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Sources of error, and their correction, in the analysis of isothermal heat conduction microcalorimetric data: applications of a newly developed test reaction

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Abstract

A recent investigation of a test reaction for isothermal heat conduction microcalorimeters, used for the determination of thermodynamic and kinetic parameters, resulted in the following recommended values for the imidazole-catalysed hydrolysis of triacetin at 298 K: the reaction rate constant, $k = (2.80 \pm 0.1) \times 10^{-6}\ \mathrm{dm^3\ mol^{-1}\ s^{-1}}$, and the reaction enthalpy change, $\Delta_R H = -91.7 \pm 3.0\ \mathrm{kJ\ mol^{-1}}$. Knowledge of these values allows the performance of a microcalorimeter to be evaluated. Thus, it may be possible to correct data for those cases in which there is mis-assignment of the true instrument baseline zero, of the upper calibration setting and of a drift in the instrument baseline. This paper describes the expected data output and its analysis in these cases. For these instances, it is possible to identify the error source and to manipulate subsequent data to produce "corrected" results. The procedures are illustrated through the use of data simulated as output. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Microcalorimetry; Test reaction; Error sources; Data correction

1. Introduction

A recent paper [1] has reported the results of an intra- and inter-laboratory investigation of a test reaction for use with isothermal heat conduction microcalorimeters used to determine both thermodynamic and kinetic parameters for reacting systems. Such a test reaction will permit traceability and validation of results for experimental systems as is described in [1]. The recommended values [1] for the reaction rate constant, k, and reaction enthalpy change, $\Delta_R H$ (hereafter referred to as H for simplicity) for the imidazole-catalysed hydrolysis of triacetin at 298 K are: $k = (2.80 \pm 0.1) \times 10^{-6}\ \mathrm{dm^3\ mol^{-1}\ s^{-1}}$ and $H = -91.7 \pm 3.0\ \mathrm{kJ\ mol^{-1}}$. The reaction is second-order over at least 100 days and proceeds to completion (i.e. no definable equilibrium position exists).

This reaction system was proposed earlier [2] as "a test and calibration process for microcalorimeters used as thermal power meters". This test reaction system is also described in [3]: a paper dealing with a range of calorimetric test reactions. In neither of these papers are values of k and H given for the reaction.

One of the applications of such a test reaction is to validate the performance of microcalorimeters [1]. This paper describes how these data may be used to identify the possible microcalorimetric situations in which erroneous data may be recorded and their

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causes. To do this, simulated microcalorimetric data is used to explore the consequences of events which lead to incorrect output. Simulated data has been used [4–6] as an effective way in which to explore the time-dependent thermal power — time data recorded in microcalorimetric experiments. The methods used to determine the thermodynamic and kinetic parameters from calorimetric observations are well documented [1,4–9].

In [1] attention is drawn to one set of *k* and *H* data which show a within-error limits agreement for *k* and out-of-limits values for *H*. Using the methods described below, it is possible to suggest a plausible explanation for these results.

In all the illustrations, simulated data output is shown for periods of 50 days. This is so that the "experimental" and "true" outputs can be clearly distinguished visually. The data from 50 h of study will however, as has been shown [7], permit determination of values of *k* and *H* that are entirely compatible with the recommended values [1] for the proposed test reaction.

2. Discussion

The discussion below refers to the manner in which a Thermometric TAM (Thermometric AB, Järfälla, Sweden: Thermal Activity Monitor) is operated.

The following theoretical examples explore the effect that different sources of instrumental error may have upon the calorimetric output obtained from a hypothetical standard test reaction and how that reaction can be diagnostic of the error and how it might correct or amend the calorimetric output and results obtained from other processes studied using the same instrument. The hypothetical standard reaction is based on the imidazole-catalysed hydrolysis of triacetin as considered previously [1]. The symbols used throughout the text use those described in [1].

2.1. Error in the upper calibration setting

If, during calibration of a calorimeter, the upper limit of the scale of study is incorrectly set, then all readings between zero and the upper limit of detection will be in error by a magnitude that is directly proportional to the percentage error in the upper calibration point. Consider a situation in which during calibration, the baseline zero is correctly set, whilst the upper setting is incorrect so that a delivered thermal power of 100 μW is in fact reported by the instrument as 110 μW. The effect this would have on the thermal power that would be observed from the hypothetical standard is simulated in Fig. 1. The solid line shows the true thermal power produced by the reaction,

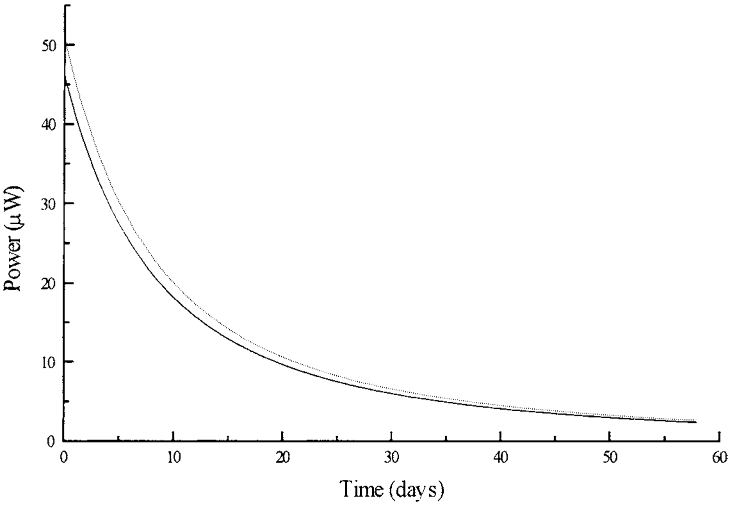

Fig. 1. Diagram illustrating the effect an error in the electrical calibration would have on the recorded signal, the solid line is the true calorimetric output of the reaction whilst the dotted line would be that recorded by the calorimeter if the upper limit in the calibration was incorrectly set (in this case an error of 10 μW in the upper limit was made).

Table 1
Parameters used to simulate data shown in Fig. 1

A_0 (mol dm^{-3})	V (dm^3)	H (kJ mol^{-1})	k (dm^3 mol^{-1} s^{-1})
0.2445	0.003	−91.7	2.80×10^{-6}

simulated using Eq. (1) to the parameters shown in Table 1, whilst the dotted line shows that which would be reported by the calorimeter. The reported initial thermal power is greater than that which is actually produced by the reaction. The baseline zero setting is not in error so, as the reaction progresses, the thermal power reported by the calorimeter will gradually converge with the true output until they meet at $dq/dt = 0$ (time $= \infty$), which is at the completion of reaction

$$\frac{dq}{dt} = -HVk\left(\frac{A_0}{1 + A_0kt}\right)^2 \tag{1}$$

Fitting the dotted line shown in Fig. 1 to Eq. (1) allows derivation of the values of H and k for the hypothetical reaction in which the electrical calibration is in error. Both A_0 and V are held constant during the fitting procedure and the results are shown in Table 2.

Although the dotted line may appear to have a greater rate of decay than the solid black line, the derived value of the rate constant is identical to the hypothetical standard. The value derived for the reaction enthalpy of -100.9 kJ mol^{-1} is significantly greater than the mean best value used to simulate the data of -91.7 kJ mol^{-1} and is well outside the standard error associated with the test reaction results. This error in the enthalpy with a correct value for the rate constant is a good indication that the scale of the calorimeter uses is incorrect whilst the baseline zero setting is correct, i.e. it is the electrical calibration setting that is in error. As it is known what the value for the reaction enthalpy should be (-91.7 kJ mol^{-1}), we can use this along with the calculated (incorrect) value of the reaction enthalpy to correct the thermal power of the calorimeter records.

Table 2
Values for k and H determined from data using an incorrectly set upper calibration point

A_0 (mol dm^{-3})	V (dm^3)	H (kJ mol^{-1})	k (dm^3 mol^{-1} s^{-1})
0.2445	0.003	−100.881	2.80×10^{-6}

Eq. (2) [6] describes the thermal power versus heat output for a simple nth-order reaction

$$\frac{dq_{\text{true}}}{dt} = -H_{\text{true}}kV\left(A_0 - \frac{q_{\text{true}}}{H_{\text{true}}}\right)^n \tag{2}$$

It follows for an incorrectly calibrated calorimeter

$$\frac{dq_{\text{obs}}}{dt} = -H_{\text{obs}}kV\left(A_0 - \frac{q_{\text{obs}}}{H_{\text{obs}}}\right)^n \tag{3}$$

when $q_{\text{obs}} = 0$ it is simple to show that Eq. (4) results

$$\frac{dq_{\text{true}}}{dt} = \frac{H_{\text{true}}}{H_{\text{obs}}}\frac{dq_{\text{obs}}}{dt} \tag{4}$$

Eq. (4) can be used to correct the thermal power, reported by any isothermal calorimeter that has an error in its upper calibration setting. For any points along the thermal power versus time curve and for any process studied within that instrument, the entire data set may be multiplied by $H_{\text{true}}/H_{\text{obs}}$ to generate the true thermal power versus time graph for the reaction. This may be illustrated by considering the error in the electrical calibration in the above theoretical example. Recall that the hypothetical calorimeter's upper calibration setting was incorrect such that a thermal power output of 100 μW is in fact reported as 110 μW.

Hence, using Eq. (4)

$$\frac{dq_{\text{true}}}{dt} = \left(\frac{-91.71}{-100.881}\right)110 = 100\,\mu\text{W}$$

It is the ratio of the true reaction enthalpy to the incorrect one which is the important factor, from this both the thermal power recorded by an incorrectly calibrated calorimeter and/or any reaction enthalpies calculated from the data may be adjusted accordingly for any reaction or processes studied using that instrument. Some instruments possess more than one calorimetric unit (e.g. the TAM has four separate calorimetric units) and these may independently be in error.

In the examples that follow the equations that describe the calorimetric output may be derived in a similar manner to that outlined above.

2.2. *Error in the baseline zero setting*

In this case, the error in the calorimetric output is caused by a shift in the baseline, either to the positive

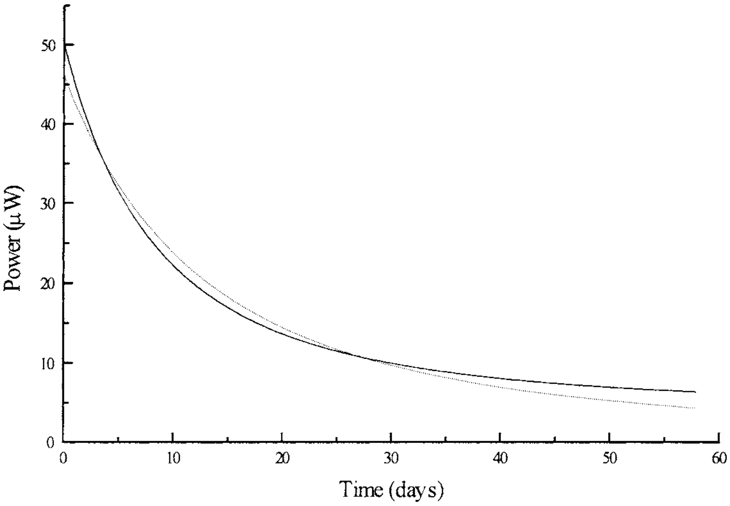

Fig. 2. The result of an attempted fit of simulated data for the hypothetical standard reaction, in which the effect of an error of +4 μW in the zero point of the calorimeter has been modeled.

or negative, so that all values reported by the calorimeter are in error by the same amount. If the data obtained from the standard reaction are fitted to Eq. (1), a satisfactory fit will not be obtained since the equation describes a second-order decay to zero (at time $= \infty$) (which the shifted data do not). This is illustrated in Fig. 2 in which all the data have been shifted up by 4 μW. The solid line is that which the calorimeter would report whilst the dotted line is the attempted fit of the data to Eq. (1) and the values obtained from the fit are detailed in Table 3. As can be seen not only is the fit unsatisfactory but also the reaction parameters yielded are far from the mean best values used to simulate the data. Here, both the values of k and of H lie well outside the standard errors reported for the test reaction.

The observed signal may be described simply in terms of the true calorimetric output plus a parameter, R, which is equal to the shift in the baseline

$$\frac{dq_{\text{obs}}}{dt} = \frac{dq_{\text{true}}}{dt} + R \tag{5}$$

Table 3
Values for k and H determined from data using an incorrect baseline zero setting

A_0 (mol dm^{-3})	V (dm^3)	H (kJ mol^{-1})	k (dm^3 mol^{-1} s^{-1})
0.2445	0.003	−138.17	1.86×10^{-6}

The signal from the test reaction may be described by a modified form of Eq. (1) which includes the extra parameter R that takes into account the shift in the baseline

$$\frac{dq}{dt} = -HVk\left(\frac{A_0}{1 + A_0kt}\right)^2 + R \tag{6}$$

The data in Fig. 2 are fitted again using Eq. (6), A_0 and V are held constant whilst H, k and R are allowed to vary. The result of this fit is shown in Fig. 3 and the values obtained for each of the parameters are shown in Table 4. As can be seen, the fitting procedure has returned the correct values of H and k as well as a value of +4 μW for R, this confirms that the error in the calorimetric signal is caused by a shift in the baseline (or zero point) of the instrument of 4 μW as a value of $R = +4$ μW allows the second-order part of Eq. (6) to be satisfied, thus generating a satisfactory fit (with a return of the correct values). Note that only one line of decay is shown, this is because the fit line overlies the

Table 4
The corrected values of k and H determined from data using an incorrect baseline zero setting and the determined correction parameter, R

A_0 (mol dm^{-3})	V (dm^3)	H (kJ mol^{-1})	k (dm^3 mol^{-1} s^{-1})	R (μW)
0.2445	0.003	−91.7	2.8×10^{-6}	4

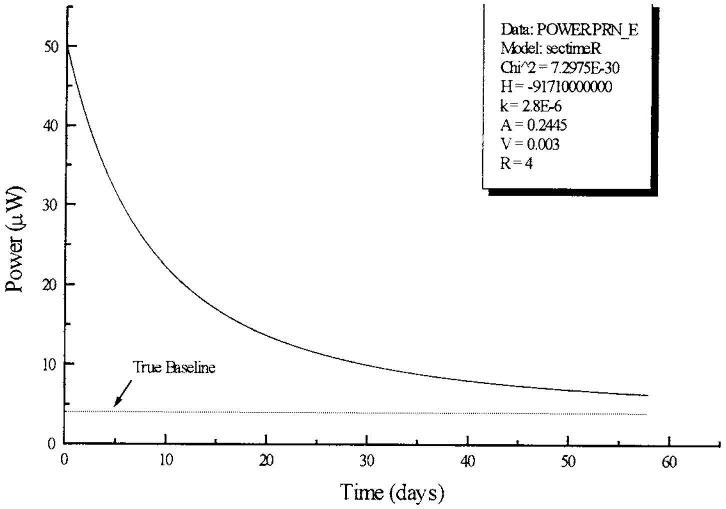

Fig. 3. The result of fitting simulated data for the hypothetical standard reaction, in which the effect of an error in the zero point of the calorimeter has been modeled, to Eq. (8).

simulated data exactly. The horizontal dotted line in Fig. 3 indicates the true position of the baseline zero setting of the calorimeter, at +4 μW.

2.3. Non-uniform error

It might be the case that the error in the observed calorimetric signal is a composite of both situations discussed above, i.e. there is both an error in the zero point of the calorimeter and in the upper limit of the scale but to different extents. Fig. 4 shows the effect that an error of +0.5 μW in the baseline zero setting and +0.3 μW in the upper setting limit of the scale would have upon the recorded signal of a theoretical reaction which, throughout its lifetime, produces a thermal power that decays from 100 to 0 μW.

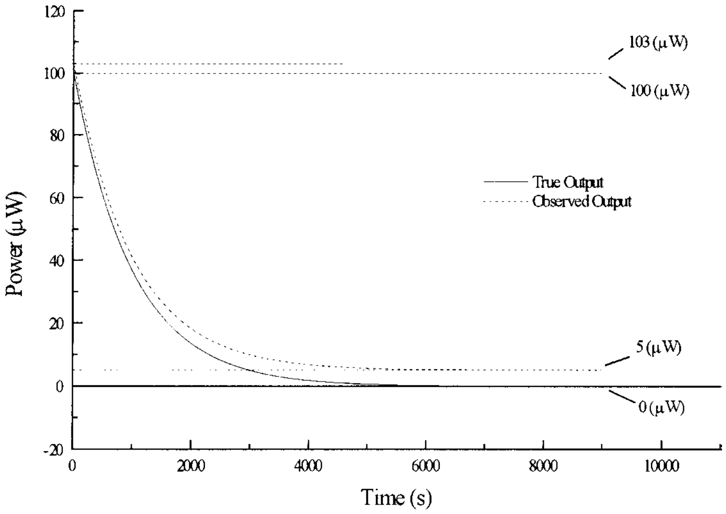

Fig. 4. Diagram illustrating the effect an error, both in the upper and lower limits, in the calibration of a calorimeter would have on the recorded output.

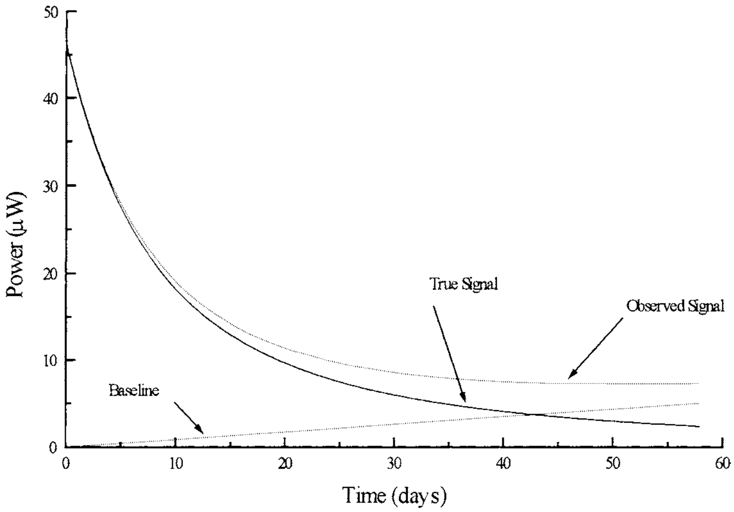

Fig. 5. Diagram illustrating the effect a drift in the baseline of the calorimeter would have on the signal recorded by the instrument.

As with the example considered above (shown in Fig. 2) a fit of the signal, which is obtained from the hypothetical standard reaction, to Eq. (1) would prove to be unsatisfactory. Instead, if the data were fitted using Eq. (6) the result would be that the error in the baseline zero setting would be reflected in the value of *R* obtained, whilst the error in the upper limit would be identified by the value of *H* derived in the fitting procedure. Once the nature and extent of the error have been identified quantified then analysis and correction of data recorded from other processes studied within the same instrument may be achieved by firstly shifting the data to an extent equal to the value of *R* (as determined in the fit of the standard test reaction) and then by correcting for the error in the electrical calibration in a manner identical to that discussed above.

2.4. Time-dependent errors

In the above examples, all the sources of error considered were constant and fixed, in many cases the error in the recorded signal may vary with time. If initially, for example, a calorimeter is correctly baseline zeroed and calibrated but over a period of time, the baseline starts to vary over time, although the initial recorded signal will be correct, as the reaction progresses the thermal power versus time curve will become distorted. The effect this would have on the hypothetical standard reaction is simulated in Fig. 5, to allow for easy illustration a high rate of change in the position of the baseline is modeled. Analysis of the data may be achieved in a similar manner to when the error in the baseline is fixed and constant (Eq. (6) except the parameter *R* is replaced by *P*(*t*) (unit of *P* is $\mu\text{W s}^{-1}$) to allow for the time-dependent variation in the baseline and is shown by Eq. (7)

$$\frac{\mathrm{d}q}{\mathrm{d}t} = -HVk\left(\frac{A_0}{1 + A_0kt}\right)^2 + P(t) \tag{7}$$

As with Eq. (6), if an adequate fit Eq. (7) is achieved with a return of the correct values of *H* and *k* (i.e. that agree with the agreed mean best values) it confirms the nature of the error and the value of *P* that is returned from the fit indicates the rate of change ($\mu\text{W s}^{-1}$) of the baseline. Once the nature of the error has been confirmed and the value of *P* determined and data obtained, using the same instrument, any process may be corrected by use of Eq. (8)

$$\frac{\mathrm{d}q_{\text{true}}}{\mathrm{d}t} = \frac{\mathrm{d}q_{\text{obs}}}{\mathrm{d}t} - P(t) \tag{8}$$

Just as the baseline can vary over time so can the upper limit of calibration of the instrument, which can lead to two further, more complex, situations. Firstly, the upper limit (as defined by, for example, electrical calibration) may drift over time. The effect this has is to introduce an ever-increasing percentage error into the calorimetric data over time. The second situation that could occur is that when both the zero point and the upper limit drift over time, leading to a similar but more complex situation to that just described. In such a case the data may be analyzed using Eq. (9), the expression $P(t)$ is as above and describes the variation in the baseline with time, whilst the expression $((\Phi_{\mathrm{upper}} + S(t))/\Phi_{\mathrm{upper}})$ accounts for the variation in the upper limit of the calibration. The parameter Φ_{upper} is the value of the upper calibration setting, i.e. if the calorimeter is supposed to be calibrated between 0 and 300 μW then Φ_{upper} will be equal to 300 μW and the parameter S is the rate of change in the upper limit of calibration (unit of S is $\mu\mathrm{W\,s^{-1}}$):

$$\frac{\mathrm{d}q}{\mathrm{d}t} = -HVk\left(\frac{A_0}{1 + A_0kt}\right)^2 \frac{\Phi_{\mathrm{upper}} + S(t)}{\Phi_{\mathrm{upper}}} + P(t) \tag{9}$$

Correction of data that is subjected to an error described by Eq. (9) may be achieved using Eq. (10)

$$\frac{\mathrm{d}q_{\mathrm{true}}}{\mathrm{d}t} = \frac{\mathrm{d}q_{\mathrm{obs}}}{\mathrm{d}t} \frac{\Phi_{\mathrm{upper}}}{\Phi_{\mathrm{upper}} + S(t)} - P(t) \tag{10}$$

In all the examples above the sources of error that might be introduced into the calorimetric signal are simple in nature and have been either fixed and constant or linearly drifting from an initially correctly calibrated instrument. In reality the two types of error may occur at the same time and the type of drift in an instrument's baseline and upper limit of calibration is likely to be more complex. Thus, it is necessary to derive more complex equations that describe the calorimetric output from the test and reference reaction in terms of the true output and parameters that describe the error. One such example is shown by Eq. (11) which contains polynomial functions of time

$$\begin{aligned}\frac{\mathrm{d}q_{\mathrm{obs}}}{\mathrm{d}t} = &- HVk\left(\frac{A_0}{1 + A_0kt}\right)^2 \\ &\times \frac{\Phi_{\mathrm{upper}} + (a + bt + ct^2 + \cdots + it^{i-1})}{\Phi_{\mathrm{upper}}} \\ &+ (z + yt + xt^2 + \cdots + jt^{j-1})\end{aligned} \tag{11}$$

In order to properly describe the various sorts of instrumental error that may be produced in calorimetric experiments, other similar equations containing different types functions might also be derived that may be applied to the calorimetric output obtained from the test reaction. It is recommended when trying to determine the performance and stability of a particular instrument, the output is firstly analyzed using just the basic calorimetric equation; Eq. (1). If a satisfactory fit is not obtained or the correct values of the reaction parameters H and k (within the S.D. of the recommended values: these are ±3% in both) are not returned, then in order to determine the nature of the error, a systematic approach to the analysis of the data should be adopted. If a satisfactory fit is obtained with a correct value (within S.D.) of the rate constant but not of reaction enthalpy then the upper limit setting of the calorimeter may be in error but the baseline zero setting correct. If the reverse is true, i.e. the fitting procedure returns the correct value for the reaction enthalpy (within S.D.) but not for the rate constant, the reported operating temperature of the calorimeter could be in error, this scenario is considered below. If however a suitable fit is not obtained a modified version of the calorimetric equation, Eq. (1), may be employed in manner described above. It is suggested however that when adding terms to the modified version of Eq. (1) this is also be done in a systematic manner, i.e. a single term as in Eq. (6) should be added first and then the fitting procedure performed again, if a satisfactory fit is still not obtained then further terms should be added one by one, the fit of the data and the reaction parameters returned being checked in each instance.

2.5. Error caused by a faulty thermostat

This is perhaps a use of the test reaction which would be employed infrequently but it merits exploration. In the event that the thermostat is faulty, the reported operating temperature of the calorimeter could be wrong. As the rates of chemical reactions are directly proportional to the temperature, this would result in an incorrect derivation of the value for the rate constant. A value of 64.30 ± 2.00 $\mathrm{kJ\,mol^{-1}}$ has been derived [6] for the activation energy of the reaction. If it is assumed that the reaction enthalpy is independent of temperature (van't Hoff isotherm), which it appears to be for the imidazole-catalysed hydrolysis of triacetin [6] then an error in the derived value of the rate constant for the test reaction whilst the derived value of the reaction enthalpy is correct could be diagnostic of an error in the reported temperature of

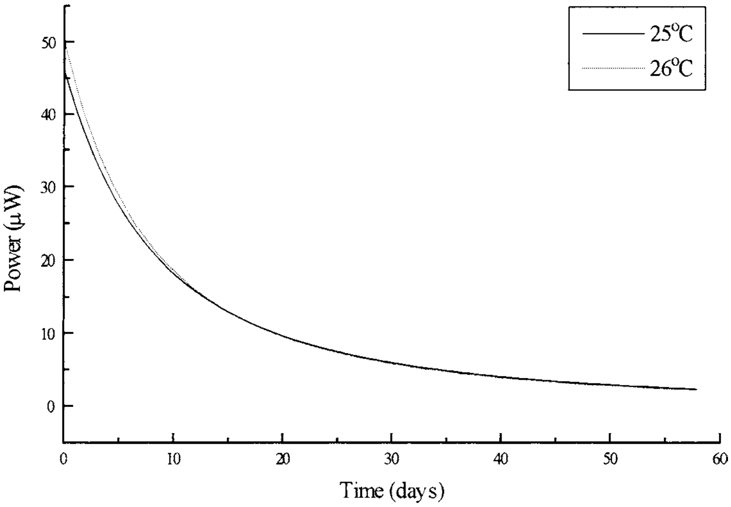

Fig. 6. Predicted thermal power vs. time graphs for the hypothetical standard reaction at 25 and 26°C.

Table 5
Values for *k* and *H* determined from data using a calorimeter with an incorrectly set thermostat temperature (see text for details)

A_0 (mol dm^{-3})	V (dm^3)	H (kJ mol^{-1})	k (dm^3 mol^{-1} s^{-1})
0.2445	0.003	−91.7	3.046×10^{-6}

the calorimeter. Fig. 6 shows the thermal power versus time graph for the hypothetical standard reaction at 25 and 26°C, as can be seen, the difference in the two thermal power versus time graphs is quite significant, the initial signal and rate of decay for the experiment performed at 26°C is greater than at 25°C. If the test reaction were to be conducted at a believed temperature of 25°C, yet the thermal power versus time trace obtained is equal to the dotted line shown in Fig. 6 then simple direct visual comparison with the solid black line which is the trace which should be obtained at 25°C (based on the mean best values reported earlier) would indicate that the instrument might be in error. Analysis of the thermal power versus time trace indicated by the dotted line in Fig. 6, using Eq. (1), yields the results shown in Table 5.

Applying the Arrhenius equation to two temperatures it is simple to show that Eq. (12) results

$$T_2 = \frac{E_a/R}{\ln(k_1/k_2) + (E_a/R)(1/T_1)} \qquad (12)$$

The actual operating temperature of the calorimeter may now be calculated

$$T_2 = \frac{7512.057}{\ln((2.8\times10^{-6})/(3.046\times10^{-6}))+(7512.057/298)}$$
$$= 298.9988 = 299\,\mathrm{K}$$

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