SOME PECULIARITIES OF THE DSC-2/-7 (PERKIN-ELMER) AND THEIR
INFLUENCE ON ACCURACY AND PRECISION OF THE MEASUREMENTS

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SUMMARY
    Perkin-Elmer power compensating differential scanning calori-
meters doesn't compensate the temperature differences totally.
Consequently the calibration factor is not constant but depends on
experimental parameters as calibration method heating rate, tem-
perature and sample mass. Though the effects are small, they
cannot be neglected for precision measurements. Furthermore a
temperature gradient in the bottom of the sample holder leads to
different temperature reading using different positions of the
sample or different sample pans. The consideration of these rather
small effects leads to a distinct increase of the accuracy and
precision of the instrument.

INTRODUCTION

    DSC-2 and DSC-7 calorimeters are widely used and well reputed.
As a consequence the user often trust blindly in the instructions
of the manufacturer. The later operation manuals only explain how
to handle the computer and the software, suggesting that the
software will fix every problem. There are no remarks about which
problems are solved in what mode. It follows from experience that
this holds for routine measurements, but that precision measure-
ments need a more particular knowledge of the peculiarities of
this type of calorimeter.

    With this knowledge it is possible to measure temperatures and
heats of a thermal event with an amazing accuracy, thus taking
advantage of the high precision of the instrument in question.

    The aim of this paper is to impart some properties of the
Perkin-Elmer calorimeter which are not mentioned in the manuals,
but should be known for to be able to perform precision measure-
ments.

SPECIAL PROPERTIES OF THE PERKIN-ELMER DSC

Measuring method

The Perkin-Elmer calorimeters are power compensating DSC. Two control circuits take care that the temperature of the sample and the reference ovens correspond to the set value (fitting to the heating rate). One circuit controls the average temperature of the sample and the reference holder. The other circuit adds a differential power which is proportional to the differential temperature between sample and reference holder, thus compensating the difference originating from thermal events in the sample.

The measuring signal of the calorimeter is an electric voltage proportional to the differential power of the second circuit. As this signal is proportional to the differential temperature, the output signal likewise is proportional to the latter. If the differential power is changed during thermal events (leading to 'peaks' in the measuring curve) thus there is a change in the differential temperature. As a result a non-zero differential power (i.e. heat flow) indicates a non-zero differential temperature. Because of the proportionality of both quantities the ordinate of the calorimeter output is likewise a heat flow and a measure for the differential temperature.

Although the Perkin-Elmer calorimeter is a power compensating one, the temperature difference between the reference and sample holders is not compensated totally. During the peak there is a temperature difference proportional to the signal. In this point the Perkin-Elmer calorimeters resemble the heat-flux calorimeters, but the actual temperature differences in power compensated calorimeters are smaller (depending on the design of the differential circuit). As a result all attributes of heat-flux-calorimeters depending on this temperature difference (ref. 1,2) can be found on the Perkin-Elmer calorimeters too, but in minor clearness. In particular the calibration factor is not a constant but depends on parameters as temperature, heat flow, heating rate and peak area. Though this effects are not very marked, they should be tested carefully and a precise calibration (including the variation of relevant parameters) should be done in case of major demands on accuracy of the measurements.

The user is advised to consider the power compensated DSC in principle as a heat-flux one with differential temperature ΔT as measuring signal, but with a lower ΔT for the same thermal event in the sample and thus lower effects being derived from this fact.

Temperature field within the sample holder

The sample and reference holders of a Perkin-Elmer DSC (fig.1a) are positioned within a aluminium block held at constant tempera- ture. As the heater is inside the sample holder and heat radiation and convection takes place at the surface of it, there is a heavy radial heat flow in the bottom of the sample holder with an attached temperature gradient. In fig.1b the temperature field of the bottom is plotted for different temperatures of the sample holder. The calculations are done with the aid of a simulation programme on the supposition that the radial heat flow increases with the cube of temperature (T^3-law of radiation).
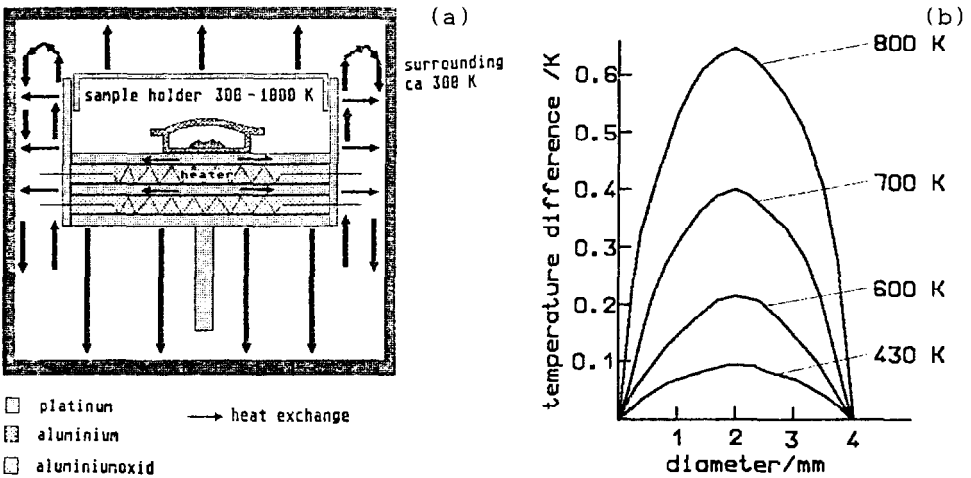

Fig.1. Perkin-Elmer DSC sample holder. (a) Construction principle. (b) Temperature field in the bottom at different temperatures.

The experimental checking of this fact was done as follows: Several very small samples (<0.2 mg) were placed in a line on the bottom of a sample pan, the first one put in the very centre, the last at the border. With this sample arrangement heating runs with the lowest possible heating rate (0.1 resp. 0.32 K/min) were performed. The result is represented in fig. 2 and 3. The results are in good agreement with the calculations represented in fig. 1b and show a significant dependence of the measured melting tempera- ture on the position of the sample in question. The differences of the measured transition temperatures ranges from 0.1 K for indium to 0.5 K for zinc. This differences are much greater than the repeatability of temperature measurements with a fixed sample position.
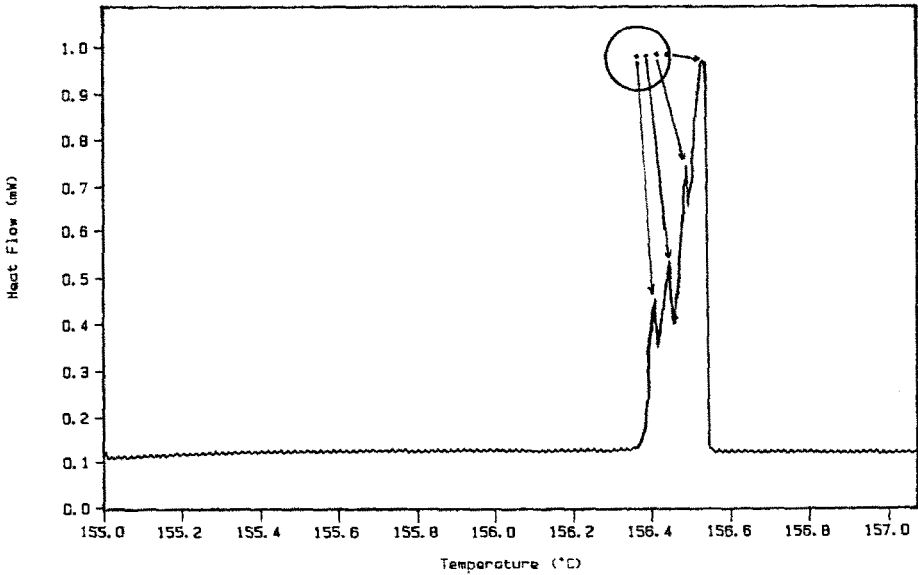
Fig. 2. Fusion of four indium samples (0.1 ... 0.3 mg) placed from centre to border of sample holder (DSC-7, 0.1 K/min).
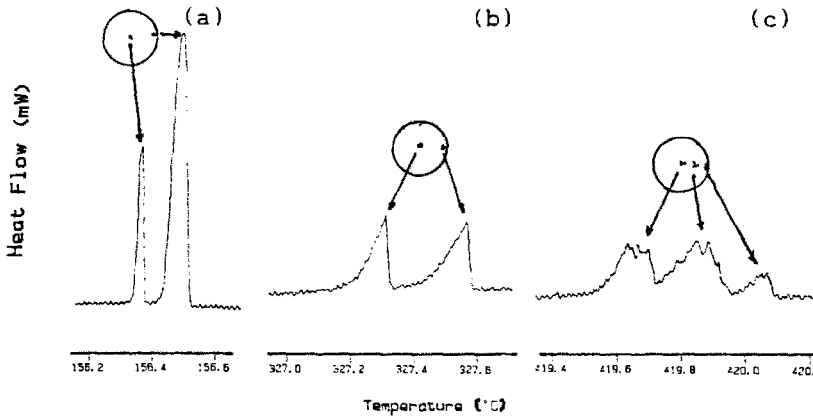

Fig.3. Fusion of samples of (a) indium, (b) lead, (c) zinc at centre and border of sample holder. (DSC-7, 0.2 K/min, ≈ 0.2 mg)

As aluminium has a much larger thermal conductivity than platinum, different sample pans (having a different contact surface) 'average' the temperature field of the bottom of the sample holder in a different manner. Any change of the sample pan, of the position of the sample inside the sample pan and of the position of the sample pan in the sample holder results in different transition-temperature measurements (fig. 4). This fact

should be reminded for precision measurements.

On the other hand the temperature field in the bottom of the sample holder (and thus in the sample pan) causes a finite width of transition peaks, which cannot be reduced further by decreasing the heating rates[1].
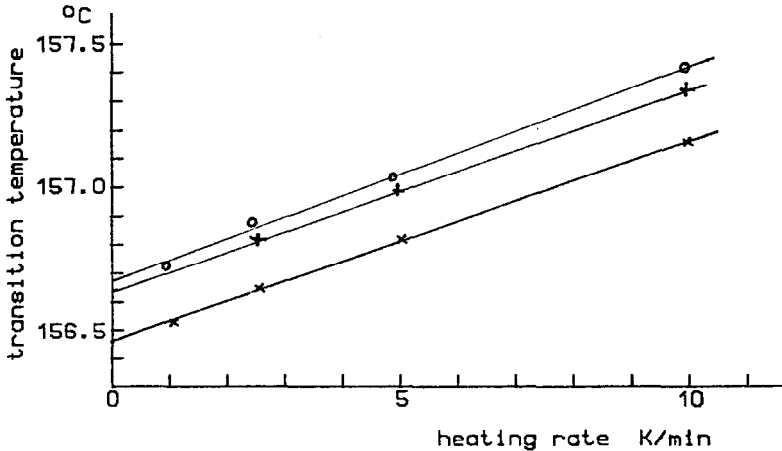

Fig. 4. Transition temperature (extrapolated onset) of three samples of indium at different heating rates. Sample change causes much larger variations of onset temperatures as the precision of the results from one sample predict.

Change of measured onset-temperature at different heating rates

Fig. 4 and 5 shows the dependence of the onset temperature on the heating rate for different materials. The function is strictly linear up to heating rates of 160 K/min, thus an extrapolation to a heating rate of zero (steady state or equilibrium transition temperature) is easy done. The slope of the line depends on the coefficient of heat transfer between sample and sample pan on the heat conductivity of the sample material. In Table 1 the slopes of some usual materials are compiled. It is highly recommended to collect such data for the calorimeter in question, for to be able to correct measuring results, got at different heating rates, before comparing them.

Temperature calibration

The Perkin-Elmer calorimeters use platinum resistance thermometers. These kind of temperature sensors have a non-linear charac-

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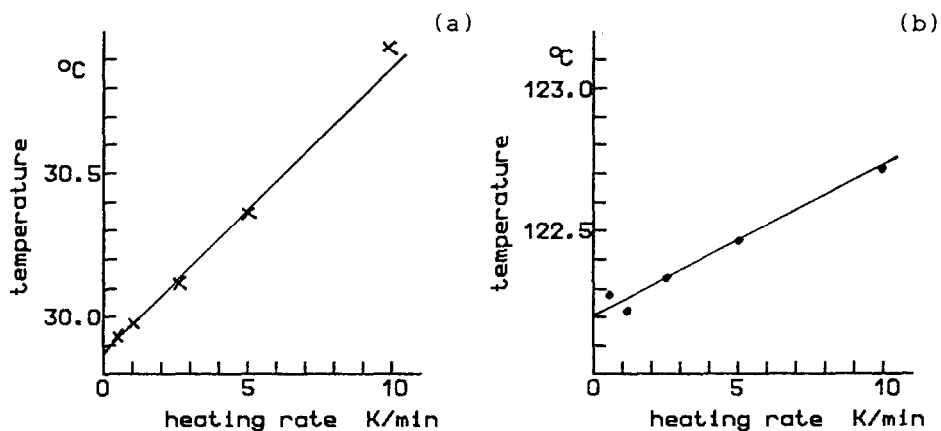[1] In the case of true heat-flux calorimeters, the peak width decreases unlimited with decreasing heating rate.

Fig. 5. Transition temperature (extrapolated onset) of (a) gallium and (b) benzoic acid at different heating rates (mass ≈5 mg).

TABLE 1

Slopes of onset versus heating rate curves for different materials (mass ≈5 mg) in a Perkin-Elmer DSC-7.

Substance	Slope [K/Kmin^{-1}]
Gallium	0.12
Indium	0.07
Tin	0.08
Lead	0.09
Average (all metals)	0.09±0.02
Diphenyl ether	0.12
Paraffine	0.08
Benzoic acid	0.05
Caffeine	0.08
Average (all non-metals)	0.08±0.03
Total average	0.09±0.02

teristic, i.e. the voltage of the sensor has to be linearized. This is done with a special circuit and several potentiometers justified in factory or by the service staff. As every man-made thing cannot be perfect and a certain change of factory settings is possible during the using, the linearisation should be checked from time to time. The procedure of temperature calibration recommended in the manuals (and implemented in the computer software) uses only two reference materials and therefore it is not suitable to test the linearity of the temperature scale. At least three reference materials with rather different transition temperatures should be taken to check the temperature calibration of the calorimeter.

In fig. 6 the temperature calibration curve of a DSC-7 is plotted. As can be seen, the accuracy of the linearisation of this special apparatus is about ±0.2 K in the tested temperature range. But as the precision of the apparatus is much higher, the accuracy of the measurements may be better than ±0.1 K with the aid of such a calibration plot.
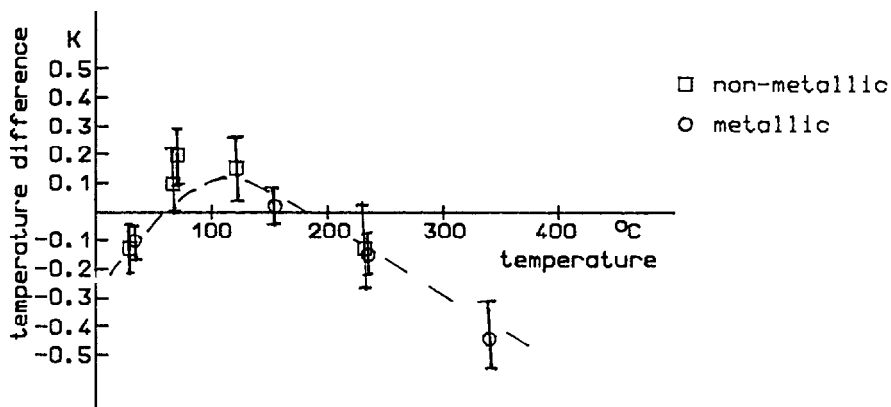

Fig. 6 Difference between measured extrapolated onset temperatur and true transition temperature for different metallic and non-metallic reference materials. The values have been corrected for a heating rate of zero. (DSC-7, mass ≈5 mg).

Heat calibration

The power compensating DSC should in principle not require any heat calibration at all, because all temperature differences are compensated immediately and the electrical differential power represents directly the differential heat flow and thus it should not be dependent ·on experimental parameters. In the case of Perkin-Elmer DSC this is not strictly true, because of the method of power compensation control, which is a pure proportional regulation. That is to say, during the transition of the sample the extra differential power ($\Delta\varphi$) (the peak in the measured curve) is coupled proportional to an extra differential temperature ($\Delta T \sim \Delta\varphi$). Thus a larger peak implies a larger temperature differ- ence between sample and reference holder. As the different temperatures of the two holders causes different heat exchange with the surroundings by radiation and convection, there is a differential heat leak depending on the differential power signal and thus on the peak area.

As a consequence the calibration factor in Perkin-Elmer DSC is

not unity and depends on sample parameters, temperature and heating rate as it is known from heat-flux DSC, which have the differential temperature as essential measuring principle. Though the effective temperature differences are much smaller in case of Perkin-Elmer DSC the resulting effects cannot be neglected and the user has to test them carefully and include them in accuracy discussions.

The following examples may show typical results from such calibration tests.

(i) Dependence of calibration factor on calibration method. Heat calibration is usually done in two ways, using enthalpy-standards (as indium) or heat-capacity-standards (as sapphire) as reference materials. The heat capacity can usually been measured with high precision and accuracy in an adiabatic calorimeter over a wide temperature range. Thus heat-capacity-standards (sapphire, platinum) are very suitable for the aim of DSC calibration. On the other hand certified enthalpy-standards are rare, as the measurement of the heat of fusion in adiabatic calorimeters take pains.
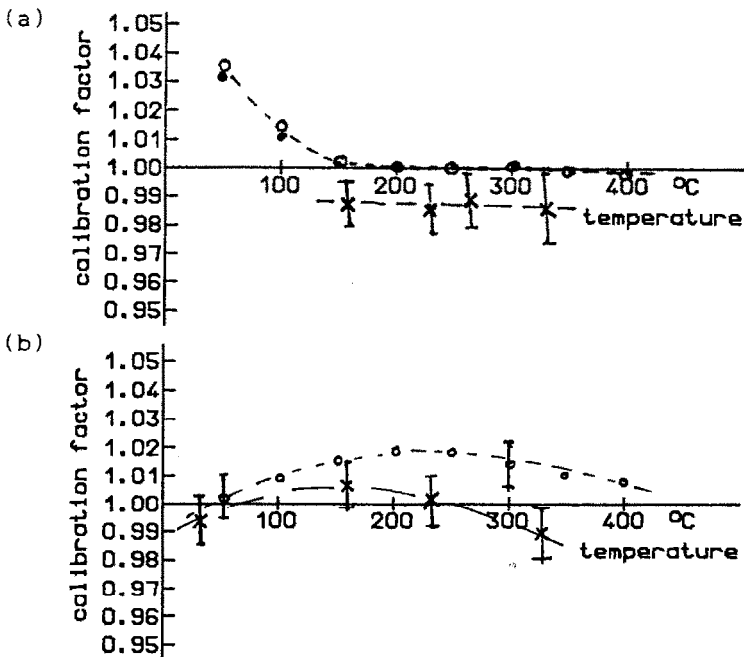

Fig. 7. Temperature dependence of calibration factor of (a) DSC-2 and (b) DSC-7, measured with a sapphire standard (, mass ≈ 100mg) and four metallic enthalpy standards (, mass ≈ 5 mg) at a heating rate of 10 K/min.

Nevertheless the magnitude of this quantity is known with suffi-
cient accuracy for some metals (indium, tin, bismuth) in order
that they can serve as reference materials for heat calibration.

Testing the calibration of a Perkin-Elmer DSC with a sapphire
standard on one hand and with different metals on the other hand
leads to the very amazing result, that there is a significant dif-
ference in the calibration factors got with both methods (1-2 per-
cent, see fig. 7). However, the differential heat flow during the
fusion of a metal sample may be hundred to thousand times larger
than the heat flow for steady state heating of a sapphire sample.
Thus even the weakest dependence of the calibration factor on the
magnitude of the differential heat flow multiplies to the measured
effect.

As a result heat-capacity-calibration (heat-flow-calibration)
should be done for heat-capacity measurements and enthalpy-
calibration (peak-area-calibration) should be done for transition
or reaction heat measurements.

(ii) <u>Dependence of calibration factor on temperature</u>. Comparing
the literature values of heat-capacity standards with the measured
values at any given temperature leads immediately to the calibra-
tion factor (for heat-capacity-calibration) and its dependence on
temperature. On the other hand the peak-area calibration is only
possible at fixed temperatures (where enthalpy standards exist)
and the temperature dependence of the calibration-factor has to
be interpolated. Fig. 7 gives the results of both calibration
methods for a DSC-7 and a DSC-2 calorimeter. As can be seen a weak
temperature dependence of the calibration factor has to be
noticed for both calorimeters, which seems to be similar for both
calibration methods.

(iii) <u>Dependence of calibration factor on heating rate and mass
of the sample.</u> Heat compensating DSC should not show any depen-
dence of the calibration factor on sample and experimental
parameters. Nevertheless such a variation can be found. Fig. 8
presents examples of measurements of the heat of fusion of samples
with different mass at different heating rates.

The measured change of the heat of fusion must be related to a
change of the calibration factor which consequently is not
completely independent from experimental parameters.

J/g

peak area

28.7

28.6

28.5

28.4

28.3

28.2

0.5 1 2 4 8 16 32 K/min

heating rate (logarithmic)
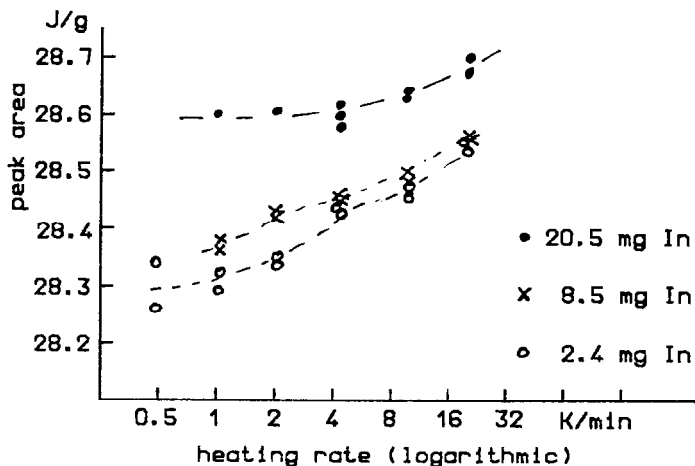
• 20.5 mg In

x 8.5 mg In

o 2.4 mg In

Fig. 8. Dependence of the measured peak area (heat of fusion of Indium) on sample mass and heating rate. (DSC-7)

CONCLUSIONS

Because of the measuring principle power compensating DSC are able to measure both heat capacities and heats of transitions or reaction with high precision. The repeatability of Perkin-Elmer DSC lies at ± 0,02 K for transition temperature, ± 0,1 % for transition heat and ± 0,5 for heat capacity measurements. Thus it is worth to look for such effects as described in this paper for to increase even the accuracy of the measurements to an amount near by the repeatability of the calorimeter.

For discussion of the accuracy of measuring results, the experimentalist should keep in view that Perkin-Elmer calorimeters may have the same flaws (coming from temperature differences between sample and reference during a transition) as heat-flux DSC have. To cover these effects the calibration procedure should be done more careful and to a greater extent as described in the manuals in order.

Neglecting the described peculiarities may restrict the accuracy of Perkin-Elmer DSC measurements to about 2 to 5 percent for heat and ± 0,3 to 1,0 K for temperature.

REFERENCES

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2 A. Marini et al., Performances of a Heat Flux DSC Cell, Thermochimica Acta, **85** (1985) 279-282.