Heat capacity determination at high temperatures by TGA/DSC Part 1: DSC standard procedures

Introduction

Several different standardized DSC measurement procedures are currently used for the determination of the specific heat capacity ($c_p$). These have been described in earlier publications [1, 2]. The introduction of the TOPEM® technique [3, 4] provides another interesting new method.

In DSC, the measured heat flow is directly proportional to the specific heat capacity. This allows $c_p$ to be calculated directly from the DSC signal ($\Phi_{\text{meas}}$). To do this, the DSC curve must be corrected by subtracting a blank curve and the masses of the crucibles should be as close as possible.

The isothermal baselines measured before and after the temperature increase should be long enough for the system to stabilize and reach stationary conditions. The results are evaluated according to standards such as ISO 11357, DIN 53765, DIN 51007 or ASTM E1269 [5–8].

$$
c_p = \frac{\Phi_{\text{sens}}}{\beta_s}
$$

where $c_s = mc$, $\beta_s$ is the heating rate (change of the sample temperature with time), $\Phi$: heat flow, $dH/dt$ is the change in enthalpy with time and in this case is called the sensible heat flow ($\Phi_{\text{sens}}$).

The measured heat flow ($\Phi_{\text{meas}}$) is the sum of the sensible and latent heat flows plus the heat flow ($\Phi_{\text{bl}}$) of the blank curve. The latent heat flow ($\Phi_{\text{lat}}$) is the sum of thermal events such as transitions or reactions.

$$
\Phi_{\text{meas}} = \Phi_{\text{sens}} + \Phi_{\text{lat}} + \Phi_{\text{bl}}
$$

Measurement of $\Phi_{\text{meas}}$ to calculate the heat capacity assumes that $\Phi_{\text{lat}}$ and $\Phi_{\text{bl}}$ are known. In $c_s$ determination, this means that other overlapping thermal events must not occur. Usually, the following two methods are employed:

The Direct method uses eq 3 to calculate the specific heat capacity.

$$
c_p = \frac{\Phi_{\text{meas}} - \Phi_{\text{bl}}}{m \beta_s}
$$

The Sapphire method is carried out according to the standard methods given above and eq 4:

$$
c_p = \frac{m_{\text{sap}} c_{\text{p,sap}}}{(\Phi_{\text{meas}} - \Phi_{\text{bl}})} - \frac{m_{\text{sap}} c_{\text{p,sap}}}{(\Phi_{\text{meas}} - \Phi_{\text{bl}}) c_{\text{p,sap}}}
$$

where $m_{\text{sap}}$, $c_{\text{p,sap}}$ and $\Phi_{\text{bl}}$ are obtained from the sapphire measurement.

<table>
<thead>
<tr>
<th>Material</th>
<th>Temperature/Literature ref.</th>
<th>500</th>
<th>550</th>
<th>600</th>
<th>1250</th>
<th>1300</th>
<th>1350</th>
<th>°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>platinum</td>
<td>9</td>
<td>0.144</td>
<td>0.145</td>
<td>0.147</td>
<td>0.16</td>
<td>0.1672</td>
<td>0.168</td>
<td>J/gK</td>
</tr>
<tr>
<td>nickel</td>
<td>10, 11</td>
<td>0.529</td>
<td>0.534</td>
<td>0.54</td>
<td>0.62</td>
<td>0.616</td>
<td>0.629</td>
<td>J/gK</td>
</tr>
<tr>
<td>sapphire</td>
<td>MT</td>
<td>1.171</td>
<td>1.185</td>
<td>1.197</td>
<td>1.29</td>
<td>1.295</td>
<td>1.299</td>
<td>J/gK</td>
</tr>
<tr>
<td>quartz</td>
<td>12, 13</td>
<td>0.777</td>
<td>0.789</td>
<td>0.732</td>
<td>0.79</td>
<td>0.793</td>
<td>0.798</td>
<td>J/gK</td>
</tr>
<tr>
<td>quartz</td>
<td>11</td>
<td>1.24</td>
<td>1.14</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>J/gK</td>
</tr>
</tbody>
</table>

Table 1. Values of specific heat capacities at different temperatures. (MT: Data taken from the STAR® software).
Both methods take the influence of different crucible masses into account.

Details and information on the use of the different methods are given in UserCom 7 [1]. This present article discusses methods for the determination of the specific heat capacity at temperatures above 500 °C and shows suitable examples.

Table 1 summarizes different \( c_p \) reference values taken from the literature to check the results. The values for quartz are relatively uncertain because the literature values differ by up to 40%.

**Experimental details**

The experiments to determine specific heat capacity at high temperatures were carried out using stable materials that could be repeatedly measured and that differed in \( c_p \), thermal conductivity, and color. Platinum and nickel were measured as pure metal disks. Different types of aluminum oxide, i.e. pieces of sapphire, powder and disks (sintered alumina) were also compared. The specific heat capacity of all three forms of aluminum oxide was assumed to be the same.

The measurements were performed with a TGA/DSC 1 equipped with the large furnace for temperatures to 1600 °C and the HSS2 sensor. The furnace was purged with nitrogen at 80 mL/min to prevent long-term oxidation of nickel.

**Calibration**

The TGA/DSC 1 was first adjusted according to the standard procedures using pure metals (Zn, Al, Au and Pd) in a 70-µL alumina crucible. If the direct method is used, the heat flow must be properly adjusted for the desired temperature range and crucibles. Since the calibration metals form alloys with platinum crucibles, the following procedure was adopted: a 30-µL alumina crucible was placed inside a 150-µL Pt crucible and the reference sample weighed into the alumina crucible. A separate crucible was used for each metal. The crucibles could be repeatedly used for calibration and adjustment. Zinc and aluminum however slowly oxidize so these samples could only used about ten times. In the case of palladium, a small amount of vaporization has to be taken into account. This was done by checking the sample weight each time.

**Crucibles and sample mass**

A series of measurements was first performed to decide which type of crucible would be best for \( c_p \) determinations. Figure 1 shows the sample temperature curve and the heat flow curves of sapphire, platinum and nickel. The lower curves show the \( c_p \) curves of platinum together with three numerical values (rounded). The values were used to calculate the results presented in Table 2.
using crucible lids. Comparison of the results of the two 150-µL crucibles (typical masses are noted in the figure) showed that the influence of the type of sample (e.g. color, thermal conductivity) was much more apparent in the alumina crucible than in the platinum crucible. This affects not only the magnitude of the heat flow but also the repeatability and accuracy of the $c_p$ measurement. Further determinations were therefore performed only using the platinum crucible.

The results showed that measurements must be performed using a lid. Platinum lids however tend to weld to platinum crucibles at temperatures above 1000 °C, especially when new crucibles are used. This can be prevented by coating the lid with a very thin film of inert material. In the measurements performed here, a thin film of Ceramabond™ (ME-71302) was applied to the underside of the lid.

Accurate $c_p$ measurements require the use of a large sample masses in order to obtain a large heat flow signals. The reproducibility of the signal must also be very good. This is the reason why the 150-µL crucibles were used because they allow a large amount of sample to be used in comparison with the mass of the crucible. The optimum amount of sample for a $c_p$ determination is when the crucible is about three-quarters full. Furthermore, the mass of sample should be chosen so that heat capacity of the sample matches the heat capacity of the sapphire reference and thus produces a similar heat flow signal. This is, however, not always possible because it depends on the density of the material (e.g. with alumina powder).

The sapphire reference consisted of several sapphire disks (4.8 mm diameter, ME-00017758).

### Temperature program

In general, a heating rate of 20 K/min was used. This is a compromise between a large heat flow signal, good temperature homogeneity within the sample, and the time for the system to reach a steady state in the dynamic segment. Optimum measurement reproducibility was achieved by performing the experiments one after the other at equal intervals. With alumina crucibles, the sample robot can ideally be used.

The method included a low and a high temperature range. This involved heating from 450 to 650 °C at 20 K/min with 10-minute isothermal phases before and after heating. This was followed by a jump to 1200 °C, an isothermal phase of 10 min, heating to 1400 °C, and another 10-minute isothermal phase (see Figure 1). The system was allowed to stabilize at 450 °C and 1200 °C before starting the measurement. The isothermal phases must be long enough for the DSC signal to stabilize before the next heating ramp begins.

### Results

#### Sapphire method

Figure 2 shows the curves obtained for a typical evaluation. The upper diagram displays the heat flow curves of platinum and sapphire. Both curves were evaluated using the “Cal, with Sapphire...” DSC function of the STAR® software. The lower diagrams show the resulting curves for the specific heat capacity of platinum separately for the lower and higher temperature ranges. Three values were automatically evaluated from the curves and are presented in the table.

Table 2 summarizes the results of the $c_p$ determinations of different materials obtained using crucible lids.
tained using the sapphire method. Three separate measurements of each sample were performed in the lower and higher temperature ranges. Each measurement of the same material was performed with the same single sample. The samples were re-inserted into the furnace each time prior to measurement. The table presents the mean values and the standard deviation of three individual values as well as the deviation from the literature values given in Table 1. The reference value for aluminum oxide was assumed to be same as that of sapphire.

The mean values of the specific heat capacities of different materials show a maximum deviation of about 10% from the corresponding reference values. The smaller values (e.g. of Pt) vary more strongly than the larger values (e.g. aluminum oxide). The results for the metals tend to deviate to larger values and for the oxides to lower values. The deviations also tend to be greater at higher temperatures than at lower temperatures. The repeatability (standard deviation) is rather better at low temperatures than at high temperatures. Comparison of the results for aluminum oxide powder and aluminum oxide lids show that the influence of packing density is hardly noticeable. In summary, a platinum crucible used with a lid gives very good results for quantitative $c_p$ determinations at high (and low) temperatures. An accuracy of $\pm 10\%$ can be expected.

**Direct method**

The measurements obtained for the sapphire method can also be used to directly determine $c_p$ values according to eq 3. The results are shown in Table 3. The large deviations indicate that this method is not suitable for $c_p$ determination.

**Conclusions**

Two standard DSC methods were used to determine $c_p$ at temperatures up to 1600 °C. In general, results from the direct method show that repeatability and absolute accuracy are strongly temperature dependent. The method cannot therefore be recommended. In contrast, the sapphire method has the great advantage that no additional calibrations are needed for special crucibles or gases. The best way to minimize the influence of the thermal conductivity of the sample and other effects is to use platinum crucibles with lids. Depending on the temperature range, measurements of pure substances are accurate to $\pm 5\%$ to $\pm 10\%$ in comparison with literature values. To achieve high reproducibility and accuracy, measurements of a series should be performed directly one after the other at constant time intervals. This is most easily done using the sample robot. Furthermore, one or two blank measurements should be performed at the beginning of a series but not used for subtraction.

**Literature**

[6] DIN 53765, Testing of plastics and elastomers; thermal analysis, DSC method, Deutsches Institut für Normung / German Institute for Standardization
[7] DIN 51007 Thermische Analyse (TA); Differenzthermoanalyse (DTA); Grundlagen, Deutsches Institut für Normung / German Institute for Standardization
[8] ASTM E1269, Determining specific heat capacity by DSC, ASTM International Westconshohocken, USA

**Publishing Note:**

This application has been published in the METTLER TOLEDO Thermal Analysis UserCom No. 27. See www.mt.com/ta-usercoms