Application of Baseline Correction Techniques to the "Ratio Method" of DSC Specific Heat Determination[1]

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ABSTRACT

The measurement of specific heat by heat flux Differential Scanning Calorimetry using the “ratio method” requires three consecutive runs (baseline, reference and sample) to be performed using identical temperature programmes. Traditionally measurements are taken as the sample of interest is subjected to a controlled heating rate, but it is also possible to perform measurements on down-ramps, and this is often worthwhile as it provides a consistency check on the up-ramp data.

In recent work at AEA Technology Windscale a Netzsch DSC-404 has been used to investigate discrepancies observed between up and down-ramp specific heat results. Based upon this experience several different “baseline correction” techniques have been developed, and have been applied to specific heat measurements on reference Sapphire samples. The performance of these “baseline correction” techniques is shown to be extremely good, even up to 1400°C.

An important conclusion is that, even in cases where agreement between up-ramp and down-ramp data is reasonable, a “baseline correction” method can still usefully be applied to improve the precision of the final results.

KEY WORDS: baseline correction techniques; Differential Scanning Calorimetry; high temperatures; ratio method; Sapphire standards; specific heat

1. INTRODUCTION

The Differential Scanning Calorimetry (DSC) method is a comparative one based upon the measurement of both a sample of interest and a reference material in which the heat input to the sample, as compared to the reference material, is measured while the sample and reference are subjected to a controlled temperature programme at a constant heating and/or cooling rate. Specific heat determination is achieved by performing three consecutive runs; baseline, reference and sample, all under identical experimental conditions. The DSC response is the temperature differential between the two crucible thermocouples and is measured during all three temperature scans. The specific heat of the sample is derived from a comparison of the deviations of the DSC responses (from the baseline) for the reference standard and the sample. Sapphire is one of the few reference standards available for specific heat determination via high temperature DSC, and its use is now well established [1,2] in providing a calibration of the DSC signal.

The two standard methods used for specific heat determination using DSC are the enthalpic and scanning or "ratio" methods. The enthalpic method automatically takes account of any baseline shift(s) that may occur between successive runs, whereas in the standard scanning method the use of faster ramp rates significantly enhances the signal response, which in turn reduces (but does not eliminate) the effect of any baseline shift(s). In order to improve the precision of the standard scanning method two techniques have been developed to detect and correct for baseline shifts that can occur.

2. STANDARD ANALYSIS METHODS

2.1 Enthalpic Method

The enthalpic method mimics the procedures used in adiabatic calorimetry, in which heating of the specimen is done over small temperature intervals at relatively slow

heating rates, and the entire area under the response curve is determined. By suitable calibration this area can be converted into an enthalpy, and division by the temperature span of the curve gives an average heat capacity corresponding to the midpoint of the temperature range [3].

2.2 Scanning Method

The scanning method is much more widely used than the enthalpic method as it is more straightforward to apply, especially over a wide temperature range. In contrast to the enthalpic method where mean values are obtained, determination of the specific heat is achieved in scanning mode at individual temperatures in the heating/cooling regime. The sample specific heat, C_P^S (in J/kg/K), is given by the following expression:

$$C_P^S(T) = \frac{m_R}{m_S}\frac{\Delta V_S(T)}{\Delta V_R(T)}.C_P^R(T) \qquad (1)$$

where $C_P^R(T)$ is the specific heat of the reference standard (J/kg/K) at temperature T; $m_{R,S}$ are the masses of the reference standard and sample; $\Delta V_{R,S}(T)$ are the voltage differences between the reference/sample curves and the baseline.

The key assumption implicit in equation (1) is that experimental conditions in the three runs are the same so that any disturbing influences, which may distort results, are eliminated. Therefore such results are not corrected for any underlying baseline shifts that *may* have occurred between any of the three measurement runs.

3. CORRECTED SCANNING METHODS

It is often stated in the literature that for the DSC method to produce reliable and reproducible results every effort must be made to duplicate experimental conditions in the three successive measurements. Provided that any baseline shifts between successive runs are small compared with the DSC voltage differences ($\Delta V_{R,S}$) the effect on the final

results will also be small, and as fast ramp rates are used (which maximise the DSC signal) this often proves to be the case. However, even in such cases an ability to detect and correct for baseline shifts is of potential benefit as a means of improving the precision of the final results. This is especially true at high temperatures where the instrument sensitivity falls off and the effects of any baseline shift(s) are more pronounced.

Specific heat determination in scanning mode is most commonly achieved by applying a controlled *heating* ramp to the sample over the temperature range of interest. It is also advisable to record data on *cooling* to determine whether any irreversible changes have occurred, either (i) to the sample, or (ii) in the experimental conditions between the measurement runs. Early work using a DSC-404 [4] with standard Sapphire samples showed that in some instances there could be a significant deviation between the heating (up-ramp) and cooling (down-ramp) specific heat results, and as no irreversible sample changes were expected (or indeed observed) the cause was attributed to changes in experimental conditions between the three successive measurement runs.

The key experimental observation was that the deviation of the up-ramp specific heat results from the accepted standard values was of opposite sign to the deviation of the down-ramp results, and more often than not the data could adequately be corrected by simply taking an average of the up-ramp and down-ramp results, weighted by the magnitude of the ramp rate (ie the faster the ramp rate the smaller the deviation).

The simplest way to explain this is in terms of an underlying baseline shift that can occur between any of the three measurement runs, and the two main assumptions underpinning the correction methods developed here, which are consistent with the above experimental observations, are that:

- the baseline shift(s) seen are due to slight changes in thermal resistance(s) in the system, so that the sign of the correction term is the same irrespective of whether it is applied to up-ramp or down-ramp data (note that this would not be true for heat capacity changes);
- the baseline shift(s) observed are small enough so that they do not have a significant effect on the instrument sensitivity.

This second assumption is a very important one in that there will come a point when the change in experimental conditions that gives rise to a baseline shift will also start to affect the instrument sensitivity, and at this stage the correction methods will start to fail. However, for the measurements reported in this paper the baseline correction methods used are shown to work very well, and this perhaps highlights a significant feature in that the baseline shifts applied did not show a strong temperature dependence. This indicates that the underlying baselines were all very similar in shape as a function of temperature, and were simply offset from one another by differing amounts.

3.1 Scanning Baseline Correction (SBC) Method

This is the simplest way of correcting specific heat data where deviations are observed between up and down-ramp data, and the basic requirement is that a temperature programme is defined with a series of up and down-ramps which have overlapping temperature ranges. On the assumption that the sample is not altered as a result of the heating ramp(s) it is possible to estimate an *effective* underlying baseline shift, $\delta_S^{eff}(T)$ between the baseline and sample runs that would be necessary to ensure equality of the up and down-ramp specific heat results. By using ± to denote either up (+) or down (-) ramp data, it is possible to define:

$$C_P^{S,\pm}(T) = \frac{m_R}{m_S}\left(\frac{\Delta V_S^{\pm}(T) - \delta_S^{eff}(T)}{\Delta V_R^{\pm}(T)}\right).C_P^R(T) \qquad (2)$$

where $\delta_S^{eff}(T)$ may be calculated by requiring that:

$$C_P^{S,+}(T) = C_P^{S,-}(T) \qquad (3)$$

This method can be viewed in crude terms as a ramp rate weighted average of up and down-ramp specific heat values.

3.2 Isothermal Baseline Correction (IBC) Method

The main disadvantage of the SBC method above is the assumption made in equation (3). However, by defining a different type of temperature programme it is possible to perform a baseline shift analysis without making such an assumption. In this method the aim is to define a scanning temperature programme with a series of fast (eg 20°C/min) up and down ramps separated by a small number of isothermal holds, ideally at equally spaced temperatures. By performing a regression analysis of the isothermal DSC voltages as a function of temperature it is possible to estimate any underlying *thermal resistive* baseline shifts that have occurred between (i) the baseline and reference runs, and (ii) the baseline and sample runs. Thus equation (1) can be modified:

$$C_P^S(T) = \frac{m_R}{m_S}\left(\frac{\Delta V_S(T) - \beta_S(T) + \beta_B(T)}{\Delta V_R(T) - \beta_R(T) + \beta_B(T)}\right).C_P^R(T) \qquad (4)$$

where $\beta_{S,R,B}(T)$ represent temperature dependent regression fits to the isothermal hold data for the sample, reference and baseline runs respectively.

A crucial feature to stress about this technique is that the effect of any applied correction on derived specific heat values is of a different sign for up and down-ramp data, and provided that the sample is not altered as a result of the thermal cycling, then *corrected* up and down-ramp results can be checked against one another for consistency.

4. MEASUREMENTS ON REFERENCE SAPPHIRE STANDARDS

A summary of the complete validation test programme performed is given below:

Test No	Identity	Mass (mg)	Comment
T10	**Baseline-1**	**0**	**First baseline run**
T11	Baseline-2	0	Repeat baseline run
T12	**Sapphire-1**	**56.3**	**First 0.5mm Sapphire run**
T13	Sapphire-2	56.3	Repeat 0.5mm Sapphire run
T14	*Sample-1*		First full *sample* run
T16	*Sample-2*		Repeat full *sample* run
T17	**Sapphire-3**	**76.6**	**First 0.7mm Sapphire run**
T18	Sapphire-4	76.6	Repeat 0.7mm Sapphire run

As a consistency check on the *sample* results the measurement programme included repeat runs of each test plus additional runs on a Sapphire standard (a different one to that used as the reference standard) following the *sample* runs. Only the results highlighted in **bold** on reference Sapphire standards are reported here to provide a comparison of the different analysis methods employed.

4.1 DSC Data

The temperature programme comprised a fast (20°C/min) heating ramp up to 800°C at which point a series of six enthalpic mode steps were performed (at a slow rate of 5°C/min) in increments of 100°C to reach a final isothermal hold temperature of 1400°C. Finally, two fast cooling ramps (of 20°C/min) were defined; the first ending with an isothermal hold at 800°C, and the second with an isothermal hold at 250°C.

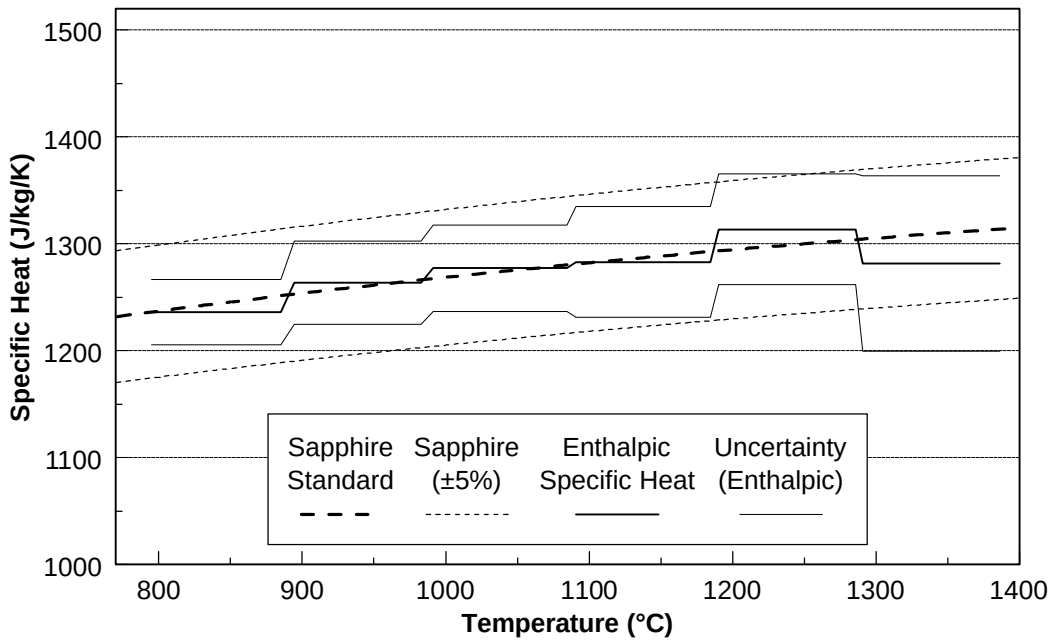
There was evidence of small but systematic baseline shifts occurring with each successive run and the cumulative effects of this were most pronounced on comparison of the Baseline-1 and Sapphire-4 data sets. A possible cause is postulated as a gradual change in geometry of the two crucible lids as at the end of the sequence of tests it was observed that the sample crucible lid (and to a lesser extent the reference crucible lid as

well) had noticeably “sagged”. The dishing of the crucible lids appears to start in the vicinity of a welded platinum tag at the centre of the lid and becomes progressively worse with prolonged exposure to high temperatures (ie a total of over 26 hours above 1000°C taking account of all the measurement runs performed).

4.2 Enthalpic Mode Results

The six enthalpic mode heating steps have been analysed using the enthalpic method, and the results are displayed in Figure 1 for the Sapphire-3 sample. These show excellent agreement with the reference standard values, and, although the *sample* data are not presented here, this also provided an excellent validation of the *sample* results.

Figure 1. Enthalpic Mode 0.7mm Sapphire Results between 800°C and 1400°C

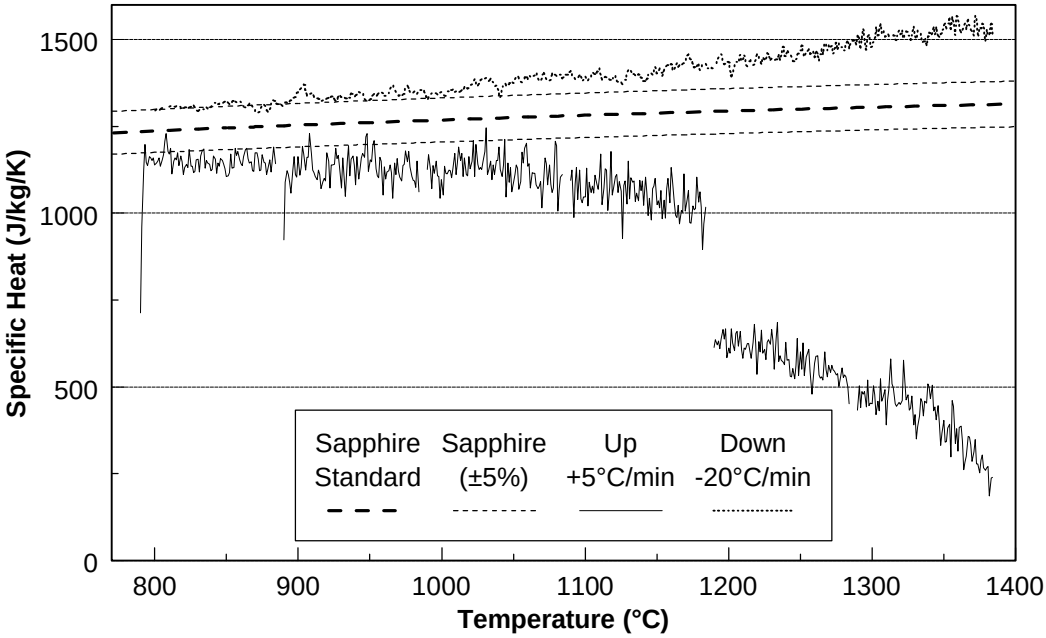


4.3 Uncorrected Scanning Mode Results

Figure 2 shows the slow up-ramp and fast down-ramp specific heat data above 800°C, calculated using equation (1), and significant deviations from the recommended values are apparent. These results display one of the classic symptoms attributable to a

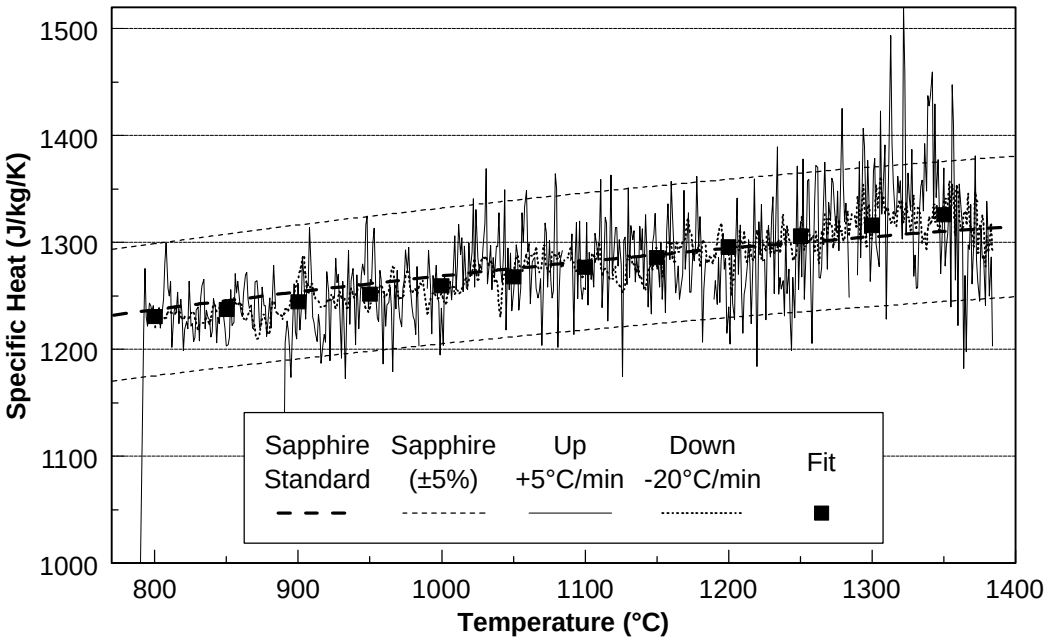
thermal resistive baseline shift in that the resultant effects are of a different sign for up and down-ramp data.

Figure 2. Uncorrected Scanning Mode 0.7mm Sapphire Results between 800°C and 1400°C



4.4 Scanning Baseline Correction Results

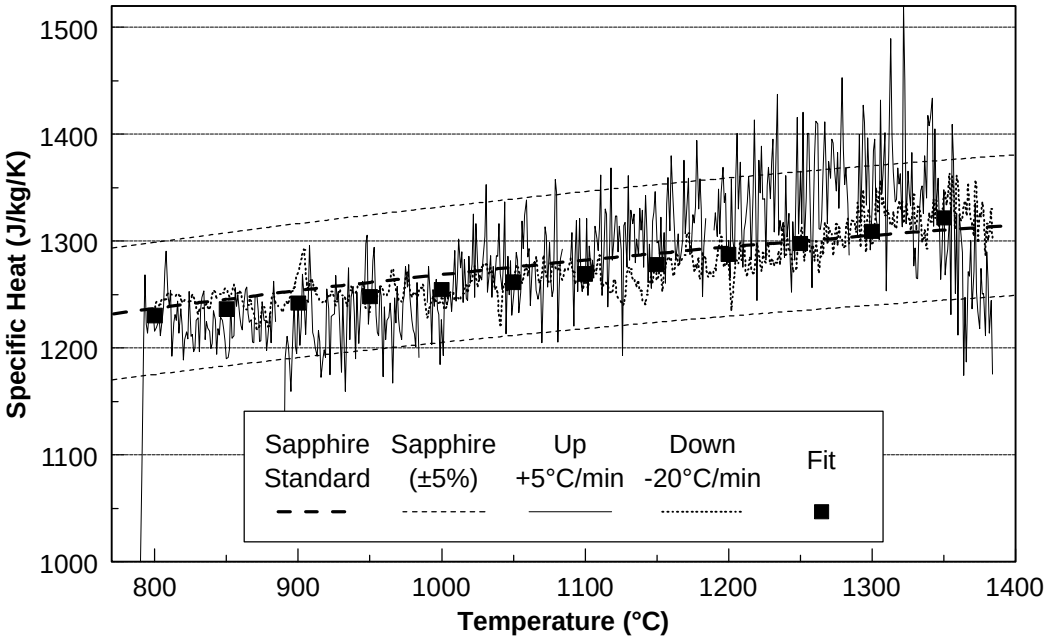
Figure 3. Scanning Mode 0.7mm Sapphire Results using Scanning Baseline Correction Method



The SBC results, given in Figure 3 for up and down-ramp data above 800°C, show excellent agreement with recommended values, and are also very similar to the results obtained via the enthalpic method.

4.5 Isothermal Baseline Correction Results

Figure 4. Scanning Mode 0.7mm Sapphire Results using Isothermal Baseline Correction Method



Quadratic fits were performed to the DSC data from the seven isothermal holds between 800°C and 1400°C, for each of the test runs separately, and the fits derived were then used to correct for baseline shifts of the Sapphire-1 and Sapphire-3 data in this temperature range. Corrected specific heat values, calculated using the IBC method via equation (4), are plotted in Figure 4. These results show excellent agreement between the slow up-ramp and fast down-ramp data, both of which are also in very good agreement with the standard reference values and the enthalpic results

4.6 Sapphire-4 Data

Although not presented here, analysis of the Sapphire-4 results also shows excellent agreement between the up and down-ramp data, both of which are in very good

agreement with results from the other two baseline correction methods. However, there is a systematic trend for the corrected results to be on average 2% higher than the standard reference values over most of the temperature range. This is perhaps an indication that the size of the baseline shift for the Sapphire-4 data (which is the largest for all the runs performed) is starting to become large enough to affect the instrument sensitivity.

5. CONCLUSIONS

As the sensitivity of the DSC-404 decreases at elevated temperatures the influence of any baseline shift becomes increasingly important, and to tackle this two new methods of analysis in the DSC scanning method have been developed to estimate and correct for instrument baseline shifts. The consistency of results obtained via the standard enthalpic method and *corrected* scanning methods of analysis is shown to be excellent, even up to 1400°C.

Based on this work the Isothermal Baseline Correction Method for DSC specific heat determination compares very favourably with the standard enthalpic method, and has important advantages in that it not only uses fast ramps to maximise the DSC signal, but also it requires fewer isothermal holds, so that both the sample and crucibles spend less time at elevated temperatures (reducing problems due to potential changes in the sample and “dishing” of the crucible lids).

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