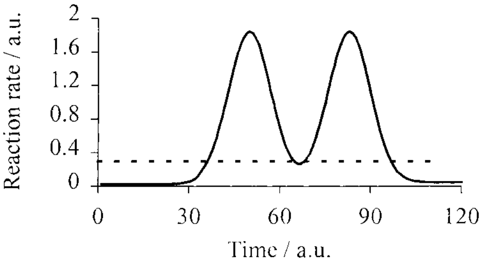

Fig. 1. Idealised schematic of a conventional linear heating thermal analysis experiment (EGA or DTG) producing two overlapping peaks of equal magnitude. The dotted line shows a 'target' rate that could be used for a subsequent CRTA experiment.

Fig. 1 shows a schematic representation of a decomposition process obtained under conventional linear heating which gives two such events of equal magnitude. It is possible to select a single 'target' reaction rate (such as that shown as a dotted line) for a subsequent CRTA experiment which would produce equal resolution for each of the two processes.

Fig. 2 shows a schematic representation of a decomposition process which produces two events (peaks) of *different* magnitude. In this case, it is impossible to select a single 'target' reaction rate for a subsequent CRTA experiment that would be appropriate for both events. A high 'target' reaction rate (dotted line U) suitable for the larger event would be too rapid to provide detailed information on the smaller event. Conversely, a lower 'target' reaction rate (dotted line L) that would be appropriate for the latter would be too

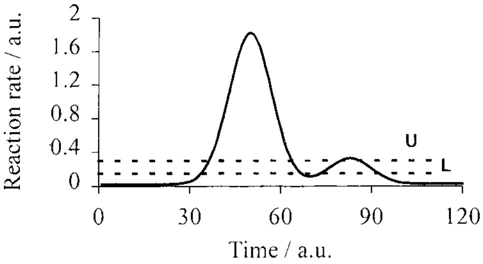

Fig. 2. Idealised schematic of a conventional linear heating thermal analysis experiment (EGA or DTG) producing two overlapping peaks of dissimilar magnitudes. The two dotted lines (H and L) demonstrate the difficulty in selecting a single 'target' rate for a subsequent CRTA experiment that would be suitable for both processes.

small for the larger event, resulting in a very long duration experiment.

3. Responsive 'peak shape' SCTA methods

An alternative SCTA method, developed by Barnes et al. [17,18] and Reading [16,19], utilises an approach where the heating rate is governed more directly by the *shape* of the DTG or EGA peak produced. This approach is aimed at overcoming the limitations of requiring a pre-selected 'target' rate by allowing the reaction itself to determine the heating regime. In this way, irrespective of the *absolute* magnitude of the peaks, the changes in heating rate will occur at the same *relative* position on each peak, i.e. at the same fraction of α.

The technique operates by real-time analysis of a peak and its derivatives, with the desired change in heating rate being triggered at a fixed percentage of the total reaction which produces the peak. Typically this involves switching from a heating period to an isothermal period, although other modifications in the heating/cooling rate are possible.

The simplest case is where the peak maximum ($d\alpha/dt$=max, $d^2\alpha/dt^2=0$) is detected, corresponding to $\alpha=0.5$ (assuming symmetrical Gaussian peaks). Note that in this case the change in heating rate triggered by detection of the peak maximum will always occur at the same *relative* value of α, regardless of the *absolute* magnitude of the peak. This approach has been shown to give improved resolution between peaks, in terms of time, with less loss in sensitivity than is the case with CRTA and SIA [1].

It is possible to extend this technique by using higher order derivatives and the relationships between these derivatives [16]. A schematic diagram of a Gaussian peak and higher orders of derivatives of α (with respect to time) is shown in Fig. 3. The first maximum of each derivative occurs at a lower value of α as the order increases, theoretically allowing the trigger in the heating rate to occur at earlier and earlier points into the process (Table 1). The total number of switching points, defined here as a maximum or minimum in the value of the derivative, also increases as the order increases and generates potential switching points at values of α ranging from 0.001 to 0.995. However, in practice, calculation of derivative orders higher than two would be increasingly difficult due to decreasing signal-to-noise ratios.

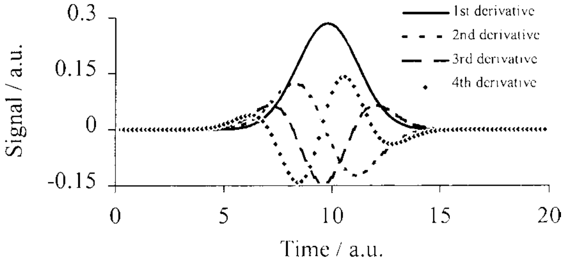

Fig. 3. Idealised EGA or DTG peak (first derivative of α w.r.t. time) and associated second to fourth order derivatives.

This approach to SCTA can be classified as 'responsive' in that it relies on detecting a point on the EGA peak (or one of its derivatives), independent of its magnitude, as it occurs.

4. Predictive 'peak-shape' SCTA methods

An alternative strategy, outlined below, can be classified as 'predictive' in that it attempts to determine a parameter, or set of parameters, that describe the shape of the entire peak from an analysis of its

Table 1
Value of α at the maxima and minima for a series of derivatives of an idealised EGA or DTG peak shown in Fig. 3

Derivative order	Value of α at consecutive peak maxima and minima				
	1st max.	1st min.	2nd max.	2nd min.	3rd max.
1 ($d\alpha/dt$)	0.500	–	–	–	–
2 ($d^2\alpha/dt^2$)	0.127	0.841	–	–	–
3 ($d^3\alpha/dt^3$)	0.032	0.443	0.942	–	–
4 ($d^4\alpha/dt^4$)	0.005	0.159	0.716	0.984	–
5 ($d^5\alpha/dt^5$)	0.001	0.044	0.388	0.873	0.995

initial stages. In this work a Gaussian peak shape is assumed as an approximation. The heating programme is then adjusted in some appropriate way to optimise the separation of this process from others that may partially overlap it. One approach would be to continuously calculate the ratio of the second and first derivative of α. For EGA, this is the ratio of the slope of the peak to the corresponding height of the peak, at time *t*.

Assuming an EGA or DTG peak can be described by a Gaussian function (Eq. (1)), its slope will be described by Eq. (2) and their ratio ($f'(x)/f(x)$) by Eq. (3)

$$f(x) = \left(\frac{1}{\sqrt{2\pi\sigma^2}}\right)\exp\left(-\frac{(x-\mu)^2}{\sigma}\right) \tag{1}$$

$$f'(x) = -\left(\frac{\sqrt{2}}{\sqrt{\pi\sigma^2}}\right)(x-\mu)\exp\left(-\frac{(x-\mu)^2}{\sigma}\right) \tag{2}$$

$$\frac{f'(x)}{f(x)} = -\left(\frac{2}{\sigma}\right)x + \left(\frac{2}{\sigma}\right)\mu \tag{3}$$

where μ is the mean; σ is the standard deviation.

Thus, a plot of Eq. (3) approximates to a straight line that gives the standard deviation (from the slope) and the mean (from the intercept) as illustrated in Fig. 4. It should, therefore, be possible to calculate these parameters from an on-line analysis of the early part of the peak and consequently to change the heating rate at a specified multiple or fraction of the standard deviation. Future advances might include the development of an algorithm defining how the heating rate should be changed as a function of standard deviation from the mean. Of course, most thermal analysis peaks are not usually Gaussian but one could derive similar types of analysis to that given above for skewed Gaussian peaks.

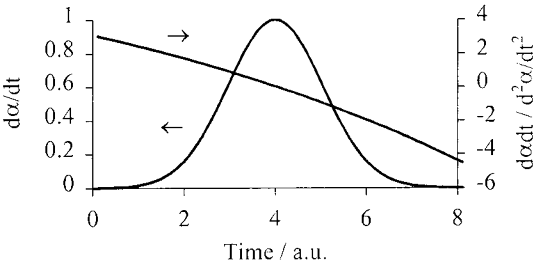

Fig. 4. Idealised EGA or DTG peak (dα/d*t*, solid line) and the ratio of this (dotted line) to its derivative $d^2\alpha/dt^2$.

An alternative would be to attempt some kind of kinetic fit to the curve. A simple procedure would be to assume first order kinetics thus giving the expression

$$\ln\left(\frac{p_h}{a_T}\right) = \ln\left(1-\frac{a_t}{a_T}\right) + \ln A - \frac{E}{RT} \tag{4}$$

where p_h is the peak height at time *t*; a_T the total area under the peak; a_t the measured area under the peak up to time *t*; *A* the pre-exponential constant; *T* the absolute temperature at time *t*; *E* is the activation energy and *R* is the gas constant.

The three unknown quantities are a_T (during the early part of the peak), *A* and *E*. There are various fitting routines that could be used to find these parameters from early data thus enabling the course of the peak to be approximately calculated and thus the fraction reacted (from a_T, the predicted quantity, and a_t, the measured quantity) without having to wait for the completion of the transformation. It would then be possible to change the heating rate as a function of fraction reacted. Where more complex functions than first order are allowed, fitting could still be used although, of course, more parameters to fit involves greater uncertainty in the result. However, where it is possible to use more complex functions of alpha, the strategy in terms of how the heating rate is changed with alpha could be varied with different reaction mechanisms. One approach to simplifying the task of fitting would be to employ a temperature modulation to calculate the activation energy directly [20]. This would then make the fitting problem trivial for a first order expression and greatly increase the certainty with which more complex alpha functions could be used.

The above two methods (i.e. responsive and predictive) are offered by way of illustration. Clearly there are a very large number of potential approaches, including using *reduced* temperature [13] instead of actual temperature, to determining the alpha function and then to find the activation energy from an Arrhenius plot. These different approaches share the common feature of attempting to characterise a reaction from its early behaviour and then impose a temperature regime that reacts to peak shape and not the absolute magnitude of the signal being used to measure the progress of the reaction.

5. Conclusions

The field of SCTA is rapidly growing as increasing numbers of workers realise its potential for higher resolution and greater insight into reaction mechanisms. The approaches outlined in this paper provide a powerful new set of temperature control strategies whose operation does not rely on the arbitrarily selection of a target rate, a drawback of many other SCTA techniques. Furthermore, the use of real-time analysis of the peak offers the potential for automatic optimisation of the resolution/experiment time ratio while reducing the dependency on experimental parameters such as sample mass. However, while we can envisage many different approaches to achieving this goal there is no current theoretical framework for the prediction of optimum strategies. We believe that the development of a proper theoretical basis for these strategies should be an important goal in the future development of SCTA.

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