TAWN tests for quantitatively measuring the resolution and sensitivity of DSCs (version 2.1)

1. Introduction

There are many properties that characterise the performance of differential scanning calorimeters (DSCs). Among the properties that directly influence the appearance of measured curves are the resolution and the sensitivity.

Here the property resolution means the ability to observe two thermal effects, which are close to one another, separated. And the property sensitivity means the ability to observe very small thermal effects. Note that sensitivity here is not interpreted as its physical definition: the size of the measured signal (electrical potential [mV]) divided by the causing physical property (heat flow [mW]); it is more a sort of signal-to-noise ratio. The interpretations of resolution and sensitivity are demonstrated in figures 1 and 2.

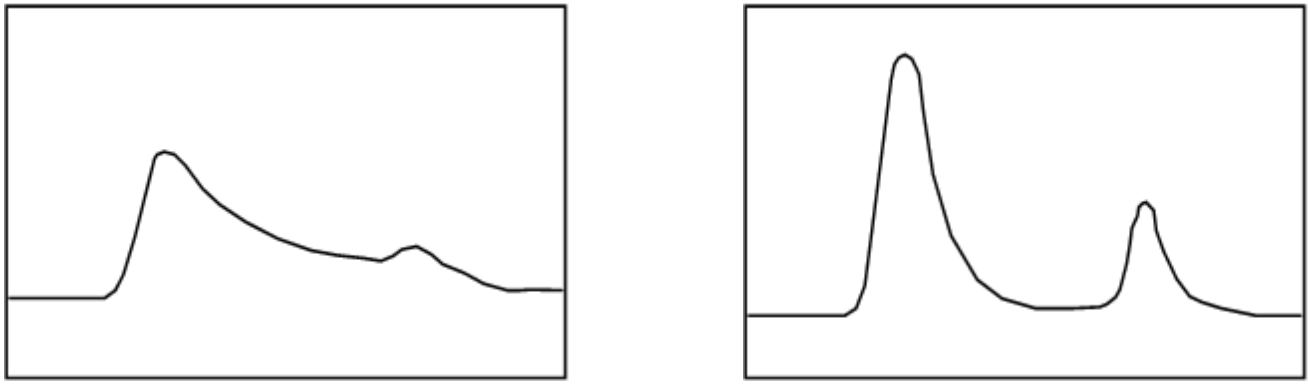

Fig. 1 - For comparable measurements in different DSCs, the DSC-curve shown in the right graph shows a better resolution than the DSC-curve shown in the left graph. Endothermic effects are plotted upwards.

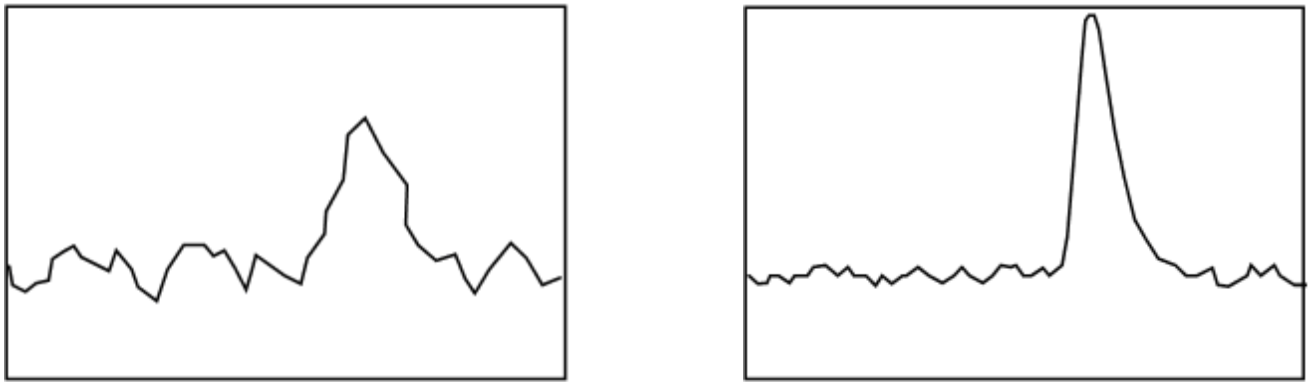

Fig. 2 - For comparable measurements in different DSCs, the DSC-curve shown in the right graph shows a better sensitivity than the DSC-curve shown in the left graph. Endothermic are effects plotted upwards.

The Dutch Society for Thermal Analysis and Calorimetry (TAWN) developed tests for quantitatively measuring the resolution and sensitivity of DSCs. These tests made it possible to compare different DSCs with respect to resolution and sensitivity [1], and the tests were adopted widely. However, since the tests were presented, the performance of modern DSC instruments has improved significantly. While the sensitivity test is still very useable, the resolution test is not discriminative any more and needs to be updated.

Marti et al. [2] published a paper on the resolution of DSCs in which some materials were evaluated as possible new test substances; n-hexatriacontane appears to be the most promising. This substance shows two phase transitions only about 2 K apart. Board members of the TAWN further investigated the applicability of n-hexatriacontane to quantitatively measure the resolution of DSCs. It was decided to provide a new test for the quantitative measurement of the resolution based on the work of Marti et al. [2]. The test for measuring the sensitivity of DSCs was only slightly updated.

In this document a detailed protocol is presented which prescribes how the measurements must be performed and how the results must be analysed. Because the resolution and the sensitivity of a DSC are not independent from one another, it is recommended to always measure the resolution and the sensitivity together.

As was also indicated in the original publication [1], the total quality of a DSC can not be determined using these test. The reason is that resolution and sensitivity are only two properties out of a large number of properties which characterise a DSC. Only a user can determine the quality of a DSC by considering all properties that are relevant to him based on his needs and wishes.

2. Protocol for measuring the resolution of a DSC

2.1. Experimental

The measurement must be performed using the following experimental parameters:

- *Crucibles*
  Aluminium standard crucibles, closed with a lid. Carefully measure the mass of the used crucibles (including the lid) and indicate this on the results form. Use the same type of crucibles for both the resolution test and the sensitivity test. For comparison reasons, crucibles with a total mass about of about 45 mg are recommended.
- *Reference*
  Empty crucible.
- *Sample*
  An amount of (5.00 ± 0.10) mg of the substance n-hexatriacontane in a crucible. This substance is a normal alkane with 36 carbon atoms in the chain. For comparison reasons, a sample with a purity of about 98% supplied by Sigma-Aldrich (H 12552) is recommended. For participation in the TAWN round robin test, the use of a sample supplied by the TAWN is mandatory. Requests for a sample can be sent by email to wim.deklerk@tno.nl.
- *Purge gas*
  Nitrogen; 50 mL/min.
  Although it is not recommended, alternatively also air can be used as a purge gas, and if the DSC cell cannot be purged, a static air atmosphere can be used.
  No other gases are allowed. Carefully indicate the atmosphere on the results form. Use the same purge gas (and flow rate) for both the resolution test and the sensitivity test.
- *Measurement mode*
  Some instruments can be operated in different modes. If this is the case, it is important that

measurements are performed in the standard mode (or most common mode). And because resolution and sensitivity are not independent from one another, the resolution test and the sensitivity test must be performed using the same mode. In addition, also other modes of operation may be used, but please treat results obtained at different modes as results obtained with different DSCs. Therefore, for each mode of operation fill in a separate results form. In any case, describe the used mode of operation as carefully as possible on the results form.

- *Temperature program*
  The temperature program must consist of at least 4 steps:
  1) Isothermal at 100 °C (373 K) for 1 min;
  2) Cool from 100 °C to 25 °C (373 K - 298 K) at a cooling rate of 10 K/min;
  3) Isothermal at 25 °C (298 K) for 1 min;
  4) Heat from 25 °C to 100 °C (298 K - 373 K) at a heating rate of 5 K/min.
  This mandatory part of the temperature is plotted in figure 3.
  The 4th step of this temperature program (heating at 5 K/min) is important for the evaluation. It must be measured using a sampling rate of 1 data point per second, or higher (sampling time ≤ 1 s).

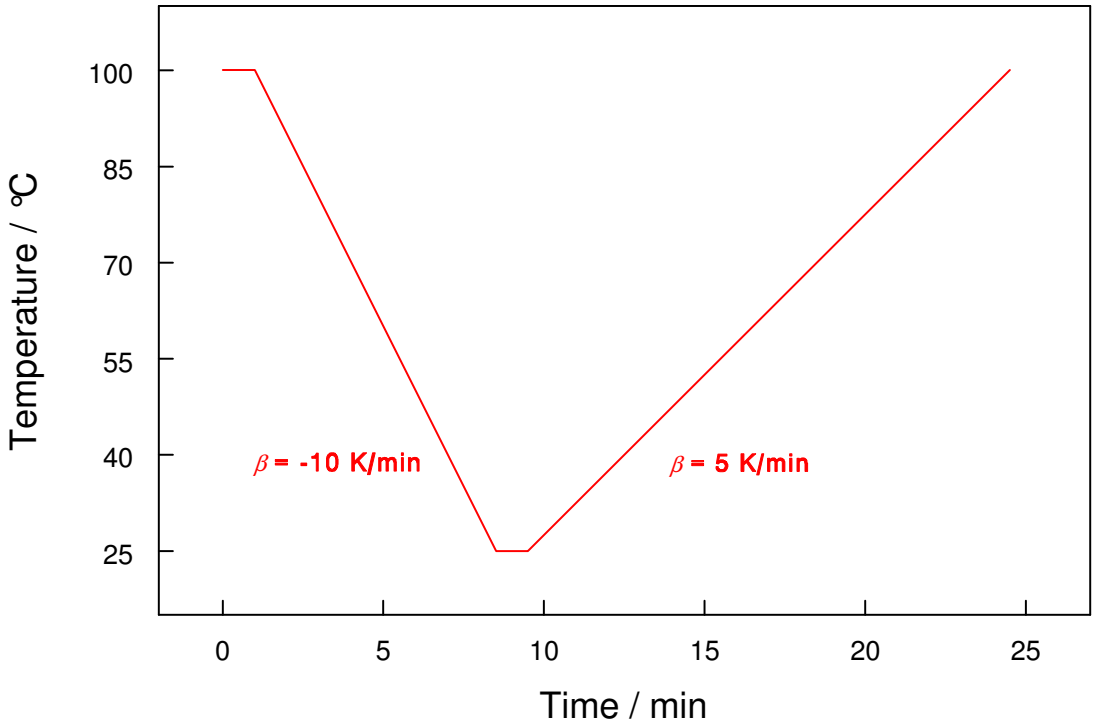

Fig. 3 - Temperature program prescribed for the resolution test. Only the mandatory part is shown.

In addition measurements may also be performed at other heating rates. Those who want to contribute to this part are specifically asked to expand the temperature program with 6 additional series of the above mentioned 4 steps, but now with different heating rates in each 4th step. Please use the following heating rates, in the given order:
10 K/min; 40 K/min; 1 K/min; 20 K/min; 3 K/min; and 5 K/min.
For heating at a rate of 40 K/min, it is recommended to use an end temperature of 120 °C (393 K).
All heating curves must be measured using a sampling rate of 1 data point per second, or higher (sampling time: ≤ 1 s).

2.2. Analysis of the results

After the measurement is performed as described in the protocol given in section 2.1, the measuring results must be presented and analysed as follows.

- The raw data[①] must be presented and analysed, without any data manipulation like smoothing or deconvolution. Do not subtract an empty pan measurement. If one wants, manipulated results can also be presented and analysed, but always in addition to the raw data. This allows to observe the effect of the data manipulation. Since the resolution and sensitivity of a DSC are not independent, when manipulation procedures are used, perform exactly the same manipulation procedures on the results of both the resolution test and the sensitivity test.
- Plot the DSC-curve that was recorded during the fourth step of the temperature program (heating at 5 K/min) in two different ways. First in a graph of the measured heat flow versus temperature, then in a graph of the measured heat flow versus time. Two significant endothermic peaks, which (in most cases) are not completely separated, should be present in the heating curves, together with some minor effects at the low-temperature side of the double peak.
- At the high-temperature side of the double peak, the recorded curve should be more or less a straight line. Here the sample is completely molten. Use this part of the curve as base line, and extrapolate the base line backwards into the transition region.
- For both not completely separated peaks, give the extrapolated onset temperatures (T_e). Evaluate the extrapolated onset temperatures as the temperatures at which the extrapolated linear parts of the ongoing sides of the peaks cross the extrapolated base line. Preferably the plot of heat flow versus temperature is used for this evaluation; see figure 4.
  And for the double peak, give the total enthalpy of transition ($\Delta_{tr}H$) evaluated from the observed curve. The total enthalpy of transition should be evaluated by peak integration; use the base line as indicated above and start the integration at the cross point of the extrapolated base line and the recorded DSC-curve (if there is no cross point in your plot, use your own integration range, and indicate this on the results form). This evaluation is preferably performed using the heat flow versus time curve.
- Use the plot of the recorded heat flow versus time to measure the peak height of the low-temperature peak of the double peak (this is the vertical distance between the maximum signal and the extrapolated base line). Also measure the valley level relative to the base line (this is the vertical distance between the signal of the valley between the two not separated peaks and the extrapolated base line). Calculate the resolution as the peak height divided by valley level[②]. Figure 5.illustrates how the values necessary for calculating the resolution are measured.
  Note that the TAWN considers the value of the resolution calculated from the heating curve at a rate of 5 K/min as *the* sensitivity of the DSC. Values calculated from heating curves at other rates (or from cooling curves) are only additional information.

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① It is recognised that hardly any modern DSC delivers real raw data. The data should be presented as 'pure' as possible, i.e. without any additional data manipulation.

② In the original resolution test [1], performed with test substance azoxyanisole, the resolution was calculated as a valley level divided by a peak height. This implied that a lower value indicated a better resolution. For this new resolution test the idea of Marti et al. [2] is followed, i.e. the resolution is calculated as peak height divided by valley level. So now a higher value of the resolution indicates a better resolution.

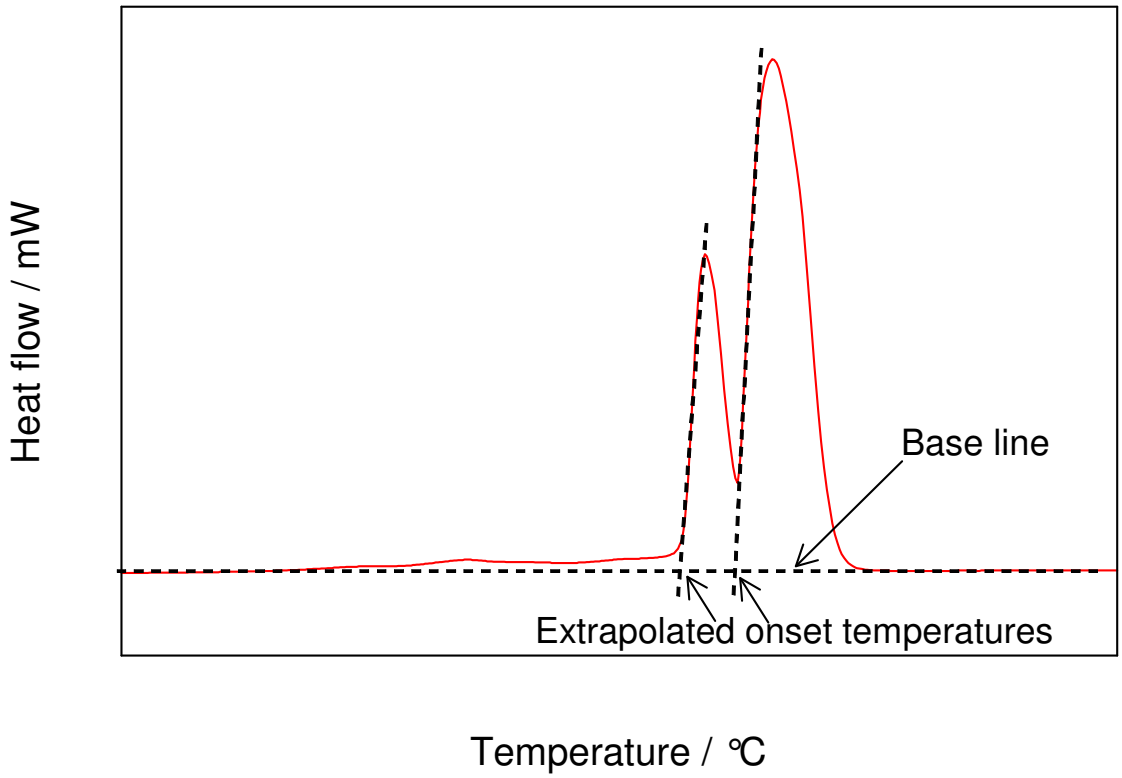

Fig. 4 - Plot of the recorded heat flow versus temperature at a heating rate of 5 K/min (endothermic effects plotted upwards). The positions of the base line and the extrapolated onset temperatures are indicated.

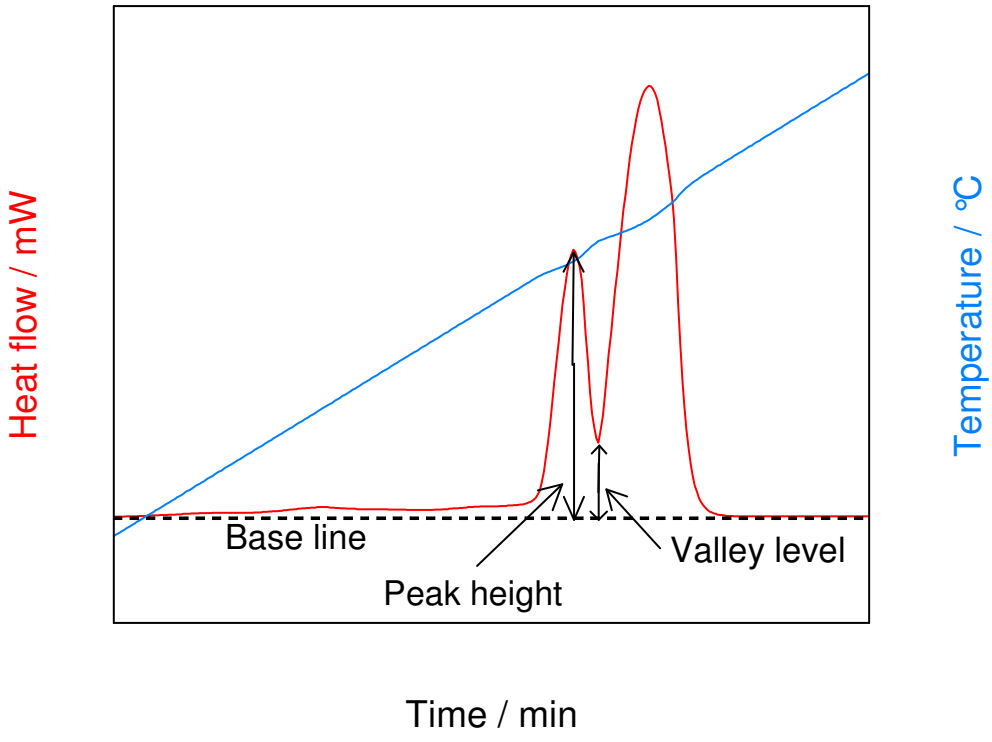

Fig. 5 - Plot of the recorded heat flow versus time at a heating rate of 5 K/min (endothermic effects plotted upwards). The values necessary to calculate the resolution of a DSC are indicated.

3. Protocol for measuring the sensitivity of a DSC

3.1. Experimental

The measurement must be performed using the following experimental parameters:

- *Crucibles*
  Aluminium standard crucibles, closed with a lid. Carefully measure the mass of the used crucibles (including the lid) and indicate this on the results form. Use the same type of crucibles for both the resolution test and the sensitivity test. For comparison reasons, crucibles with a total mass about of about 45 mg are recommended.
- *Reference*
  Empty crucible.
- *Sample*
  An amount of (0.25 ± 0.02) mg of the substance 4,4'-azoxyanisole (other names: p-azoxyanisole or 4,4'-azoxydianisole) in a crucible. For comparison reasons, a sample with a purity of about 98% is recommended (available from e.g. Sigma-Aldrich). For participation in the TAWN round robin test, a standard sample can be supplied by the TAWN on request.

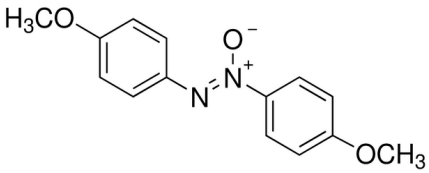

Fig. 6 - Structural formula of the substance 4,4'-azoxyanisole.

- *Purge gas*
  Nitrogen; 50 mL/min.
  Although it is not recommended, alternatively also air can be used as a purge gas, and if the DSC cell cannot be purged, a static air atmosphere can be used.
  No other gases are allowed. Carefully indicate the atmosphere on the results form. Use the same purge gas (and flow rate) for both the resolution test and the sensitivity test.
- *Measurement mode*
  Some instruments can be operated in different modes. If this is the case, it is important that measurements are performed in the standard mode (or most common mode). And because resolution and sensitivity are not independent from one another, the resolution test and the sensitivity test must be performed using the same mode. In addition, also other modes of operation may be used, but please treat results obtained at different modes as results obtained with different DSCs. Therefore, for each mode of operation fill in a separate results form.
  In any case, describe the used mode of operation as carefully as possible on the results form.
- *Temperature program*
  The temperature program must consist of at least 2 steps:
  1) Isothermal at 130 °C (403 K) for 5 min;
  2) Heat from 130 °C to 140 °C (403 K - 413 K) at a heating rate of 0.1 K/min.
  Additionally a third step may be applied to measure the sensitivity on cooling:
  3) Cool from 140 °C to 130 °C (413 K - 403 K) at a cooling rate of 0.1 K/min.
  A plot of the prescribed temperature program is given in figure 7. Preferably the curve recorded during the second step (and additionally also the curve recorded during the third

step) must be recorded at a sampling rate of 1 data point per second (i.e. sampling time 1 s)[3]. If this is not possible, use a sampling rate as close as possible to this value and clearly indicate the used sampling rate on the results form.

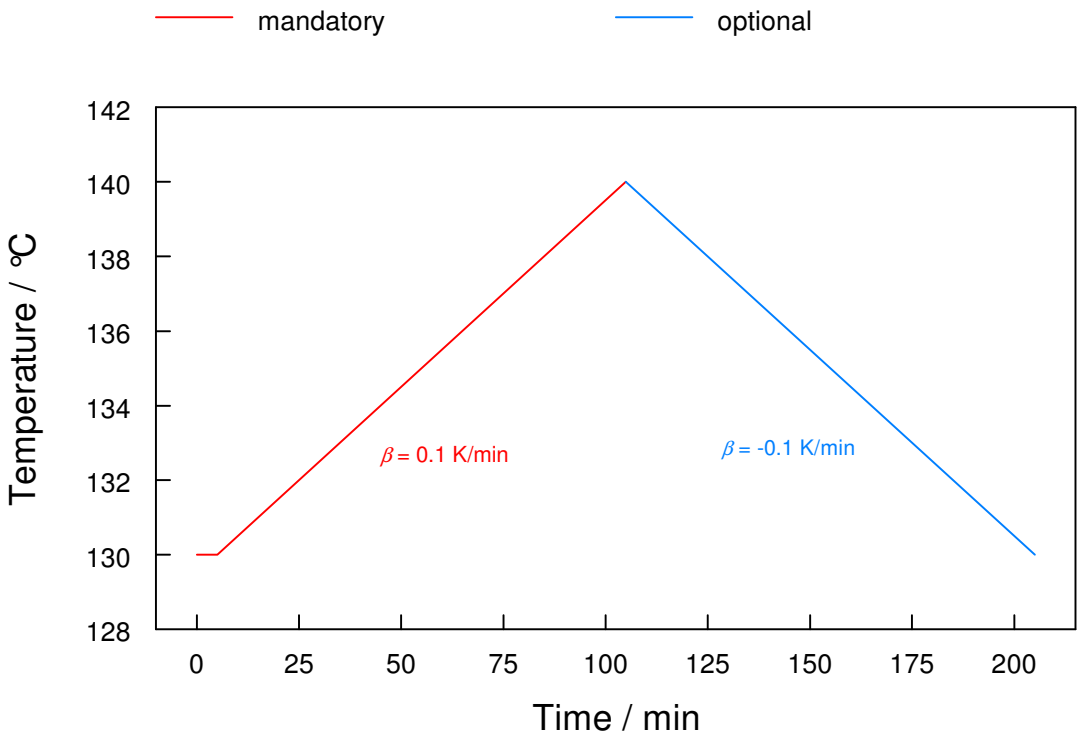

Fig. 7 - Temperature program prescribed for the sensitivity test. The optional cooling part is also shown.

3.2. Analysis of the results

After the measurement is performed as described in the protocol given in section 3.1, the measuring results must be presented and analysed as follows.

- The raw data[4] must be presented and analysed, without any data manipulation like smoothing or deconvolution. Do not subtract an empty pan measurement. If one wants, manipulated results can also be presented and analysed, but always in addition to the raw data. This allows to observe the effect of the data manipulation. Since the resolution and sensitivity of a DSC are not independent, when manipulation procedures are used, perform exactly the same manipulation procedures on the results of both the resolution test and the sensitivity test.
- Plot the DSC-curve that was recorded during the second step of the temperature program (heating at 0.1 K/min). If appropriate, also plot the DSC-curve that was recorded during the third step of the temperature program (cooling at 0.1 K/min).
  The horizontal axis of both plots should display the temperature, the vertical axis should display the heat flow. A single endothermic peak should be present in the heating curve. If the cooling curve was also recorded, this should display a single exothermic peak.

[3] In the original paper [1] a sampling rate of 1 data point per 10 s was prescribed. Experience has learned that a higher sampling rate is required for a better reproducibility.
[4] It is recognised that hardly any modern DSC delivers real raw data. The data should be presented as 'pure' as possible, i.e. without any additional data manipulation.

- For each peak, give the extrapolated onset temperature (T_e) and the enthalpy of transition ($\Delta_{tr}H$) evaluated from the observed peaks.
- On the low-temperature side of the transition, use data points over a range of 2 K to draw a linear line which represents the mean base line and extrapolate this line into the transition region. The base line should be (almost) horizontal. If this is not the case, a linear base line correction may be applied.
  Over the same temperature range of 2 K, draw parallel to this mean base line two other lines, such that all recorded data points are trapped within these two lines. Measure the vertical distance between these two lines (the top-to-top noise level). Also measure the peak height as the distance between the peak maximum (or minimum) signal and the signal of the extrapolated mean base line at the peak maximum temperature T_p. Calculate the sensitivity as the peak height divided by the top-to-top noise level. The procedure for calculating the sensitivity is graphically displayed in figure 8.
  Note that the TAWN considers the value of the sensitivity calculated from the heating curve as *the* sensitivity of the DSC. The value calculated from the cooling curve is only additional information.

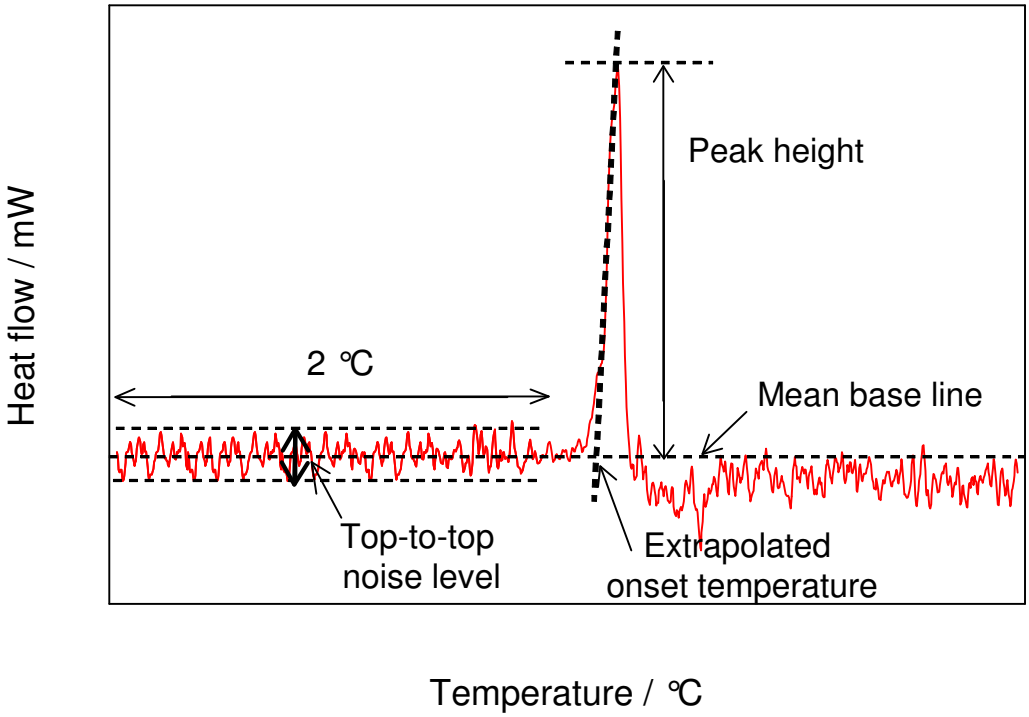

Fig. 8 - Graphical display of the procedure to calculate the sensitivity of a DSC.

References

1. P.J. van Ekeren, C.M. Holl and A.J. Witteveen, *A comparative test of Differential Scanning Calorimeters*, J. Therm. Anal. 49 (1997) 1105-1114.
2. E. Marti, E. Kaisersberger and W.-D. Emmerich, *New aspects of Thermal Analysis. Part I. Resolution of DSC and means for its optimization*, J. Therm. Anal. Calorim. 77 (2004) 905-934.