Measuring specific heat capacity

1. Measuring specific heat capacity

The specific heat capacity, often referred to as the specific heat, is a measure of the amount of energy required to raise the temperature of 1 g (or 1 mole) of a substance by 1 K. The symbol used is \( c_p \), or \( C_p \) for the molar quantity. The ‘p’ in the lower position stands for ‘at constant pressure’. The SI units for the specific heat capacity are J g\(^{-1}\) K\(^{-1}\) (also J/g K) or J mol\(^{-1}\) K\(^{-1}\) (also J/mol K).

Usually the specific heat is not measured during first order transitions in the physical state (e.g. melting), where it can be infinitely large. The values for solids and liquids range from 0.1 to 5 J g\(^{-1}\) K\(^{-1}\). The specific heat of most substances increases with increasing temperature; the measurement is therefore often performed over a relatively large temperature range.

Some examples at 25 °C:

<table>
<thead>
<tr>
<th>Substance</th>
<th>Alumina</th>
<th>Aluminum</th>
<th>Lead</th>
<th>Polystyrene</th>
<th>Water</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wert [J g(^{-1}) K(^{-1})]</td>
<td>0.895</td>
<td>0.776</td>
<td>0.129</td>
<td>1.3</td>
<td>4.18</td>
</tr>
</tbody>
</table>

With the STAR\(^\text{TM}\) Software, 4 different possibilities for the determination of the specific heat are available, each with its own advantages and disadvantages. The various methods will be described later on in detail. First of all, here is a survey of the various temperature programs:

- Direct method
- Steady state ADSC
- Sapphire method
- ADSC
1.1 General information about measurement conditions

DSC cell
The FR55 must be well ‘burned-in’ (e.g. 10 minutes at 600 °C with air flow in order to remove any volatile impurities). After this cleaning process the sensor sits very tightly, which is a further requirement for accurate \( c_p \) measurements. Any ash or dust is carefully blown away with compressed air (dust under the crucible leads to poor reproducibility of DSC curves). With the sample changer, the 34 recesses on the turntable must be freed regularly from any dust.

Temperature calibration
Since the specific heat is a function of temperature, the temperature should be calibrated (checked) in the measurement range to be used and if necessary adjusted. In addition, the heating rate enters into the result in both the direct and the steady-state methods. The heating rate is only right if the temperatures are correct.

Tau lag adjustment
This is a prerequisite for accurate melting point determinations, but is of no great importance for the accuracy of \( c_p \) measurements.

Type of crucible
Up until now most experience has been gained with the 40 \( \mu l \) standard aluminium crucibles. Previous measurements with the tall Al crucibles (160 \( \mu l \)) gave poorer \( c_p \) values in spite of the increased signal obtained with the larger sample amount. The new lighter Al crucibles (20 \( \mu l \)) are advantageous because the sample can be pressed down against the bottom of the crucible, thereby improving the thermal contact. This is particularly important for temperature modulated methods. The disadvantage is the poorer mechanical stability. This can lead to a deformation of the crucible when it is used repeatedly in the sample changer (reference crucible). In addition the crucible is unsuitable for use with volatile samples because it can not be hermetically sealed.

Reference crucible
The reference crucible remains in the same position for all measurements. If it does not have a centering pin then its exact orientation should be checked visually from time to time. An atmosphere of static air or 50 ml nitrogen per minute is usual.

Sample preparation
Good contact with the bottom of the crucible is important. The situation is ideal with liquid samples and with flat disks. Powder samples of medium particle size (about 0.1 mm) are also good. Very fine powders often contain a lot of air, which makes them poor thermal conductors; they can usually be compacted with a PTFE rod. Samples of low thermal conductivity give \( c_p \) values that are about 5% too low. It is important that the bottoms of the crucibles are flat and not deformed.
Sample quantity
The size of the measurement signal is proportional to the sample amount. This means, in principle, with \( c_p \) measurements (except ADSC): the larger the sample the better. One should try to obtain a signal of at least 5 mW (maximum about 10 mW). This requires a 30 mg sample with a \( c_p \) of 1 J/gK at a heating rate of 10 K/min.

For \( c_p \) measurements with sinusoidal temperature modulation, signal amplitudes of 1 mW are optimal; with a temperature program of amplitude of 1 K and a cycle time of 1 min this corresponds to a sample of about 15 mg.

Weighing accuracy
Weighing errors are important in any \( c_p \) measurement. A microbalance such as the MT5, which was used for all the measurements in this work, is best.

Blank curves
All accurate \( c_p \) measurements should be blank curve corrected. The measurement of several blank curves is recommended before the sample measurements. The first two are to condition the measuring cell. The third is used for the calculation (the STARe Software always uses the most recent blank curve of the relevant method; if this is an outlier it should be deleted from the database).

Heating rate
A heating rate of 10 K/min is normally used for classical \( c_p \) measurements. Time-saving heating rates of 20 K/min give good results. A larger temperature range is required because about 1 minute is needed to reach a state of dynamic equilibrium. Reliable \( c_p \) values can only be obtained in this region.

1.2 The direct method
This is based on the 'dynamic definition' of the specific heat and is equal to the heat flow \( HF \) divided by the heating rate \( \beta \) and the sample mass \( m \).

Possible errors:
1. Blank curve correction: this is essential because an asymmetry of up to about 2 mW can occur. Compared with a sample signal of 10 mW, for example, an error of 20 % would arise if the blank curve correction was not applied.
2. Accuracy of the calorimetric calibration (\( E_{in} \)): an error limit of 1 % is aimed for. The weighing error may therefore only be about 0.1 % (5 mg in 5 mg). In particular, when using the automatic sample changer, it is recommended that the previously flattened indium sample be pressed tightly in the middle of the Al standard crucible with a PTFE rod (place the crucible on a hard, absolutely flat surface, e.g. a glass plate). This ensures that the sample remains in the middle of the crucible even when measurements are performed repeatedly.
3. Temperature function of \( E_{rel} \): the response curve between 0 °C and 250 °C that is stored in the STARe Software has an error limit of 3 %. A more accurate function with a maximum error of 1 % in this temperature range is being developed. At much lower or higher temperatures the error is somewhat larger.
4. Reproducibility of the sample and blank curves: the reproducibility of the blank curve corrected measurement curve is around ±0.1 mW with the FRSS sensor. These values are valid for temperature range of 50 °C to 200 °C and for a preconditioned measuring cell (reject the first two blanks). The measurement uncertainty is therefore ±2 % with a sample signal of 5 mW.

Total error (only those that can not be avoided according to sections 2. to 4. above): the total error is approximately equal to the square root of the sum of the squares of the individual errors i.e. the square root of \( 1^2 + 2^2 + 3^2 = 3.7 \% \) (with the new \( E_{rel} \) temperature function the square root of \( 1 + 2^2 + 1 = 2.5 \% \)). In addition the sample weighing errors must also be taken into account. Series of measurements in the range 50 °C to 200 °C with samples of good thermal conductivity show errors of -5.5 % to +2.0 %.
1.3 The ‘steady state’ ADSC

In this method the sample is subjected to a periodic heating and cooling program (sawtooth). The heating and cooling rates lie between 2 K/min and 10 K/min and need not be identical. A segment should last at least 2 minutes so that the sample is in a state of dynamic equilibrium (steady state). Samples of poor thermal conductivity require 4 to 5 minutes. The evaluation routine Math/Steady State ADSC Cp performs a cp determination towards the end of each segment (analogous to the direct method).

The blank curve is measured with an empty crucible of the same mass as for a sample in order to avoid additional smoothing of the automatic blank curve (identification e.g. blank curve sample weight 0 mg).

Possible errors:
The possible errors are similar to those of the direct method. The measurement signals are somewhat smaller due to the lower heating rates. The reproducibility of the DSC signal is however better because of the shorter segments. With the new Ew temperature function we expect an error of about 2.5 %.

1.4 The saphire method

The saphire method for cp determination has been used for more than 30 years. The DSC signal of the sample is compared with the DSC signal of the calibration sample of known specific heat. Both curves are blank curve corrected (automatic blank curve correction).

A total of three measurements are made:
1. Blank (crucible without lid on both sides, the reference crucible remains in the same place for all measurements),
2. Calibration (crucible with lid, the difference in mass compared with the crucible of the blank measurement isothermal segments of 5 minutes. The evaluation can use as many segments as desired.

Possible errors:
The saphire cp standard technique makes errors in Ew and Ew irrelevant. There is only the reproducibility of the sample and the saphire curves to consider. With the FRS5 sensor, the reproducibility of the blank curve corrected measurement curve is ±0.1 mW. This value is valid for the temperature range 50 °C to 200 °C with a preconditioned measuring cell (reject the first blank). The measurement uncertainty with a sample signal of 5 mW is therefore ±2 %. The total error (square root of the sum of the squares of the individual errors) is the square root of (2^2 + 2^2) = 2.8 %. In addition, the weighing errors of the sample and the saphire must be taken into account. Series of measurements with samples of good thermal conductivity gave errors of -1.4 % to +0.7 % in the range 50 °C to 200 °C. It is advantageous to measure segments not larger than 100 °C to 200 °C. If a wider temperature range is of interest, then it is better to divide it up into segments of maximum 200 °C separated by isothermal segments of 5 minutes.

1.5 ADSC with a sinusoidal temperature program

In alternating DSC (ADSC) the temperature is varied sinusoidally as a function of time and is superimposed on the average heating rate. The heat capacity of the sample gives rise to a periodic measurement signal. The blank curve corrected amplitude is proportional to the heat capacity.

A heat capacity calibration standard is required just as with the saphire method. It consists of the lid of the crucible. The cp temperature functions of all Mettler crucible materials are stored in the STAR database. There are 3 measurements to be performed:
1. Blank (crucible without lid on both sides, the reference crucible remains in the same place for all measurements)
2. Calibration (crucible with lid, the difference in mass compared with the crucible of the blank measurement
3. Sample (in the crucible with lid with similar mass (difference < 20 mg) as for the calibration). The evaluation routine Math/ADSC \( C_p \) determines the amplitude using Fourier analysis. In addition to the formula shown in figure 4, the signal damping is compensated mathematically by the phase change of the sample measurement.

Possible errors:
The error possibilities are similar to those of the sapphire method. The calibration heat capacity is however quite small (corresponds to the mass of the lid). It is better to use smaller samples with ADSC in order to keep the signal damping low. For the same reasons high frequencies are not used. Normally the cycle time is not less than 1 minute. The average heating rate lies between -5 K/min and +5 K/min (the maximum heating and cooling rates of the method must be lower than the maximum heating and cooling rates of the modules).

An amplitude of 1 K is normally used.

1.6 Comparison of the four different methods

<table>
<thead>
<tr>
<th></th>
<th>Direct</th>
<th>Steady State</th>
<th>Sapphire</th>
<th>ADSC (Sine)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Principle</td>
<td>heat flow divided by the heating rate and sample mass</td>
<td>comparison with a ( C_p ) standard that is subjected to the same temperature program</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Accuracy attainable</td>
<td>±5 % 1)</td>
<td>±4 % 1)</td>
<td>±2 %</td>
<td>±3 %</td>
</tr>
<tr>
<td>Disadvantages</td>
<td>• not very accurate</td>
<td>• not very accurate</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>• long measurement time</td>
<td>• long measurement time</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>• 3 measurements required, can be run at 20 K/min however</td>
<td>• 3 measurements required, long measurement time</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>• frequency dependent</td>
<td>• frequency dependent</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Advantages</td>
<td>• shortest measurement time</td>
<td>• yields also quasi isothermal ( C_p )</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>• highest accuracy for standards: DIN 51007 ASTM E 1269</td>
<td>• yields quasi isothermal ( C_p )</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>• ( C_p ) also during non-reversing reactions</td>
<td>• ( C_p ) also during non-reversing reactions</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>• in modern trend</td>
<td>• in modern trend</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Automatic blank curve</td>
<td>yes</td>
<td>no</td>
<td>yes</td>
<td>no</td>
</tr>
<tr>
<td>Software options required</td>
<td>specific heat</td>
<td>Method window, Relative loop, Mathematic, ADSC</td>
<td>specific heat</td>
<td>Method window, Relative loop, ADSC ( C_p )</td>
</tr>
</tbody>
</table>

1) With the new \( E_\infty \) temperature function (in version 5.12) of the DSC sensor FRS5, 2.5 % to 3 % can be attained.

Publishing Note:
This application has been published in the METTLER TOLEDO Thermal Analysis UserCom No. 7.
See [www.mt.com/ta-usercoms](http://www.mt.com/ta-usercoms)