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THE TEMPERATURE CALIBRATION OF SCANNING CALORIMETERS

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(Recommendation of the working group "Calibration of Scanning Calorimeters" of the Gesellschaft für Thermische Analyse e.V. (GEFTA)*, FRG)

PURPOSE AND SCOPE OF APPLICATION OF THE RECOMMENDATION

The present recommendation allows the correct temperature calibration of scanning calorimeters irrespective of the instrument type. The procedure is elucidated in the section "Temperature calibration procedure" and briefly substantiated in the section "Grounds for the recommendation for temperature calibration"; in the annex of this section a concrete calibration example is given for illustration.

It is the purpose of this recommendation to unify the methods hitherto used and, thus, to avoid errors liable to compromise the reliability of the results obtained by other methods. The GEFTA working group "Calibration of Scanning Calorimeters" intends to supplement the present recommendation by a list of substances for temperature calibration. Until this list is published, the substances referred to in the International Temperature Scale of 1990 (ITS-90) and those recommended by the International Committee of Weights and Measures (CIPM) should be used. The metals indium and tin used for calibration in the example (annex) are fixed point materials of the ITS-90; lead was used within the scope of the IPTS-68 valid before; the substances (metals and non-metals) used for subsequently checking the calibration were selected irrespective of the list to be established.

Though the present recommendation has been formulated only for scanning calorimeters, it should be applied by analogy to the temperature calibration of instruments for differential thermal analysis (DTA).

DOCUMENTS TO BE TAKEN INTO ACCOUNT

Temperature scale in force:

- The International Temperature Scale of 1990.
  Metrologia 27 (1990), No. 1
- Supplementary Information on the ITS-90.
  Published by: International Committee of Weights and Measures (CIPM)
- Techniques for Approximating the International Temperature Scale of 1990. Published by: International Committee of Weights and Measures (CIPM)

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DEFINITION OF CONCEPTS

Temperature calibration means the unique assignment of the temperature indicated by the instrument to the true temperature. The true temperature is defined in accordance with the temperature scale in force (ITS-90) by fixed points of suitable substances, suitable measuring instruments and calculation prescriptions. The temperature measured by the instrument must normally be derived from curves of measured values, extrapolation to zero heating rate being necessary.

It should be borne in mind that for the definition of the temperature scale static methods are used which in a scanning calorimeter can always be realized only approximately. Furthermore, the location of temperature measurement in the calorimeter is never the location of the sample. In dynamic measurements, this leads to a systematic error which is a function of test parameters. The calibration method described in the following allows for these particular features in a general way which is independent of the instrument type and enables unmistakable and comparable measurements of the temperature of any thermal event to be carried out.

Temperature values in K are used with the symbol T and values in °C with the symbol t. In quantity equations, T is generally used for temperatures.

DEFINITION OF CHARACTERISTIC TEMPERATURES

In an endothermic event, the calorimeter records the heat flux signal as a function of temperature; this is schematically represented in Fig.1. The section of the curve between T_i and T_f is defined to as *peak*.

In practice, various methods are applied to *interpolate* the *base line* between the initial and the final peak temperature. To determine the extrapolated peak onset and peak offset temperature, the linear extrapolations of the *initial* and *final base line* are used.

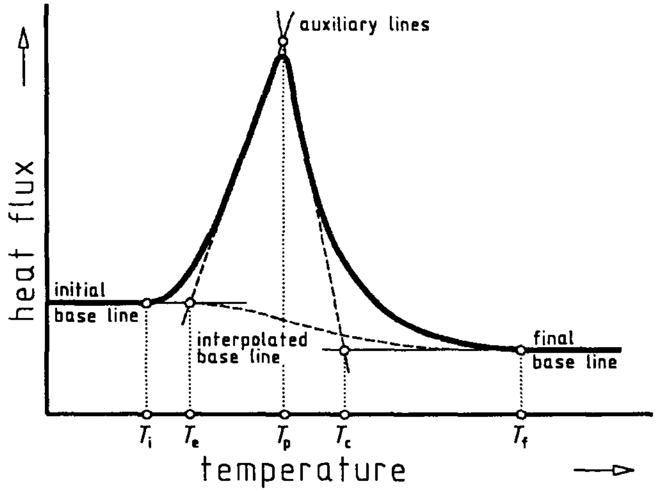


Fig.1. Definition of characteristic temperatures of a peak

The *auxiliary lines* are drawn through the (almost) linear section of the two peak slopes, either as inflectional tangents or as fitted lines. The distinction between the two methods is of no significance for practical calibration, as the resulting differences are smaller than the repeatability error of the measurement results.

T_i: *Initial peak temperature*
Here the curve of measured values begins to deviate from the (extrapolated) initial base line.

T_e: *Extrapolated peak onset temperature*
Here the auxiliary line through the ascending peak slope intersects the linearly extrapolated initial base line.

T_p: *Maximum peak temperature*
This is the maximum value of the difference between the curve of measured values and the *interpolated* base line (not necessarily the absolute maximum of the curve of measured values).

T_c: *Extrapolated peak offset temperature*
Here the auxiliary line through the descending peak slope intersects the linearly extrapolated final base line.

T_f: *Final peak temperature*
Here the curve of measured values reaches again the (extrapolated) final base line.

TEMPERATURE CALIBRATION PROCEDURE

- From the list of calibration substances recommended, at least three substances are selected which cover the temperature range in question.
- Of each of these substances, several samples of a specified weight are taken whose masses should more or less correspond to the mass recommended for the respective calorimeter and used for routine measurements.
- With these samples the event is to be measured at at least five different heating rates β in 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 peak onset temperature T_e is determined.
- It is to be checked whether the temperatures 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 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 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.

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. It is therefore necessary to prepare a calibration table or curve for all heating rates used, which contains the difference between the sample temperature and the indicated temperature, as a function of the heating rate. These corrections are normally insignificant at small heating rates but at heating rates greater than 5 K/min, they can reach considerable values and, in addition, depend on the kind and mass of the sample. To prepare this table or curve, the results of the calibration experiments can be used, but it is also possible to use suitable pure substances in order to determine the relative shifts of the temperatures as a function of the heating rate. In this case, these substances are to be used as in the case of calibration.

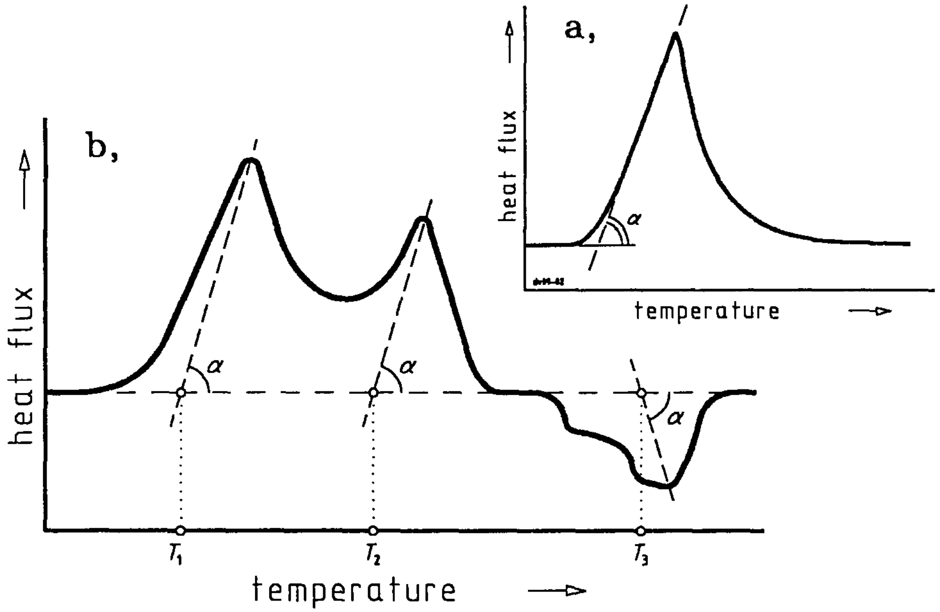


Fig.2. Determination of characteristic temperatures of a complex event. When the scaling is the same, the auxiliary lines (dashed) have the same slope
a) calibration experiment
b) complex event

In order to assign correct temperatures to individual characteristic parts of complex thermal events, at finite heating rates, auxiliary lines must be drawn at the angle α to the interpolated base line (Fig.2). The correct angle α is obtained from the calibration experiment at the respective heating rate, providing the axes are identically scaled. If not, the slope of the auxiliary line must be converted.

Note 1:

In exothermic events, due to the heat released, the sample temperature is higher than that indicated by the instrument. As at present calibration substances for exothermic events are not yet generally available, the amount of this error cannot be exactly determined. It is therefore suitable to assign a temperature only to the beginning of the exothermic event.

Note 2:

The procedure above allows also cooling curves to be correctly calibrated, providing a corresponding correction is made. It is to be taken into account that in this case the sample temperature is higher than the indicated temperature, i.e. that the sign of the correction value to be applied must be opposite to that for heating. For the rest, the calibration table must be derived from the table for heating, as no suitable substances are at present available for cooling calibration. This is why characteristic temperatures for cooling curves cannot be determined as exactly as those for heating.

GROUNDS FOR THE RECOMMENDATION FOR TEMPERATURE CALIBRATION

The recommendations for the temperature calibration of differential scanning calorimeters hitherto formulated assume that the temperature indication is calibrated at a standard heating rate (e.g. 10 K/min). This procedure cannot be recommended for the following reasons:

- The temperature fixed points of the ITS-90 are defined for phase equilibrium (i.e. for zero heating rate).
- In the scanning calorimeter there are always temperature differences between the location of temperature measurement and the location of the sample, which disappear only at zero heating rate. At a finite heating rate, the temperature measured is not equal to the sample temperature.
- Calibration at a finite heating rate leads to a temperature correction which is unsymmetrical for heating and cooling measurements. As suitable substances are not available, a correction table or curve for cooling measurements cannot be prepared.
- For a finite heating rate, the extrapolated peak onset temperature is a function of the thermal conductivity of the sample and of the heat transfer between sample and sample pan. The calibration is therefore not independent of the substance.
- The correction table or curve for other heating rates is not easy to derive and must therefore be redetermined each time the calibration heating rate is changed.

From among the characteristic temperatures of the peak solely the extrapolated peak onset temperature T_e is to be used for defining the temperature scale. The initial peak temperature T_i cannot be exactly determined; the temperature of the peak maximum T_p and the extrapolated peak offset temperature T_c largely depend on the mass, layer thickness and thermal conductivity of the sample. This means that they are a function of the substance and cannot be uniquely reproduced; the same applies to the final peak temperature T_f. T_e depends to a relatively small extent on the sample parameters so that it is possible with the restrictions referred to in the recommendation (e.g. equal weight of substance and similar substances) to prepare a correct calibration table or curve which will also be valid for cooling rates (with a somewhat greater uncertainty).

As it is not absolutely sure for scanning calorimeters that there is a linear relationship between the temperature-analogue signal and the temperature of the sample, this must be checked. For this purpose, at least three fixed points on the temperature scale in the range in question are required.

For heat flux DSC's, the extrapolated onset temperature T_e of a peak is more or less a function of the sample's location in the sample pan and the location of this pan in the measuring system. As the heat transfer between sample and sample pan can change due to fusion, and this might influence the extrapolated peak onset temperature T_e, each sample must be subjected to at least two subsequent measurements to determine this effect.

As shifting of the extrapolated peak onset temperature T_e does not always take place linearly with the heating rate, to ensure safe extrapolation to the zero heating rate, test measurements are to be carried out in the range of interest at at least five different heating rates, including the smallest possible one.

Different substances normally show different interdependencies between the extrapolated peak onset temperatures and the heating rate. For the preparation of a correction table or curve reflecting this relationship, pure substances with fast transitions in the temperature range of interest and properties as similar to those of the materials to be investigated as possible should be used. This is to ensure that any dependence of the extrapolated peak onset temperature and the slope of the auxiliary line on the kind (metal, non-metal, organic substance) and thermal conductivity of the materials to be investigated is detected. As temperature calibration has already been completed at this moment, the materials to be used here need not belong to the calibration substances; it will be sufficient if they show a well reproducible, narrow peak whose shift with the heating rate is the sole phenomenon to be determined.

ANNEX

Example of the temperature calibration of a differential scanning calorimeter (DSC-7, Perkin Elmer Corp.) with subsequent test measurements. The samples were contained in sealed aluminium pans (sample mass: approx. 5 mg).

(a) Temperature calibration

For temperature calibration the metals indium, tin and lead were used. Indium and tin count among the fixed point materials of the ITS-90. Lead was a secondary fixed point material of the IPTS-68 and was used here so as to have three calibration materials in not too great a temperature range.

The measurements necessary for temperature calibration yielded the results given in Table 1.

TABLE 1

Temperature calibration using indium, tin (fixed point materials of the ITS-90) and lead (secondary fixed point material of the IPTS-68). t_e: extrapolated peak onset temperature

Calibration substance	Sample No.	Measurement No.	Heating rate in K/min	t_e in °C
indium	1	1	10.0	156.21
	1	2	10.0	156.16
	2	1	10.0	156.25
	2	2	10.0	156.21
	1	1	5.0	155.81
	2	1	5.0	155.91
	1	1	2.5	155.65
	2	1	2.5	155.67
	1	1	1.0	155.64
	2	1	1.0	155.65
	1	1	0.5	155.52
	2	1	0.5	155.65
	2	2	0.5	155.53
	1	1	0.1	155.49
	2	1	0.1	155.50
tin	1	1	10.0	232.35
	1	2	10.0	232.18
	2	1	10.0	232.06
	1	1	5.0	231.81
	2	1	5.0	231.69
	1	1	2.5	231.54
	2	1	2.5	231.41
	1	1	1.0	231.33
	2	1	1.0	231.22
	1	1	0.5	231.28
	2	1	0.5	231.12
	1	1	0.1	231.26
	2	1	0.1	231.12
lead	1	1	10.0	328.22
	1	2	10.0	327.50
	1	3	10.0	327.52
	2	1	10.0	327.95
	2	2	10.0	327.87
	1	1	5.0	327.10
	1	2	5.0	327.09
	2	1	5.0	327.42
	1	1	2.5	326.94
	2	1	2.5	327.23
	1	1	1.0	326.76
	2	1	1.0	326.97
	1	1	0.5	326.78
	2	1	0.5	326.95
	1	1	0.1	326.75
	2	1	0.1	326.93

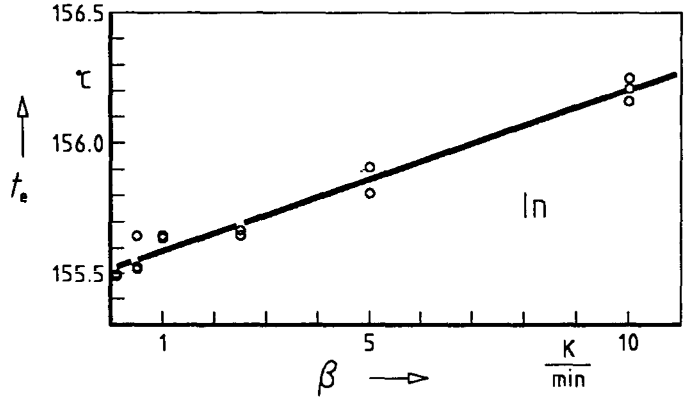
From the calibration results (Table 1) the dependence $t_e(\beta)$ shown in Figs.A1 to A3 is obtained. The following values are given:

$t_e(\beta \rightarrow 0)$	extrapolated peak onset temperature t_e extrapolated to $\beta = 0$
t_{tr}	true temperature (fixed point temperature t_{fix} or value from literature)
$\Delta T_{corr}(\beta = 0) = t_{tr} - t_e(\beta \rightarrow 0)$	correction to be applied to $t_e(\beta \rightarrow 0)$ in order to obtain t_{tr}

(For indium and tin, $t_{tr} = t_{fix90}$ (ITS-90); for lead, the temperature t_{fix68} given in the IPTS-68 was converted to the ITS-90).

For this calorimeter the relationship $t_e(\beta)$ is in good approximation linear. The dependence of the correction $\Delta T_{corr}(\beta = 0)$ on the temperature $t_e(\beta \rightarrow 0)$ is represented in Fig. A4.

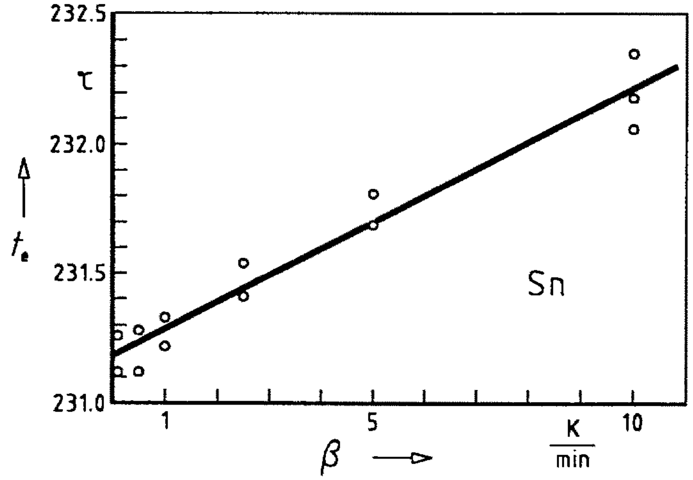
The calorimeter was calibrated using the measurement results (potentiometer, software).



$t_e(\beta \rightarrow 0)$ = 155.523 °C $t_{tr} = t_{fix90}$ = 156.5985 °C

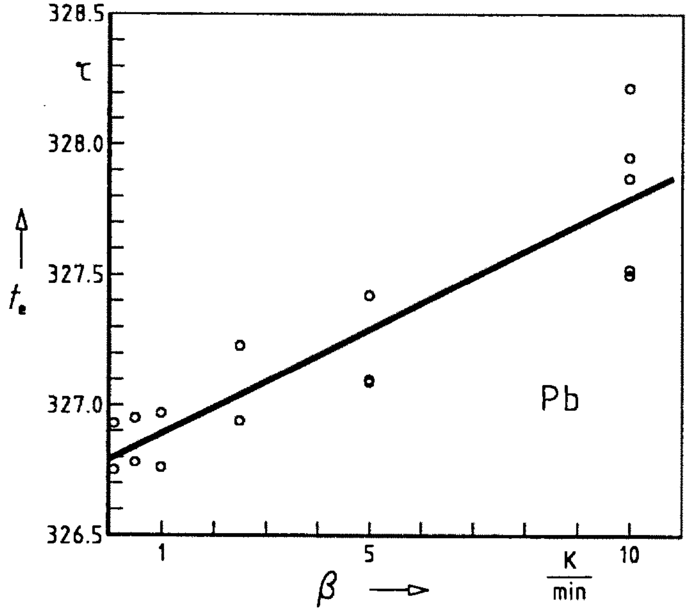
$\Delta T_{corr}(\beta = 0)$ = 1.075$_5$ K

Fig.A1. Dependence of the extrapolated peak onset temperature t_e on the heating rate β for indium



$t_e(\beta \to 0)$ = 231.184 ℃ $t_{tr} = t_{fix90}$ = 231.928 ℃
$\Delta T_{corr}(\beta = 0)$ = 0.744 K

Fig.A2. Dependence of the extrapolated peak onset temperature t_e on the heating rate β for tin



$t_e(\beta \to 0)$ = 326.793℃ t_{tr} = 327.462℃
$\Delta T_{corr}(\beta = 0)$ = 0.669 K

Fig.A3. Dependence of the extrapolated peak onset temperature t_e on the heating rate β for lead

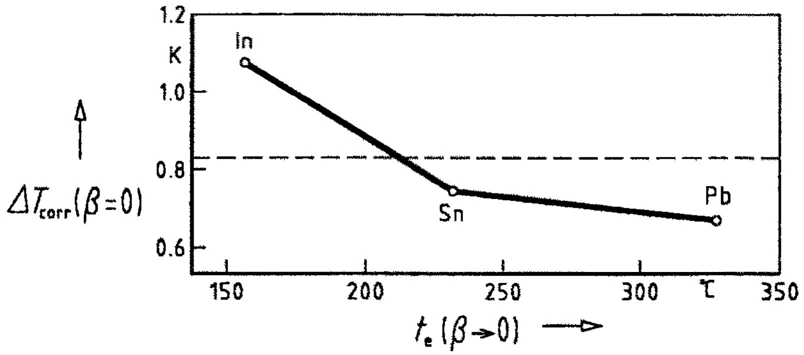


Fig.A4. Dependence of the correction $\Delta T_{corr}(\beta=0)$ on temperature as a result of calibration with indium, tin and lead

(b) Test measurements for determining the dependence of the extrapolated peak onset temperature on the heating rate

The calibrated calorimeter (cf. section a)) was used to measure the respective dependence $T_e(\beta)$ with different test substances. The substances used for calibration were also employed for the test measurements in order to check the accuracy of the calibration, for the calibration does not lead to entire conformity in the calibration points but only to a best possible approximation. The results are given in Table 2. In addition the following values are given:

$\Delta T_{tot} = t_{tr} - t_e(\beta)$	total correction at the heating rate β
t_{tr}	true temperature (t_{fix} or value from literature)
$t_e(\beta)$	extrapolated peak onset temperature at the heating rate β
$t_e\,(\beta\to 0)$:	extrapolated peak onset temperature t_e extrapolated to $\beta = 0$
$\Delta T_{corr} = t_{tr} - t_e\,(\beta\to 0)$:	correction to be applied to $t_e\,(\beta\to 0)$

(The values for ΔT_{tot} have been rounded to one decimal, the values for ΔT_{corr} to maximally two decimals).

TABLE 2

Measurement results for determining $t_e(\beta)$ for different substances

Substance	$t_e(\beta)$ in °C	Heating rate in K/min	ΔT_{tot} in K	
diphenyl ether	27.05	0.5	- 0.2	t_{tr}=26.86°C
	27.10	1.0	- 0.2	$t_e(\beta \to 0)$=26.93°C
	27.20	2.5	- 0.3	
	27.73	5.0	- 0.9	ΔT_{corr}=-0.07 K
gallium	29.92	0.5	- 0.1	$t_{tr}=t_{fix90}$=29.7646°C
	29.97	1.0	- 0.2	
	30.11	2.5	- 0.3	$t_e(\beta \to 0)$=29.85°C
	30.35	5.0	- 0.6	
	30.94	10.0	-1.2	ΔT_{corr}=-0.09 K
$C_{33}H_{68}$ (A)	67.35	0.5	0	t_{tr}=67.4°C
	67.36	1.0	0	
(paraffin)	67.47	2.5	- 0.1	$t_e(\beta \to 0)$= 67.3°C
	67.66	5.0	- 0.3	
	68.06	10.0	- 0.7	ΔT_{corr}=0.1 K
$C_{33}H_{68}$ (B)	70.98	0.5	0.1	t_{tr}=71.1°C
	70.98	1.0	0.1	
(paraffin)	71.10	2.5	0	$t_e(\beta \to 0)$=70.91°C
	71.27	5.0	- 0.2	
	71.70	10.0	- 0.6	ΔT_{corr}=0.2 K
benzoic acid	122.28	0.5	0.1	t_{tr}=122.34°C
	122.23	1.0	0.1	
	122.34	2.5	0	$t_e(\beta \to 0)$=122.22°C
	122.46	5.0	- 0.1	
	122.72	10.0	- 0.4	ΔT_{corr}=0.12 K
indium	156.63	0.5	0	$t_{tr}=t_{fix90}$=156.5985°C
	156.67	1.0	- 0.1	
	156.80	2.5	- 0.2	$t_e(\beta \to 0)$=156.53°C
	156.96	5.0	- 0.4	
	157.32	10.0	- 0.7	ΔT_{corr}=0.06 K
	158.01	20.0	- 1.4	
	159.34	40.0	- 2.7	
	162.17	80.0	- 5.6	
	168.60	160.0	-12.0	
tin	232.18	0.5	- 0.2	$t_{tr}=t_{fix90}$=231.928°C
	232.21	1.0	- 0.3	
	232.34	2.5	- 0.4	$t_e(\beta \to 0)$=232.12°C
	232.52	5.0	- 0.6	
	233.01	10.0	- 1.1	ΔT_{corr}=-0.19 K
caffeine	236.30	0.5	- 0.2	t_{tr}=236.1°C
	236.30	1.0	- 0.2	
	236.36	2.5	- 0.3	$t_e(\beta \to 0)$=236.24°C
	236.67	5.0	- 0.6	
	236.96	10.0	- 0.9	ΔT_{corr}=-0.1 K
lead	327.99	0.5	- 0.5	t_{tr}=327.462°C
	328.00	1.0	- 0.5	
	328.17	2.5	- 0.7	$t_e(\beta \to 0)$=327.93°C
	328.32	5.0	- 0.9	
	328.81	10.0	- 1.3	ΔT_{corr}=-0.47 K

For each substance the dependence $T_e(\beta)$ can be represented with sufficient accuracy by a fitted line of the mean slope $\Delta T_e/\Delta\beta$. These slopes are compiled in Table 3 for the substances investigated.

TABLE 3

Mean slopes $\Delta T_e/\Delta\beta$ for the test substances investigated

Substance	$\Delta T_e/\Delta\beta$ in $K/(K \cdot min^{-1})$
gallium indium tin lead	0.11 0.07 0.09 0.09
mean value for metals	0.09±0.02*
diphenyl ether paraffin $C_{33}H_{68}$ benzoic acid caffeine	0.15 0.08 0.05 0.07
mean value for organic substances	0.09±0.04
total mean value	0.09±0.03*

*standard deviation

At a heating rate of, for example, 10 K/min a mean shift

$[T_e(\beta) - T_e(\beta \rightarrow 0)]$ of 0.9 ± 0.3 K

is obtained; the actual shift can be between 0.5 and 1.5 K according to the heat transfer between substance and pan. For a more accurate temperature measurement, the slope $\Delta T_e/\Delta\beta$ must be separately determined for the substance in question.

If T_e is measured at a heating rate β, the total correction ΔT_{tot} is to be applied to $T_e(\beta)$ in order to obtain T_{tr}.

Be $\Delta T_{tot} = T_{tr} - T_e(\beta)$

With $T_{tr} = T_e(\beta \rightarrow 0) + \Delta T_{corr}$

and $T_e(\beta) - T_e(\beta \rightarrow 0) \approx \beta \cdot \Delta T_e/\Delta\beta$

$\Delta T_{tot} \approx \Delta T_{corr} - \beta \cdot \Delta T_e/\Delta\beta$

and, thus $T_{tr} \approx T_e(\beta) + \Delta T_{tot}$

are obtained.

Both determining quantities for ΔT_{tot} (ΔT_{corr} and $\Delta T_e/\Delta\beta$) can be determined by test measurements as described. For $\Delta T_e/\Delta\beta$, either the mean values of Table 3 can be used in approximation or the results of the $T_e(\beta)$ measurement carried out with the substance to be investigated can be taken over.