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REMARKS ON THE CALIBRATION OF DIFFERENTIAL SCANNING CALORIMETERS

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The development of methods for temperature and heat calibration of DSC and DTA supported by the German Society of Thermal Analysis (GEFTA) are presented. Reasons are given for the recommendation of the temperature calibration method, which refers to the valid international temperature scale (ITS 90) and takes into account the fact that the fixpoints of this scale are defined in two phase equilibrium.

Furthermore the hard problems with the heat flow and peak area calibration of DSC are described and the methods are presented to come to realistic and sufficient results. Thus both traditional (with the aid of C_p – and enthalpy – reference materials) and electrical calibration are critically discussed. Today's best values of suitable materials for heat calibration are reported.

Introduction

Calibration means the definite coordination of the magnitude of a measured quantity and the 'true one'. For calorimeters the quantities in question are the temperature and the heat or heat flow. As qualitative DTA apparatus are not suitable for quantitative heat measurements, they need only temperature calibration, a procedure similar to that of DSC. Thus we can proceed without naming DTA separately.

There are still no procedures for the temperature and heat calibration of DSC's, which are definitely backed up both theoretically and experimentally. The results of investigations carried out in this respect must be taken into account in the relevant calibration regulations, and they also show the basic limits set to the reliability of measurements. To which extent DSC's are capable of being calibrated depends on the quality of the DSC measuring system and on operational parameters as well as on the availability of precisely measured reference materials. The fundamentals of the apparative side were described elsewhere [1]. But it should be mentioned that no complete theory of DSC exists up today which could describe the DSC performance in any

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detail. The situation of calibration is on the other hand quite satisfactory. Certified materials are either not available or the certified data of substances available are not thermodynamic equilibrium values but mean values weighed in one way or the other. At last one should take in mind, that the overall uncertainty of the calibration yields the smallest possible systematic uncertainty of the measurements.

Temperature calibration

Calibration means the unequivocal assigment of the temperature 'indicated' by the instrument to the 'true' temperature.

The 'true' temperature is defined by fixed points with the aid of reference substances. It is reasonable to use as reference substances, if possible, the substances serving the realization of the fixed points of the International Temperature Scale (ITS) [2].

The 'indicated' (or measured) temperature must be taken from the output of the instrument usually this is a graph or plot. Thus we have to define a method to find the 'measured temperature' in a clear-cut way. It is highly recommended not to trust on temperatures automatically calculated with built-in computer software. At least interactive construction on the terminal screen should be possible to influence the calculations.

After calibration procedure has been completed, either the potentiometer provided for this purpose will be adjusted until the temperature indicated corresponds to the true one, or adaptation will be ensured via the internal computer program (in a way usually not apparent to the user), or a graph or table is established showing the relation between the indicated and the true temperatures.

Any calibration already carried out by the manufacturer must be checked. Regular calibrations provide important information about the repeatibility error and any long-term systematic variations (drift). (It should be noted that repeatibility error is not the same as uncertainty of measurement.)

Temperature calibration procedure

The following procedure is elaborated and recommended of the German Society of Thermal Analysis (GEFTA) [3]. On the one hand it takes into consideration the known properties of differential scanning calorimeters and their influence on peak evaluation results, and on the other hand this calibration connects directly to the fixed points of the International Temperature Scale (ITS).

Definition of peak temperature

The temperature of any process in the sample must be determined from the measured curves. For phase transitions the calorimeter plots are represented normally by a 'peak' which is shown in Fig. 1. From all characteristic temperatures of a peak only the 'extrapolated peak onset temperature' T_e is nearly independent of sample parameters. The other characteristic temperatures, especially the peak maximum temperature depends heavily on sample mass and shape. Thus only the extrapolated onset temperature should be taken for calibration.

The extrapolated onset temperature T_e is defined as the intersect between an auxiliary straight line through the ascending slope of the peak and the linearly extrapolated initial base line (Fig. 1).

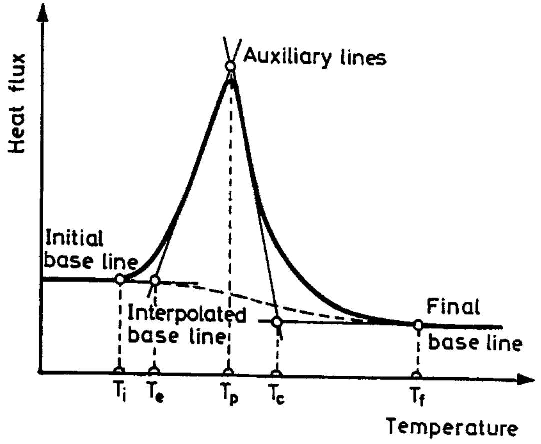

Fig. 1 Definition of characteristic temperatures of a peak

The auxiliary line is constructed either as tangent at the point of inflection or as fitted line through the (almost linear) section of the peak flank. For temperature calibration, the difference of these two methods is of no significance within the scope of the repeatibility error.

Procedure

- From the list of calibration substances recommended, at least three substances should be selected which cover the temperature range in question.

- Of each of these substances, several samples of a specified weight are taken whose masses should correspond to the mass recommended for the respective calorimeter and used for routine measurements.
- With these samples the event is to be measured at least five different heating rates within the range of interest, including the smallest possible one. At each heating rate, at least two experiments are to be carried out.

For each of the peaks obtained the extrapolated onset temperature T_e is determined.

- It is cheeked whether the temperature T_e thus obtained differ significantly between the first and the second experiment or whether they are a function not only of the heating rate but also of other sample parameters (e. g. the mass or position of the sample).
- If not, T_e will be represented as a function of the heating rate and extrapolated to zero heating rate. The value obtained is compared with the respective (fixed point) temperature of the ITS T_{fix}.
- Any difference obtained either serves as a basis for changing the calibration of the instrument to be carried out according to the manufacturer's specifications or is allowed for to put in a calibration table or curve. Should T_e be a function not only of the heating rate but also of other parameters, these dependencies are also to be represented accordingly.

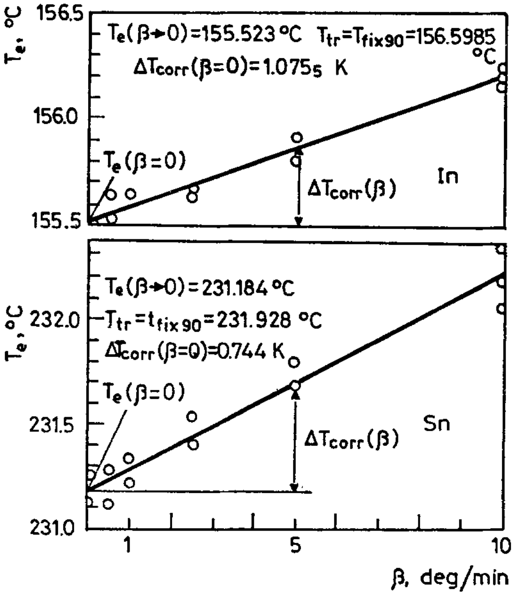

Fig. 2 T_e as a function of heating rate

This completes the temperature calibration. It strictly applies only to zero heating rate. At finite heating rate, the sample temperature is lower than the indicated temperature. In each case, a table (or graph) should be made up which shows the variation of the indicated temperature (or of that read from the measured curve) in relation to the true temperature at different heating rates. The formulas are as follows (Fig. 2):

$$\Delta T_{\mathrm{corr}} = T_{\mathrm{fix}} - T_{\mathrm{e}}$$

$$\Delta T_{\mathrm{corr}} = \Delta T_{\mathrm{corr}}\,(\beta = 0) + \Delta T_{\mathrm{corr}}\,(\beta)$$

$$\Delta T_{\mathrm{corr}}\,(\beta = 0) = T_{\mathrm{fix}} - T_{\mathrm{e}}\,(\beta = 0)$$

The true temperature of a measured transition can be calculated:

$$T_{\mathrm{true}} = T_{\mathrm{e}} + \Delta T_{\mathrm{corr}} \qquad \text{or} \qquad T_{\mathrm{true}} = T_{\mathrm{e}}\,(\beta = 0) + \Delta T_{\mathrm{corr}}\,(\beta = 0)$$

Reference materials

The international temperature scale (ITS) is defined on the one hand by ‘fixed points’, i.e. temperatures of two phase equilibrium of pure substanc-es, and on the other hand by a table or function of resistances of the platinum thermometer. As the fixed points lies under permanent international control, the transition temperatures of these materials are very suitable for temperature calibration, no more certificate than purity is necessary.

Substances from ITS 90 fixed point table [2] which can be used for temperature calibration of DSC are listed in Table 1. As can be seen almost the whole interesting temperature region is covered.

Table 1 Temperature fixed points of ITS 90

Substance	T_{fix90} in K	in °C
Triple point of mercury	234.3156	–38.8344
Triple point of water	273.16	0.01
Melting point of gallium	302.9146	29.7646
Solidification point of indium	429.7485	156.5985
Solidification point of tin	505.078	231.928
Solidification point of zinc	692.677	419.527
Solidification point of aluminium	933.473	660.323
Solidification point of silver	1234.93	961.78
Solidification point of gold	1337.33	1064.18
Solidification point of copper	1357.77	1084.62

We highly recommend to use these substances for calibration and to desist from other, however, certified materials. Nevertheless substances should be as pure as possible ($\geq$ 99.999 percent).

Arguments in support of this calibration procedure

The up to now existing recommendations concerning the temperature calibration of DSC's (e.g. ASTM E 967-83, ASTM E 794-85) and the specification of most manufacturers take a standard heating rate (e.g. 10 deg/min) as a basis of temperature calibration. This method cannot be recommended since:

* Every temperature of a first order phase transition and thus also the temperature of the fixed points if the International Temperature Scale are defined in phase equilibrium only, i. e. static at zero heating rate.
* Only at zero heating is the sample temperature equal to the measured temperature, in every other case there is an unknown difference which depends on sample parameters (mass, thermal conductivity, surface and thickness).
* For a finite heating rate, the extrapolated onset temperature (and all the more every other characteristic peak temperature) is a function of the thermal conductivity of the sample and of the heat transfer between sample and sample pan. Such a calibration is thus not independent of the substance chosen.
* Different heating rates require different corrections; shifting of T_e is not always linear to the heating rate and different materials have a different slope of the correction curve (cf. Fig. 2), thus ΔT_{corr} (β) depends on the sample in question.
* The correction tables or curves for other heating rates cannot straight forward been calculated from such an isolated calibration. Thus a separate experimental determination is needed each time the calibration heating rate is changed.

As we don't have any reference substance for cooling experiments (because of the supercooling effects at freezing of pure materials) a cooling temperature calibration is not easy. But a temperature calibration due to $\beta = 0$ as described above holds in the case of heat flux DSC also for cooling experiments. Because of symmetry in heat transport phenomena the correction term ΔT_{corr} ($\beta = 0$) is the same and the correction due to the heating rate $\Delta T(\beta)$ is also the same but has the opposite sign.

In the case of power compensating DSC this symmetry cannot be assumed without further ceremony. As an example, for Perkin-Elmer DSC-2 and DSC-7 a significant difference of the temperature scales (extrapolated to zero rate) for heating and cooling experiments can be found [4].

There is no more need to use 'certified' reference substances of different kind (metallic, organic, inorganic) for to calibrate the temperature scale of DSC due to the class of the material with the unknown transition in question, since all possible differences cancel out at zero heating rate.

Using metallic materials as reference materials reduces problems originating from the grain size, impurities and instability of other inorganic and organic materials.

The above described temperature calibration method is indeed a rather time consuming one, but it has a lot of advantages resulting in a distinct higher accuracy of the measured temperatures.

Heat calibration

By means of heat calibration, the proportionality factor between the measured heat flux Φ_m and the real heat flux Φ_r and between the measured exchanged heat q_m and the heat really transformed q_r is to be determined:

$$\Phi_r = K_\Phi \cdot \Phi_m \qquad (1a)$$

$$q_r = K_q \cdot q_m \qquad (1b)$$

This calibration is carried out either directly as 'heat flux calibration' in the (quasi-) steady state by

- electric heating
- known heat capacity of the calibration sample

or as 'peak area calibration' by integration over a peak which represents a known heat $q_r = \Phi_r dt = K_q \Phi_m dt$, by means of

- electrical heating
- phase transition (melting) of a pure substance.

As $q_r = \int \Phi_r dt$ and $q_m = \int \Phi_m dt$, K_Φ should be equal to K_q. But in reality this is not the case as K_φ depends (i) on temperature and (ii) on heat flow [1, 5]. Consequently Eq. 1a may be integrated, but K_Φ (T, Φ) is not allowed to be put outside the integral

$$q_r = \int \Phi_r (t)\, dt = \int K_\Phi (T(t), \Phi_m (t)) \cdot \Phi_m(T(t)) dt \neq K_\Phi \cdot \int \Phi_m (T(t)) dt \qquad ((2)$$

On the other hand from Eq. 1b is valid:

$$q_r = K_q \cdot q_m = K_q \cdot \int \Phi_m dt \tag{3}$$

Comparing equations 2 and 3 yields that K_q is not equal to K_Φ but a kind of integral average of all K_Φ values due to the $\Phi(t)$ function of the peak. Practically the difference between the two calibration factors is not very large ($<10\%$ depending on the apparatus) nevertheless separate calibrations should be done.

Another consequence of the theory of DSC [1] is that the thermophysical behaviour of the calibration sample and the sample to be measured must be as similar as possible. As this is possible only approximately, systematic deviations exist, which must be estimated and included in the overall uncertainty of measurement.

Heat flux calibration

In almost all DSC's commercially available, a heat flux signal Φ_m is internally assigned to the actual measured signal ΔT. (When the measured signal is read out as voltage (in mV), the following applies analogously, Φ_m being replaced by ΔU). The heat flux calibration defines the functional relation between Φ_m and the heat flux Φ_r absorbed or emitted by the sample:

$$\Phi_r = K_\Phi (X) \cdot \Phi_m \tag{4}$$

(steady state, Φ_m with subtracted base line, X: any parameter).

The proportionality factor (calibration factor, calibration function) K_Φ usually depends on parameters such as temperature and of course also on heat flux. In some DSC's, K_Φ is made unity by electronic or software means. In these cases, too, the relation between Φ_m and Φ_r must be carefully checked.

Electrical calibration

The installation of an electric calibration heater in the place of the sample or inside the sample, offers the following advantages:

* The electric power (heating power) can be measured easily and with high accuracy $\Phi_r = P_{el} = U \cdot i$.

* Heat fluxes of differing intensity can be generated without change of the calibration set-up.
* Adjustment of the steady state can be maintained for any period of time desired; the resulting conditions are most similar to those of a C_p measurement.
* The heater can be switched on or off at any temperature desired so that the position of the base line can also be checked in between.
* By appropriate presetting of the development of the heating rate with time, measurement effects (peaks) can be 'repeated' (simulated) so that heat fluxes leading to such a peak can be assigned without deconvolution procedures.
* The time constant of the measuring system can be easily determined.

The disadvantages of the electric calibration heater are the following:

* The heater can hardly be installed in the small crucibles of a disk-type measuring systems.
* Heaters permanently installed in measuring systems are not situated at the sample location; this leads to systematic errors.
* Heat fluxes in the wires (heat-leak) lead to systematic uncertainty (observe thermal symmetry of sample and reference side).
* Wires have a non-zero resistance and thus an additional heat production i^2R_{wire} occurs.

Ideally the calibration heater should have a large resistance compared with that of the wires. On the other hand the wires should be as thin as possible to avoid additional heat flows.

C_p-calibration

Heat flux calibration can also be carried out with a sample of known heat capacity. The following is valid for the heat flux absorbed by the sample in (quasi-) steady state:

$$\Phi_r = C_p \cdot \beta \text{ (without reference sample)} \tag{5}$$

so that

$$K_\Phi (T) = C_p (T) \cdot \beta / (\Phi_m(T) - \Phi_{b1} (T)) \tag{6}$$

The advantages of this calibration method are as follows:

* Applicable in all DSC's.

* Calibration at the sample location.
* No wires required and thus no heat leak.
* Reference materials with certified C_p-values available.

The disadvantages are:

* Calibration cannot be switched off in between, i. e. checking of the base line is not possible during the run (leads to uncertainties in $\Phi_m - \Phi_{b1}$).
* Temperature profile inside the sample yields a 'mean C_p' due to the (sample depending) temperature interval.

Peak area calibration

In peak-area calibration a known heat q_r (disappeared or consumed) is compared with the area of the resultant peak:

$$q_r = K_q(T) \cdot \int [\Phi_m(t) - \Phi_{b1}(t)] dt = K_q \cdot A \qquad (7)$$

The integral A is the peak-area. Integration must be carried out over the whole peak in order that contributions of terms with the 1st or higher derivatives of the measured signal do not play a role.

Electrical peak-area calibration

If electrical calibration is possible the advantages listed for the heat flux calibration apply analogously to peak area calibration. Additional advantages are:

* Peaks of suitable size can be produced. By appropriate presenting of the development of the heating power with time, measurement effects (peaks) can be 'traced' (simulated).
* Measurement effects (peaks) can be 'encompassed' during the run by similar calibration peaks.

The disadvantages are the same as those stated in section 'Electrical calibration'. Attention must be paid that electrical calibration is carried out only over a small temperature interval.

Peak area calibration with enthalpy references

Peak area of DSC's is usually carried out by means of the heats of fusion of pure substances.

The advantages of this method are as follows:

* Applicable in all DSC's.
* Calibration at the sample location.
* No wires required.
* Simultaneous temperature and heat calibration is possible with some reference materials.

The disadvantages are:

* Calibration practicable only at discrete temperatures.
* No adaptation to a certain peak profile is possible.
* Systematic uncertainties due to the special shape of the sample temperature curve $T_S(t)$ during the calibration procedure.
* Uncertainties resulting from the determination of the area (definition of the integration limits and shape of the base line).

A very important remark on the relation between enthalpy difference ΔQ has to be taken into consideration. The enthalpy difference of a phase transition of a substance is a difference of two functions of state and thus well defined. But in a calorimeter in fact the heat exchanged (during the transition) is measured which is not a function of state and thus may depend on the path of the reaction. The thermodynamic connection of these quantities is as follows. The first law reads:

$$\mathrm{d}U = \mathrm{d}Q + \mathrm{d}A + \Sigma \mathrm{d}E_1$$

($\mathrm{d}U$: change of internal energy, $\mathrm{d}Q$: heat exchanged, $\mathrm{d}A$: work exchanged, $\mathrm{d}E_1$: additional exchanged forms of energy)

With the definition of enthalpy $H = U + pv$ and thus $\mathrm{d}H = \mathrm{d}U + p\mathrm{d}V + v\mathrm{d}p$ and the restriction that work only should be exchanged as volume work ($\mathrm{d}A = -p\mathrm{d}V$) we get $\mathrm{d}H = \mathrm{d}Q + v\mathrm{d}p + \Sigma\mathrm{d}E_1$. If we set pressure p = const. and no more energy forms (as surface energy, electrical energy etc.) to be exchanged we get $\mathrm{d}H = \mathrm{d}Q$ and thus $\Delta H = \Delta Q$.

That is, the measured heat of transition is only equal to the enthalpy difference, if we have such conditions that the pressure is constant (no vapour pressure change!) and no other energy forms changed during phase transition, i.e. no change of surface energy, no change of deformation energy, no change of cohesion energy between sample and crucible and so on.

Furthermore it should be called in mind, that the enthalpy function is defined for infinite phases and the process of phase transition must be done quasi static (reversible). As a result the demands on enthalpy references for calibration are:

- Very pure substances with well known ΔH of transition.
- Large grains (single crystals as the best) which show no other phenomena than phase transition.
- Calibration should be done at low heating rates.

As these demands cannot be performed in practice the calibration may include uncertainties due to these conflicts. The magnitude of it cannot be generally predicted because of the missing of proper investigations. From round robin results an estimation of the uncertainty of about 1 percent seems to be realistic.

The calibration procedure with the aid of the phase transition heat is as follows:

* Selection of calibration substances which cover the desired temperature range and whose thermophysical characteristic data are similar to those of the sample.
* Weighing-in of such masses which approximately generate a heat effect as is found in normal measurements.
* Adjustment of customary heating rates. (Be careful in the case of reference substances which melt close to the start temperature: the quasi-steady state must have been reached, the effects due to the start must have faded; apply lower heating rate if necessary.)
* Evaluation of peak (area and extrapolated onset temperature T_e).
* Determination of $K_q(T_e)$, drawing of a calibration curve or establishing of a table, or input of measured data into calorimeter according to the manufacturer's specifications (potentiometer or in software).
* Estimation of the uncertainty of the calibration (uncertainty of the weighing, of the base line, of the integration limits, of the values for the heat of fusion taken from the literature; the estimated uncertainty from theoretical considerations must be taken into account.
* Measurement of the repeatibility errors of the calibration factors (or calibration curve). This repeatibility error must be clearly smaller than the estimated overall uncertainty of the calibration (see above). The repeatibility error is the smallest possible uncertainty of caloric measurements.

The same calibration procedure is applied to power compensation DSC's, however in this case, calibration with one reference material is in general sufficient (e.g. Indium) as the calibration factor depends on temperature only to a minor extend.

Reference materials for heat calibration

For heat flow calibration air inert substances with well known specific heat capacity should be selected. Mostly an α-Alumina single crystal (Al_2O_3, sapphire) is employed, but platinum and copper (in inert atmosphere) are also suitable. For recommended C_p-values of these substances see [6].

For peak area calibration pure substances with well known transition heat should be chosen. The precise measurement of the heat of transition needs adiabatic calorimeters. Such precise results are available for only a few substances. When several independent measurements have been carried out on one substance, the ranges of uncertainty stated often do not overlap so that the estimate of the best value and of the overall uncertainty is problematic. Nowadays the heats of fusion of pure metals seem to be the most reliable ones (Table 2). The uncertainties of the heat of fusion stated are based on measurements of the Physikalisch-Technische Bundesanstalt Braunschweig (FRG) [7, 8]. and on an evaluation of data found in the literature [9, 10]. Two substances are also suitable for temperature calibration as they define fixed points of ITS 90.

Table 2 Best values of recommended enthalpy references

Substance	Fusion temperature, °C	Specific heat of fusion, J/g
Indium	156.5985	28.58 ± 0.11 (0.4 %)
Tin	231.928	60.46 ± 0.3 (0.5 %)
Bismuth	271.403	53.26 ± 0.6 (1.1 %)

Concluding remarks on heat calibration

Different calibration factors for heat flow and heat (peak area) measurements must be taken in consideration and thus be measured separately. It must be expected that the heat flow calibration factor depends on heat-flow itself. This should be checked with aid of two samples with a large (but well known) difference in heat capacity or by a build in electric heater.

The peak area calibration factor may depend on sample mass, heating rate, peak shape and size, temperature and other parameters. This dependencies should be tested during first calibration and the results of these checks must be taken into account for valuation of uncertainty of any measurement.

On principle the heat calibration run should be as similar as possible to the measuring run. The best is to simulate the measured peak by proper variation of the current into a build in electrical heater.

Because of the systematic error sources due to the construction principle heat-flux DSC yields results in heat measurements with an uncertainty of about 5 percent, which may be decreased by very careful special calibration.

For power compensating DSC the uncertainty of heat measurements is about 1 to 2 percent.

Heat flow or heat capacity measurements in heat-flux DSC is always problematical, usually the uncertainty must be considered to be 10 to 20 percent. Higher accuracy needs a great expense of calibration.

Power compensating DSC are normally able to measure heat capacities with an uncertainty of 3 to 5 percent, which may be decreased to 1 percent.

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Zusammenfassung — Methoden zur Temperatur- und Enthalpiekalibrierung von DSC und DTA Instrumenten werden dargestellt. Dieses Forschungsvorhaben wurde von der Gesellschaft für Thermische Analyse (GEFTA) unterstützt. Gründe werden dargelegt, weshalb die Temperaturkalibrierung auf Referenzsubstanzen abgestützt werden soll, die in der Internationalen Temperaturskala (ITS90) aufgeführt sind.

Ebenso wird das schwierige Unterfangen der kalorischen Kalibrierung mit mehreren unterschiedlichen Methoden erläutert, und geeignete Referenzsubstanzen werden vorgestellt.