Thermal Analysis Application

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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/gK) or J mol^{-1} K^{-1} (also J/mol K).

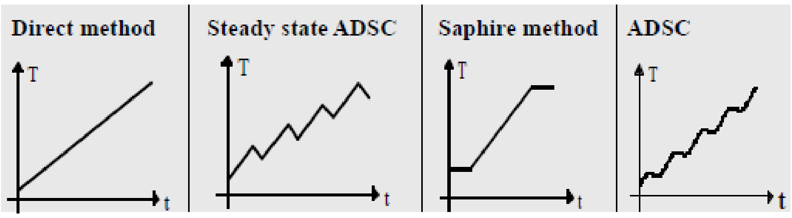
Usually the specific heat is not measured during first order transitions in the physical state (e.g. melting), where it can be infinitely large.

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:

Substance	Alumina	Aluminum	Lead	Polystyrene	Water
Wert [J g^{-1} K^{-1}]	0.895	0.776	0.129	1.3	4.18

With the STAR^e 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:



1.1 General information about measurement conditions

DSC cell

The FRS5 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.

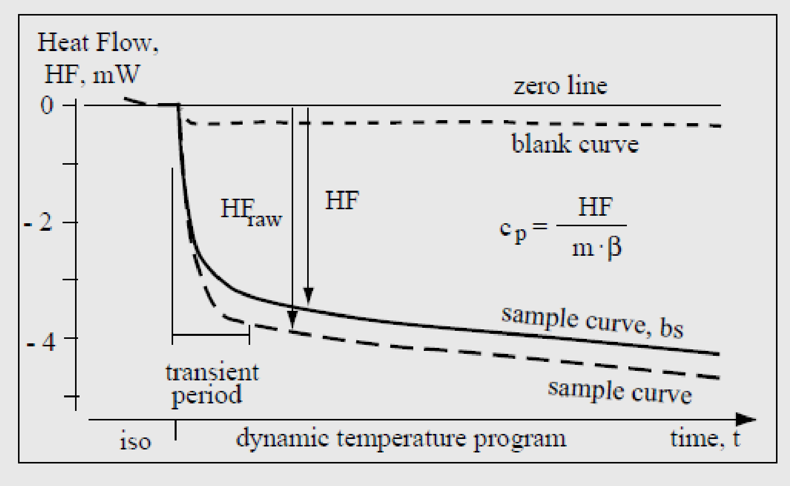


Fig. 1: The heat flow HF is obtained from the raw DSC signal HF_{raw} by blank curve subtraction (bs). The evaluation should begin after the state of dynamic equilibrium has been reached.

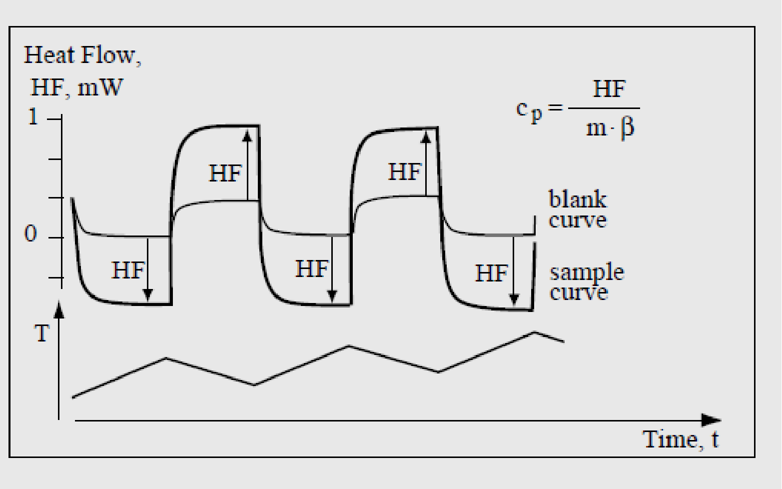


Fig. 2: The sawtooth temperature program shown below produces the DSC curves shown above. The blank curve is subtracted from the sample curve, so that the evaluation method Math/Steady State ADSC C_p can convert the difference of the heat flows HF to c_p.

Type of crucible

Up until now most experience has been gained with the 40 µl standard aluminum crucibles. Previous measurements with the tall Al crucibles (160 µl) gave poorer c_p values in spite of the increased signal obtained with the larger sample amount. The new lighter Al crucibles (20 µl) 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.

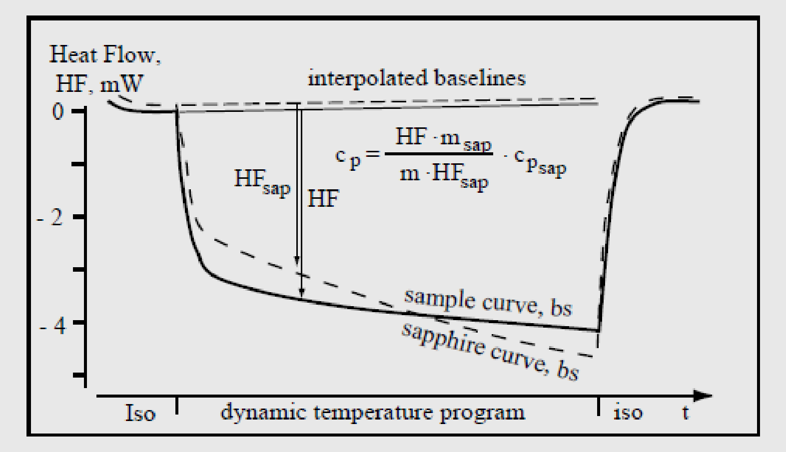


Fig. 3: The blank curve corrected sample and saphire measurements are shown. The interpolated baseline between the isothermal levels at the start and end temperatures is automatically calculated in order to improve the accuracy of the heat flow HF. The literature values for the c_p of saphire as a function of temperature function are included in the evaluation program.

Sample quantity

The size of the measurement signal is propotional 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 measuremnts 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 STAR^e 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 the specific heat and is equal to the heat flow HF divided by the heating rate ß and the sample mass m.

Possible errors:

1. Blank curve correction: this is essential because an assymetry 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 µg 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 STAR^e 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 FRS5 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 $1 + 2^2 + 3^2 = 3.7$ % (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 c_p 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 E_{rel} temperature function we expect an error of about 2.5 %.

1.4 The saphire method

The saphire method for c_p 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: blank (empty crucible), saphire (3 small saphire disks of 4.8 mm diameter, ME 17 558 as the calibration sample) and the sample itself. A blank curve correction is in this case also essential.

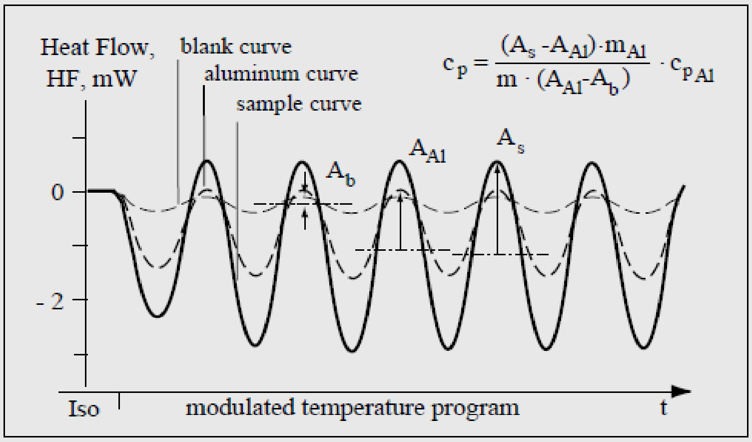


Fig. 4: The evaluation routine Math/ADSC Cp determines the phase-correct amplitude differences (1. blank curve, 2. calibration curve, 3. sample curve). The equation for the c_p determination includes the difference of the amplitudes because the crucible lid that serves as the c_p standard is also measured with the sample.

Possible errors:

The saphire c_p standard technique makes errors in E_{In} and E_{rel} 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 seperated by isothermal segments of 5 minutes. The evaluation can use as many segments as desired.

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 periodical 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 c_p temperature functions of all Mettler crucible materials are stored in the STAR^e 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

is entered as the sample weight),
3. Sample (in the crucible with lid with similar mass (difference < 20 µg) 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 possibilites are similar to those of the saphire 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.

The longer measurement times (3 to 10 times), compared with the saphire method, are only justified if the specific heat is to be measured (also isothermally) during chemical reactions or certain physical transitions. Please note: the Al crucibles are only suitable for certain chemical reactions. Series of samples with good conductivity gave errors in the range -2.5 % and +3 %.

1.6 Comparison of the four different methods

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

1) With the new E_{rel} 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**