PREDICTION CONFIDENCE FOR SMALL SCALE THERMAL TESTING OF MATERIALS

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Small scale tests such as DSC and Carius (10 g) tube are used to derive information on heat and gas output from possible decompositions, so are important tools for hazard assessment of materials, particularly for early screening of the behaviour of materials in development where only small quantities may be available for destructive testing. Such data may be used in the assessment of operations such as drying and distillation.

Some materials exhibit autocatalytic behaviour which is not dependent on scale, but only on time and temperature. By plotting reciprocal absolute temperature against logarithm of induction time it is possible to fit a line and extrapolate to lower temperatures. This shows how long material may be safely stored before thermal decomposition might be expected. The extrapolation is necessary because laboratory measurements of induction times can last for minutes, hours or even days, despite being at elevated temperatures, whereas at the temperatures of interest induction time will be weeks, months or even years – time scales which cannot reasonably be simulated in the laboratory. By using standard statistical methods the prediction interval can be plotted. This can be used to help judge appropriate safety factors for such extrapolations.

Time to Maximum Rate (TMR) is used to give a feel for the rate of a reaction runaway when it is not autocatalytic, and what type of emergency response is appropriate. This features two parameters (heat output and activation energy) which are derived from experiment, and both will have confidence intervals which should be factored into the final measure of TMR. Plotting the confidence and prediction intervals gives a better feel for the uncertainty in an estimate, particularly how it increases the further from the measured data, than just relying on the R^2 value as is common.

The paper also contains some examination of the repeatability of the experimental points used for the derivation, and the associated error in these measurements, and looks at how error is distributed at the various temperatures.

DEFINITION OF TIME TO MAXIMUM RATE.

One safety metric that is used for chemical reactions to classify the types of control required to avoid runaway reaction is the time to maximum rate under adiabatic conditions (Townsend and Tou, 1980).

TMR can be used as an indicator of the type of control systems that should be present (Dixon-Jackson, 2010):

i. For TMR greater than 24 hours rehearsed organizational controls and procedures can be suitable if the available measures can cope with the severity.
ii. For TMR between 8 and 24 hours automated control measures should be present to cope with deviations (this means that the decision is not left in the hands of a human who may be tempted to or pressurised into prioritising production until it is too late, and the process is beyond the point of no return).
iii. For TMR less than 8 hours – either the process should be changed, or venting must be present.

Another way of looking at this can be found in Ciba guidance (1993) where TMR is used to assess the probability of a problem having already assessed the reaction severity. Decomposition was considered to become critical when the TMR fell below 24 hours, with the range 8−24

hrs considered as medium probability and less than 8 hrs[1] as high probability.

TMR is can be estimated from the following equation:

$$TMR_{ad} = \frac{C_p R T_0^2}{\dot{q}(T_0) E_a}$$

The unknowns in this equation are E_a (activation energy for Arrhenius form kinetics) and $\dot{q}(T_0)$ (the peak power output at a given temperature). Generally these are determined by isothermal DSC experiments looking for the peak power output.

Heat release rate is assumed to be given by (see *Keller et al.*)

$$\dot{q} = k_\infty \exp\left(\frac{-E_a}{RT}\right) f(c)(-\Delta H_R)$$

Subject to some assumptions about constant conversion, zero order kinetics and other parameters remaining constant with temperature this can be linearised by a natural log conversion to

$$\ln \dot{q} = \ln k' - \frac{E_a}{RT}$$

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[1]8 hrs is assumed to be 1 shift

And hence plotting $\ln \dot{q}$ as a function of $\frac{1}{T}$ we get a line with a slope of $\frac{-E_a}{R}$. So from the regression for a line of the form $y = \hat{a} + \hat{\beta}x$ we can estimate heat release rate and activation energy.

To extrapolate for values of the heat release rate we use a prediction interval of the form (this is in many statistical books, for example Montgomery and Peck)

$$\hat{a} + \hat{\beta}x \pm t\sqrt{\frac{s^2(x_0) - \bar{x}}{s_{xx}} + \frac{1}{n} + 1}$$

See Figure 1 for an example of a plot showing the confidence intervals (parameters have all been calculated using 'R' statistical software). This shows the typical behaviour where the width is narrow in the middle of the experimental data and increases as we move away from the centre of mass. The confidence intervals are quite rightly much wider as we move (extrapolate) away from the known data. To support such extrapolations we should have a physical model and an understanding of what may change and violate the model outside our collected data.

This prediction interval includes terms for the variance, the number of experimental points and the t statistic, which takes account of the degrees of freedom derived from the number of experimental points and the number of parameters in the model. So as the number of points increases the width of the prediction interval should decrease. See Figure 2 for an example of the calculated prediction interval where only 3 points have been used for the regression (this figure is over the same range as Figure 1, and uses 3 of the 5 points used for Figure 1). This is further compared in Figure 3 where in an expanded area of the plot the regression for 5 points (red line – as shown in Figure 1) has been plotted with the prediction interval, and the regression from 3 of the points (as shown in Figure 2) is also plotted which is shown exceeding the 5 point prediction interval.

The variance is also included in the calculation of the prediction interval, and in a conventional least squares fit will be calculated from the points plotted. However, each of these points is not an absolute, but is an experimental estimate of a value and there is an associated uncertainty or error associated with each point. Strictly for least squares estimation the errors should be normally distributed, and of constant variance across the range.

Similarly the activation energy will also have an uncertainty associated with it and the appropriate form of the confidence interval for this is that for a slope which is of the form

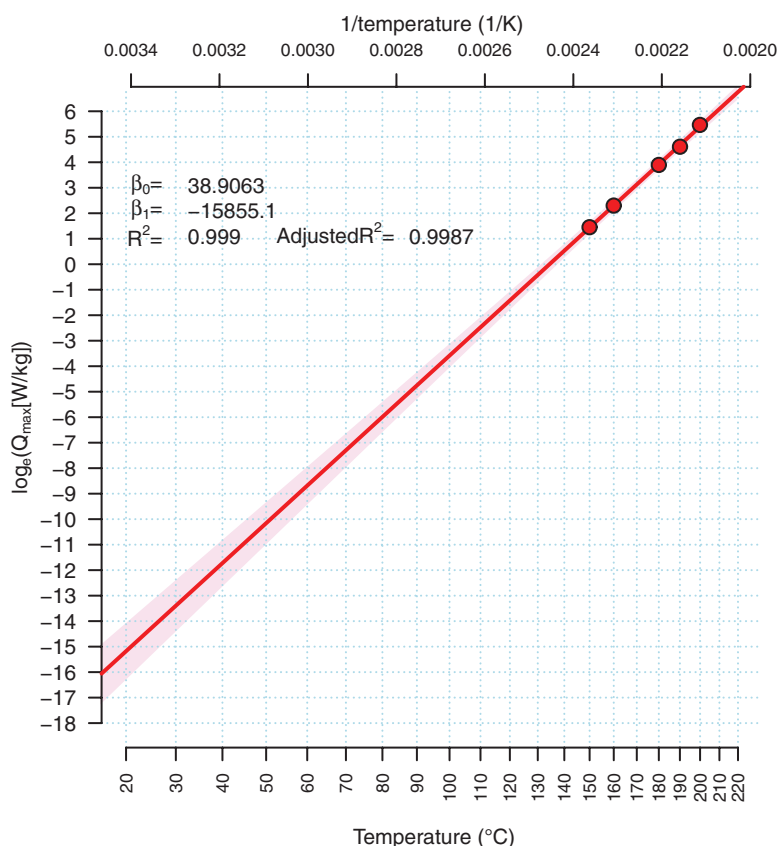$$\hat{\beta} \pm t \times standard\ error\ of\ slope$$

Figure 1. Predicting heat release vs temperature, showing 95% prediction interval
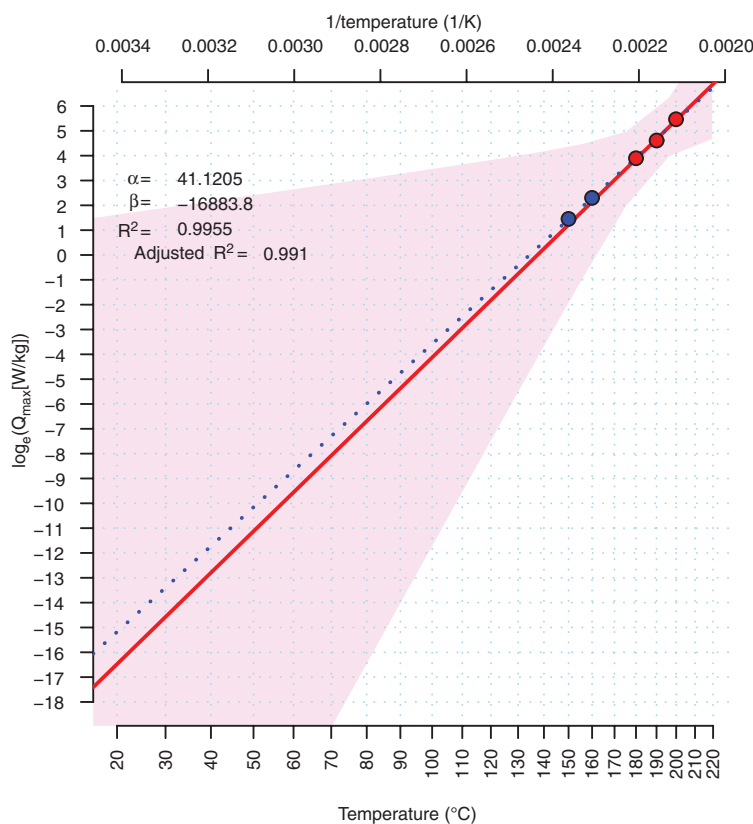
Figure 2. Prediction Interval (95% confidence) if only 3 points are used. Blue line shows prediction using all 5 points

For this particular example this gives us an estimated activation energy of $132\,kJ/mol \pm 7.7$. If we used only three points for our prediction this uncertainty would be much greater.

Putting the estimates of activation energy and heat release rate together with a heat capacity allows us to calculate TMR at various temperatures. Heat capacity generally increases with temperature, and can be difficult to determine on a system that decomposes, such as those we are necessarily interested in; it may be necessary to estimate suitable values. Using a smaller value such as from a lower temperature than the temperature of interest will err on the safely conservative side since this will lead to a lower value of calculated TMR.

TMR has been calculated across a range of temperatures and is shown in Figure 4. Uncertainty limits have been plotted on the graph too using the bands as calculated above, although the minimum or maximum values of each should not be combined, rather the maximum gradient (hence activation energy) matches with the minimums in predicted heat release rate and vice versa.

Some example values are 52 hrs at 110°C (range 33–83), 19 hrs at 120°C (range 12–29) and 7 hrs at 130°C (range 5–11 hrs). Alternatively this can be given as a range of temperatures for a given TMR so TMR (8 hr) is approximately 125–133°C or TMR (24 hr) is approximately
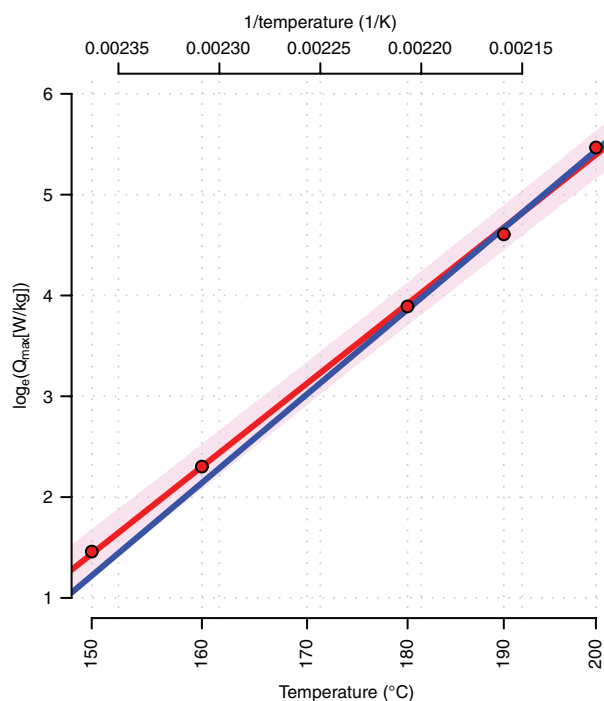

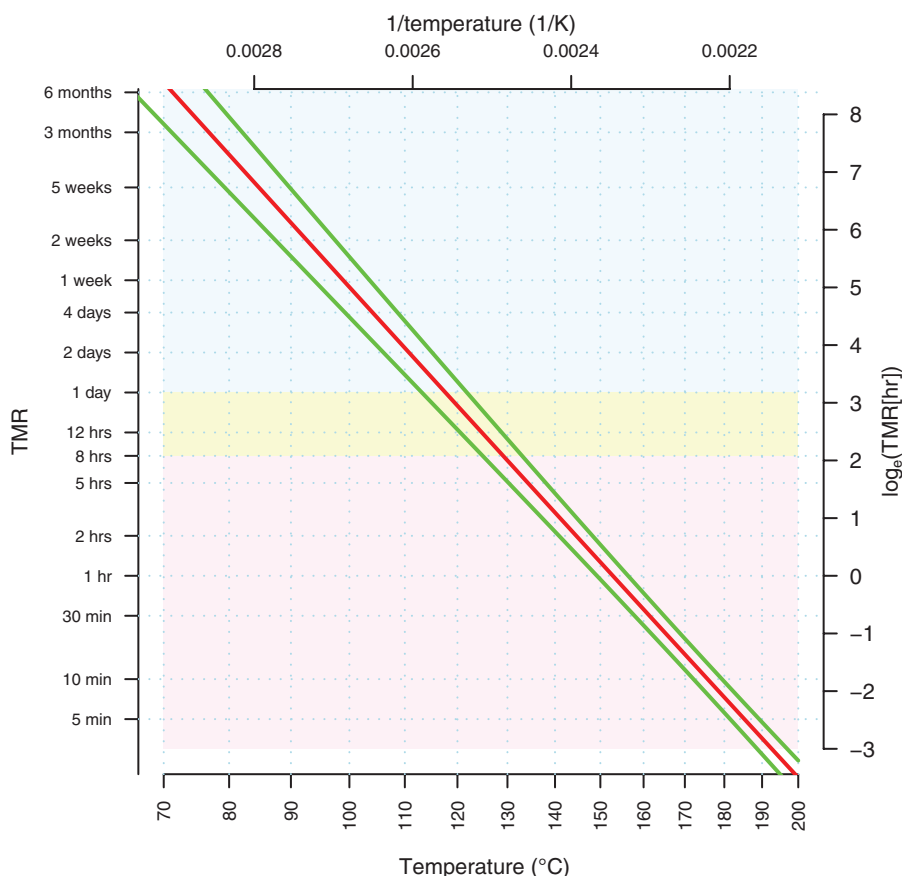**Figure 3.** Fit showing 3 point and 5 point predictions (and prediction intervals for 5 point line)

Figure 4. Predicted TMR across a range of temperatures with confidence intervals

113–122°C. With such ranges it is clearly inappropriate to give these values to any greater degree of precision.

DISCUSSION ON TMR

TMR gives the time to maximum rate assuming loss of control and as noted above there are approximate time bounds given to signify the appropriate type of control measures. It is not a precise measure, as is emphasised by the analysis above, so should not be quoted to inappropriate degrees of precision.

In using the number one important aspect can be missed which is this is the time to maximum rate, not a measure of how long one has to respond. Depending on the nature of the reaction, the amount of heat or gas released and the plant configuration maximum rate may be a tolerable event, or complete destruction of the plant may have occurred well before maximum rate is achieved. This measure looks at one facet of reaction runaway, and to appropriately design a process it is necessary to look at other facets too hence working with a more complete data set. For example it could be useful to use the concept of a point of no return which would take more account of the specific plant configuration and the ability to remove heat.

ONSET/INDUCTION TIME

For auto-catalytic reactions it is possible to measure induction time in small scale isothermal experiments. The natural logarithm of induction time is plotted as a function of the reciprocal of absolute temperature and a line fitted to the data to extrapolate to the temperature range of interest. Similarly to the analysis on TMR we can use a prediction interval and an example is shown in Figure 5.

VARIABILITY IN EXPERIMENTAL DATA

The examples shown have all used DSC data, specifically isothermal runs. No data for repeatability was available for isothermal DSC, but some repeatability data was available for ramped DSC testing (Arthur), and this can give a feel for the intrinsic variability in data points. Examples of maximum detected power are shown in Figure 6, and onset temperature in Figure 7. These plots are all fresh repeat runs for the same system.

CONCLUSIONS

By using some standard statistical methodologies it is possible to put some uncertainty bands around predicted data such that we do not get carried away with our precision.
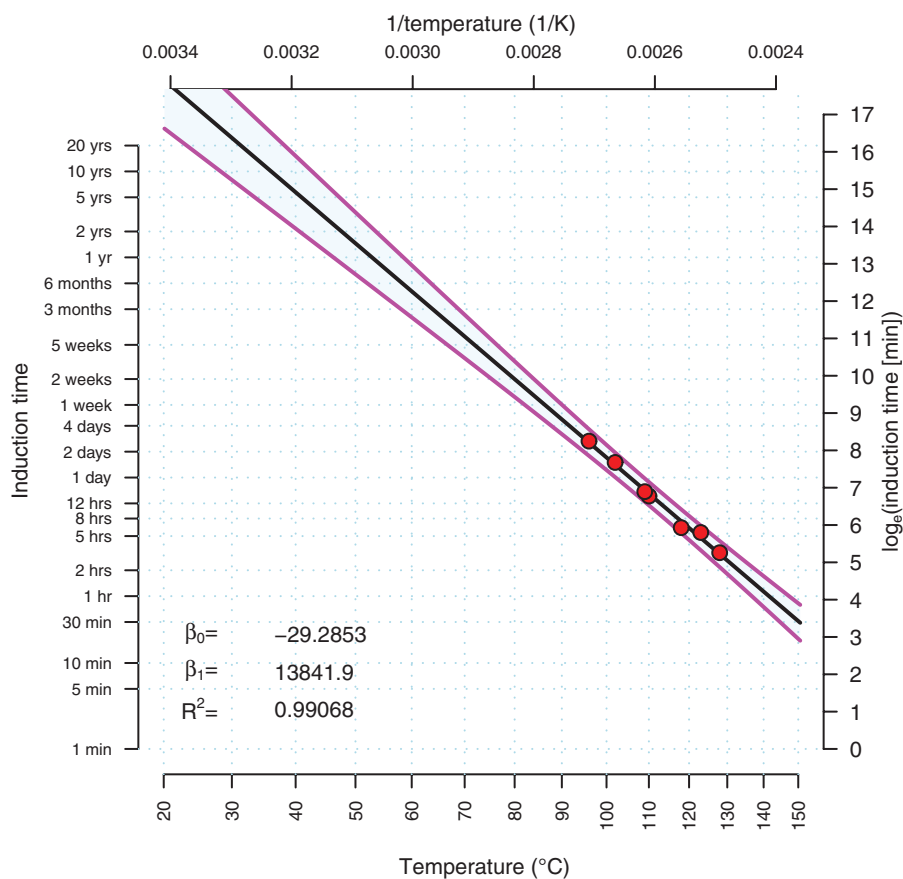
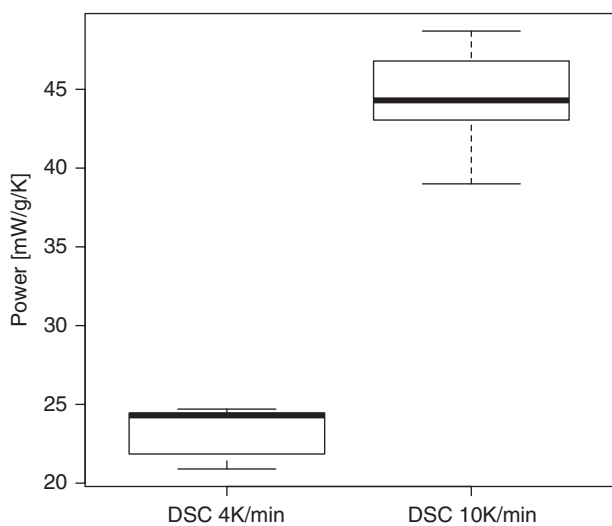**Figure 5.** Plot for induction time showing 95% prediction intervals

Figure 6. Comparison of maximum power outputs detected for repeat runs on the same system
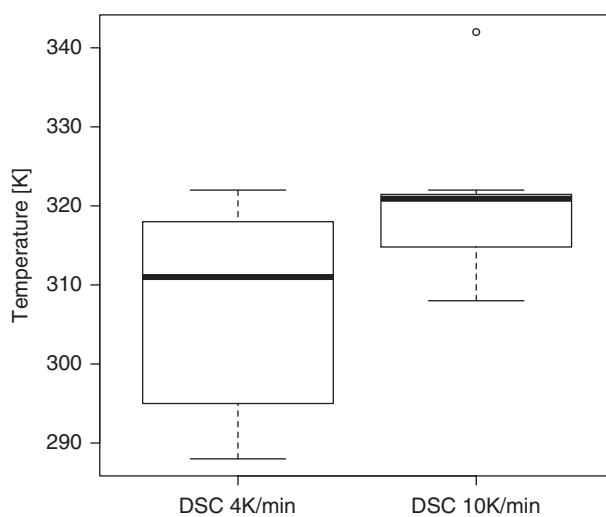

Figure 7. Rampled DSC comparison of detected onsets for repeated runs on same system

These predictions can be improved in confidence if more data points are available, as close to the desired prediction zone as possible. However, even then we should be aware of possible behaviour change between experimental conditions and the desired prediction region.

The R^2 values for the lines plotted were all high, but the prediction intervals could vary widely. R^2 is often very high for small numbers of points, and measures how the line fits those points. It is not a measure of how confident we should be in extrapolating the line, prediction intervals and confidence intervals on the line slope are more appropriate measures.

Experimental data is always an estimate of a value and has a degree of variability, we should remain aware of that and not be overawed by the graphical displays and slick printouts from modern computerised data collection equipment. Pleasing graphical displays do not add to the intrinsic precision and accuracy of the measured data, that is a function of the detector.

NOMENCLATURE

C_p	heat capacity [J kg^{-1} K^{-1}]
E	activation energy [J mol^{-1}]
n	number of data points
$\dot{q}$	heat release rate [W kg^{-1}]
R	universal gas constant [Jmol^{-1}K^{-1}]
s^2	experimental variance
S_{xx}	sum of squares for x
t	'Student's critical t value – dependent on number of degrees of freedom
T	absolute temperature [K]
T_0	initial temperature
TMR$_{ad}$	Time to Maximum rate under adiabatic conditions
x	explanatory or independent variable
$\hat{\alpha}$	estimated intercept
$\hat{\beta}$	estimated slope
ΔH_R	heat of reaction

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