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Plastics — Differential scanning calorimetry (DSC) —

Part 1:
General principles

Plastiques — Analyse calorimétrique différentielle (DSC) —

Partie 1: Principes généraux

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Foreword

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The committee responsible for this document is ISO/TC 61, *Plastics*, Subcommittee SC 5, *Physical-chemical properties*

This third edition cancels and replaces the second edition (ISO 11357-1:2009), 3.7.2 of which has been technically revised.

ISO 11357 consists of the following parts, under the general title *Plastics — Differential scanning calorimetry (DSC)*:

- *Part 1: General principles*
- *Part 2: Determination of glass transition temperature and glass transition step height*
- *Part 3: Determination of temperature and enthalpy of melting and crystallisation*
- *Part 4: Determination of specific heat capacity*
- *Part 5: Determination of characteristic reaction-curve temperatures and times, enthalpy of reaction and degree of conversion*
- *Part 6: Determination of oxidation induction time (isothermal OIT) and oxidation induction temperature (dynamic OIT)*
- *Part 7: Determination of crystallization kinetics*

Introduction

ISO 11357 describes thermoanalytical DSC test methods which can be used for quality assurance purposes, for routine checks of raw materials and finished products or for the determination of comparable data needed for data sheets or databases. The procedures given in ISO 11357 apply as long as product standards or standards describing special atmospheres for conditioning of specimens do not specify otherwise.

Plastics — Differential scanning calorimetry (DSC) —

Part 1:
General principles

SAFETY STATEMENT — Persons using this document should be familiar with normal laboratory practice, if applicable. This document does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user to establish appropriate safety and health practices and to ensure compliance with any regulatory requirements.

1 Scope

ISO 11357 specifies several differential scanning calorimetry (DSC) methods for the thermal analysis of polymers and polymer blends, such as

- thermoplastics (polymers, moulding compounds and other moulding materials, with or without fillers, fibres or reinforcements),
- thermosets (uncured or cured materials, with or without fillers, fibres or reinforcements), and
- elastomers (with or without fillers, fibres or reinforcements).

ISO 11357 is intended for the observation and measurement of various properties of, and phenomena associated with, the above-mentioned materials, such as

- physical transitions (glass transition, phase transitions such as melting and crystallization, polymorphic transitions, etc.),
- chemical reactions (polymerization, crosslinking and curing of elastomers and thermosets, etc.),
- the stability to oxidation, and
- the heat capacity.

This part of ISO 11357 specifies a number of general aspects of differential scanning calorimetry, such as the principle and the apparatus, sampling, calibration and general aspects of the procedure and test report common to all following parts.

Details on performing specific methods are given in subsequent parts of ISO 11357 (see Foreword).

2 Normative references

The following documents, in whole or in part, are normatively referenced in this document and are indispensable for its application. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 472, *Plastics — Vocabulary*

ISO 80000-5, *Quantities and units — Part 5: Thermodynamics*

3 Terms and definitions

For the purposes of this document, the terms and definitions given in ISO 472 and ISO 80000-5 and the following apply.

3.1
differential scanning calorimetry
DSC

technique in which the difference between the rate of flow of heat into a specimen crucible containing the specimen and that into a *reference crucible* (3.3) is derived as a function of temperature and/or time while the specimen and reference are subjected to the same controlled temperature programme in a specified atmosphere using a symmetrical measurement system

Note 1 to entry: It is common practice to record, for each measurement run, a curve in which temperature or time is plotted as the abscissa and *heat flow rate* (3.4) difference as the ordinate. The endothermic and/or exothermic direction is indicated on the DSC curve.

Note 2 to entry: According to the principles of thermodynamics, energy absorbed by a system is considered positive while energy released is negative. This approach implies that the endothermic direction points upwards in the ordinate and the exothermic direction downwards (see Figures 1 and 2). It also has the advantage that the direction of thermal effects in plots of *heat flow rate* (3.4) and specific heat is consistent.

3.2
calibration material

material for which one or more of the thermal properties are sufficiently homogeneous and well established to be used for the calibration of a DSC instrument or for the assessment of a measurement method

3.3
reference crucible

crucible used on the reference side of the symmetrical crucible holder assembly

Note 1 to entry: Normally, the reference crucible is empty.

Note 2 to entry: In special cases, such as the measurement of highly filled or reinforced polymers or specimens having a heat capacity comparable to that of the crucible, a suitable material can be used inside the reference crucible. This reference material should be thermally inactive over the temperature and time range of interest and its heat capacity should be similar to that of the specimen. In the case of filled or reinforced products, the pure filler or reinforcement can be used, for example.

3.4
heat flow rate

quantity of heat transferred per unit time ($\mathrm{d}Q/\mathrm{d}t$)

Note 1 to entry: It is expressed in watts (W) or milliwatts (mW).

Note 2 to entry: The total quantity of heat transferred, Q, corresponds to the time integral of the heat flow rate:

$$Q = \int \frac{\mathrm{d}Q}{\mathrm{d}t}\,\mathrm{d}t$$

3.5
change in heat
ΔQ

quantity of heat absorbed (endothermic, ΔQ positive) or released (exothermic, ΔQ negative) within a specified time, t, or temperature, T, range by a specimen undergoing a chemical or physical change and/or a temperature change:

$$\Delta Q = \int_{t_1}^{t_2} \frac{\mathrm{d}Q}{\mathrm{d}t}\,\mathrm{d}t$$

or

$$\Delta Q = \frac{60}{\beta}\int_{T_1}^{T_2} \frac{\mathrm{d}Q}{\mathrm{d}t}\,\mathrm{d}T$$

where

ΔQ is expressed in joules (J) or as a specific quantity, Δq, expressed in joules per amount of material in grams ($\mathrm{J \cdot g^{-1}}$) or joules per amount of material in moles ($\mathrm{J \cdot mol^{-1}}$);

β is the constant heating or cooling rate, $\mathrm{d}T/\mathrm{d}t$, expressed in kelvins per minute ($\mathrm{K \cdot min^{-1}}$).

Note 1 to entry: If measurements are made at constant pressure, ΔQ corresponds to the change in enthalpy, ΔH.

3.6
specific heat capacity at constant pressure

c_p

quantity of heat necessary to raise the temperature of unit mass of material by 1 K at constant pressure:

$$c_p = \frac{1}{m} \times \left(\frac{\mathrm{d}Q}{\mathrm{d}T} \right)_p$$

or

$$c_p = \frac{1}{m} \times \frac{60}{\beta} \times \left(\frac{\mathrm{d}Q}{\mathrm{d}t} \right)_p$$

where

$\mathrm{d}Q$ is the quantity of heat, expressed in joules (J), necessary to raise the temperature of an amount of material of mass m, expressed in grams (g), by $\mathrm{d}T$ kelvins at constant pressure;

β is the heating rate, expressed in kelvins per minute ($\mathrm{K \cdot min^{-1}}$);

c_p is expressed in joules per gram per kelvin ($\mathrm{J \cdot g^{-1} \cdot K^{-1}}$).

Note 1 to entry: c_p may also be expressed in joules per mole per kelvin ($\mathrm{J \cdot mol^{-1} \cdot K^{-1}}$) when the amount of material, m, is expressed in moles.

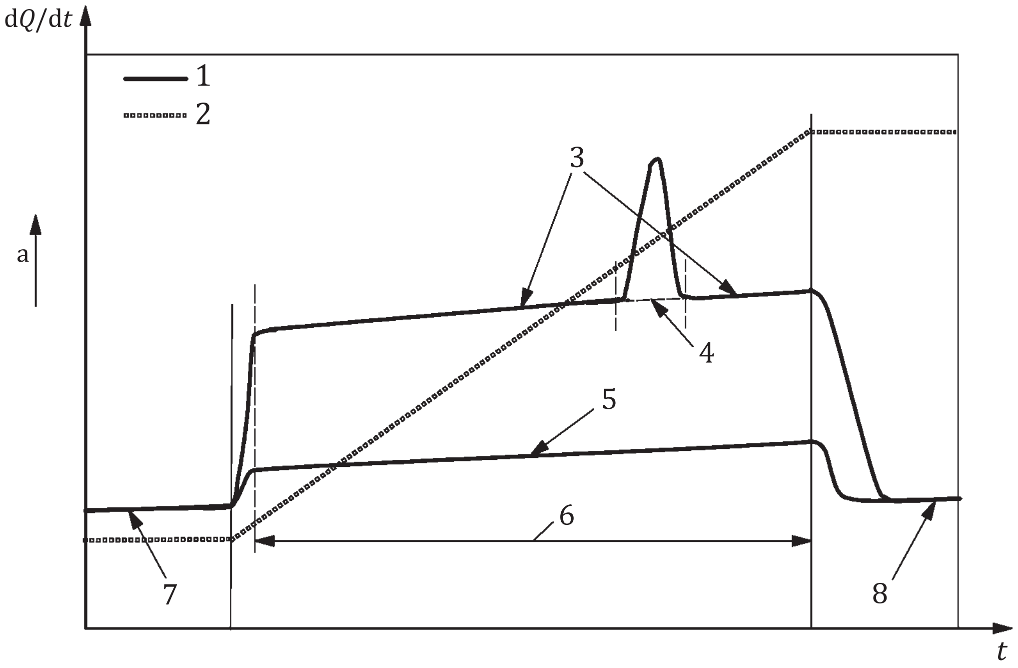
Note 2 to entry: When analysing polymers, ensure that the measured specific heat capacity does not include any heat change due to a chemical reaction or a physical transition.

3.7
baseline

part of the recorded curve in which no reactions or transitions take place

Note 1 to entry: This can be an isothermal baseline when the temperature is maintained constant or a dynamic baseline when the temperature is changed in accordance with a controlled temperature programme.

Note 2 to entry: The baselines defined in 3.7.1 to 3.7.3 refer to the quasi-stationary range only, i.e. when the instrument is operating under stable conditions shortly after starting and shortly before ending the DSC run (see Figure 1).



Key

dQ/dt	heat flow rate	4	virtual baseline
T	temperature	5	instrument baseline
t	time	6	quasi-stationary range
1	dQ/dt vs t (or T)	7	isothermal start baseline
2	T vs t	8	isothermal end baseline
3	specimen baselines	a	Endothermic direction.

Figure 1 — Schematic drawing showing baselines

3.7.1

instrument baseline

curve obtained using only empty crucibles of identical mass and material in the specimen and reference positions of the DSC cell

Note 1 to entry: The instrument baseline is required for heat capacity measurements.

3.7.2

specimen baseline

DSC curve obtained outside any reaction or transition zone(s) while the instrument is loaded with both the specimen in the specimen crucible and the *reference crucible* (3.3)

Note 1 to entry: In this part of the curve, the difference in *heat flow rate* (3.4) between the specimen crucible and the *reference crucible* (3.3) depends solely on the heat capacity of the specimen and the *instrument baseline* (3.7.1).

Note 2 to entry: The specimen baseline reflects the temperature dependence of the heat capacity of the specimen.

Note 3 to entry: For heat capacity determinations, a dynamic DSC curve is required and, in addition, the *instrument baseline* (3.7.1) and the isothermal start and end baselines (see Figure 1).

3.7.3
virtual baseline

imaginary line drawn through a reaction and/or transition zone assuming the heat of reaction and/or transition to be zero

Note 1 to entry: Assuming the change in heat capacity with temperature to be linear, the virtual baseline is drawn by interpolating or extrapolating the specimen baseline in a straight line. It is normally indicated on the DSC curve for convenience (see Figures 1 and 2).

Note 2 to entry: The virtual baseline drawn from peak onset, T_i, to peak end, T_f, (the peak baseline) allows the determination of the peak area from which the heat of transition can be obtained. If there is no significant change in heat capacity during the transition or reaction, the baseline can be drawn simply by connecting the peak onset and peak end by a straight line. If significant heat capacity changes occur, a sigmoidal baseline can be drawn.

Note 3 to entry: Extrapolated and interpolated virtual baselines will not necessarily coincide with each other (see Figure 2).

3.8
step

abrupt positive or negative change in the height of a DSC curve, taking place over a limited temperature range

Note 1 to entry: A step in the DSC curve can be caused by, for example, a glass transition (see Figure 2).

3.8.1
step height

difference between the heights of the extrapolated baselines before and after a step, measured at the time or temperature corresponding to the point on the DSC curve which is equidistant between the two baselines

3.9
peak

part of the DSC curve which departs from the *specimen baseline* (3.7.2), reaches a maximum or minimum, and subsequently returns to the *specimen baseline* (3.7.2)

Note 1 to entry: A peak in the DSC curve may indicate a chemical reaction or a first-order transition. The initial departure of the peak from the *virtual baseline* (3.7.3) corresponds to the start of the reaction or transition.

3.9.1
endothermic peak

peak in which the rate of flow of heat into the specimen crucible is greater than that into the *reference crucible* (3.3)

Note 1 to entry: This corresponds to a transition which absorbs heat.

3.9.2
exothermic peak

peak in which the rate of flow of heat into the specimen crucible is less than that into the *reference crucible* (3.3)

Note 1 to entry: This corresponds to a transition which releases heat.

3.9.3
peak area

area enclosed by a peak and the interpolated *virtual baseline* (3.7.3)

3.9.4

peak height

greatest distance in the ordinate direction between the interpolated *virtual baseline* (3.7.3) and the DSC curve during a peak

Note 1 to entry: The peak height, which is expressed in watts (W) or watts per gram (W/g), is not necessarily proportional to the mass of the specimen.

3.9.5

peak width

distance between the onset and end temperatures or times of a peak

3.10

characteristic temperatures, *T*, and times, *t*

values for temperature and time obtained from the DSC curve

Note 1 to entry: See Figure 2.

Note 2 to entry: For all types of DSC instrument, a distinction needs to be made between two different categories of temperature:

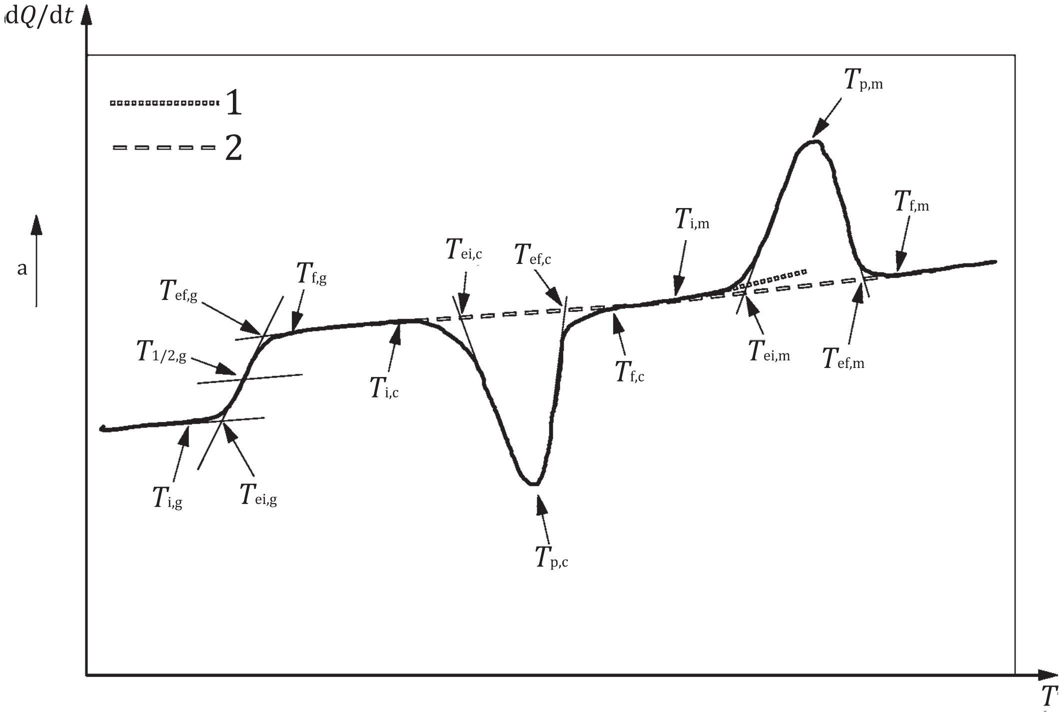
— the temperature at the reference position;

— the temperature at the specimen position.

The reference position temperature is the one preferred for plotting thermograms. If the specimen position temperature is used, then this information will need to be included in the test report.

Note 3 to entry: Characteristic temperatures are expressed in degrees Celsius (°C), relative temperatures and temperature differences in kelvins (K) and characteristic times in seconds (s) or minutes (min) (see Figure 2).

Note 4 to entry: The DSC curve can also be plotted using time, *t*, as the abscissa instead of temperature, *T*.



Key

dQ/dt	heat flow rate	1	extrapolated baseline
T	temperature (or t, time)	2	interpolated baseline

Characteristic temperatures

The first subscript, or pair of subscripts, denotes the position on the DSC curve with respect to the step or peak:

— onset temperature	T_i	first detectable departure of curve from extrapolated start baseline;
— interpolated or extrapolated onset temperature	T_{ei}	(for a peak) point of intersection of interpolated virtual baseline and tangent drawn at point of inflection of near side of peak or (for a step) point of intersection of extrapolated start baseline and tangent drawn at point of inflection of step;
— midpoint temperature	$T_{1/2}$	half-height of a step;
— peak temperature	T_p	greatest distance between curve and virtual baseline during a peak;
— interpolated or extrapolated end temperature	T_{ef}	(for a peak) point of intersection of interpolated virtual baseline and tangent drawn at point of inflection of far side of peak or (for a step) point of intersection of extrapolated end baseline and tangent drawn at point of inflection of step;
— end temperature	T_f	last detectable deviation of curve from extrapolated end baseline.

The second subscript indicates the type of transition:

g	glass transition
c	crystallization
m	melting

[a] Endothermic direction.

Figure 2 — Typical DSC curve (schematic)

4 Basic principles

4.1 General

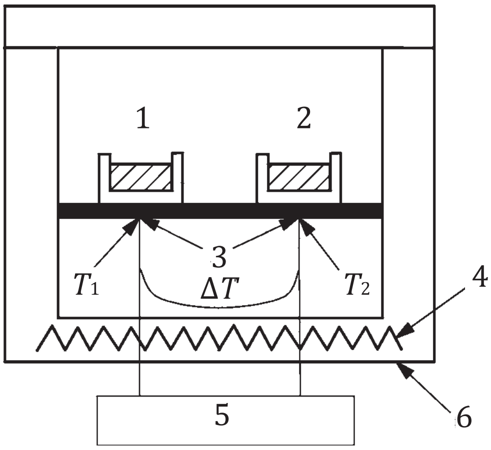
The difference between the rate of heat flow into a specimen and that into a reference crucible is measured as a function of temperature and/or time while the specimen and the reference are subjected to the same temperature-control programme under a specified atmosphere.

Two types of DSC can be carried out: heat-flux DSC and power-compensation DSC.

4.2 Heat-flux DSC

The specimen and reference positions are subjected to the same temperature-control programme by a single heater. A difference in temperature, ΔT, occurs between the specimen position and the reference position because of the difference in heat capacity between the specimen and the reference. From this temperature difference, the difference in the rates of heat flow into the specimen and reference positions is derived and is normally recorded against the temperature of the reference, T_{ref}, or against time.

A schematic drawing of a heat-flux DSC instrument is shown in Figure 3.



Key

1	specimen position	6	surrounding oven
2	reference position	T_1	temperature at specimen position (T_{specimen})
3	thermocouples	T_2	temperature at reference position (T_{ref})
4	single heater	ΔT	temperature difference between specimen and reference positions
5	measurement circuit for T_{specimen}, T_{ref} and ΔT		

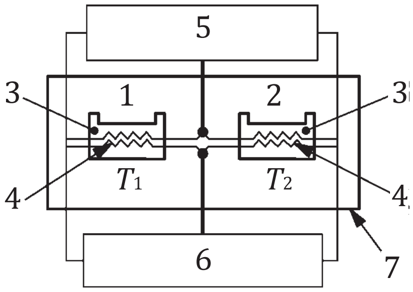
Figure 3 — Schematic diagram illustrating the basic principles of heat-flux DSC

4.3 Power-compensation DSC

In power-compensated DSC, individual heaters are used for the specimen and reference positions. The difference in electrical power required to maintain both the specimen position and the reference position at the same temperature is recorded against temperature or time, while each position is subjected to the same temperature-control programme.

For power-compensated isoperibolic calorimeters, the surrounding temperature (i.e. the temperature of the heat sink) has to be kept constant.

A schematic drawing of a power-compensation DSC instrument is shown in Figure 4.



Key

1	specimen position
2	reference position
3	thermometers
4	individual heaters
5	measurement circuit for T_{specimen} and T_{ref}
6	heat-flux compensation circuit
7	surrounding heat sink
T_1	temperature at specimen position (T_{specimen})
T_2	temperature at reference position (T_{ref})

Figure 4 — Schematic diagram illustrating the basic principles of power-compensation DSC

5 Apparatus and materials

5.1 Differential scanning calorimeter, with the following features:

a) A symmetrical crucible holder assembly which has holders for the specimen and reference crucibles.

b) The capability to generate constant heating and cooling rates suitable for the intended measurements.

c) The capability to maintain the test temperature constant to within ± 0,3 K or less for at least 60 min.

d) The capability to carry out step heating or step cooling.

NOTE Normally, this is achieved by a suitable combination of linear heating or cooling and constant-temperature regimes.

e) The capability to maintain a constant purge gas flow rate controllable to within ±10 % over a range of flow rates (e.g. 10 ml·min^{-1} to 100 ml·min^{-1}).

NOTE The actual gas flow rate will depend on the design of the instrument used.

f) A temperature range in line with the experimental requirements.

g) A heat flow rate range of ±100 mW or more.

h) A recording device capable of automatically recording the measured curve of heat flow rate against temperature and time.

i) The capability to measure temperature signals with a resolution of ±0,1 K and an accuracy of ±0,5 K or better.

j) The capability to measure time with a resolution of ±0,5 s and an accuracy of ±1 s or better.

k) The capability to measure heat flow rates with a resolution of ±0,5 μW and an accuracy of ±2 μW or better.

5.2 Crucibles, for the specimen and reference positions. They shall be of the same type, made of the same material and have similar masses. They shall be physically and chemically inert to the specimen, the calibration materials and the purge gas under the measurement conditions (see Annexes C and D).

NOTE 1 If required, small variations in crucible mass can be arithmetically corrected for, given the specific heat capacity of the crucible material.

Crucibles should preferably be made of a material with a high thermal conductivity, e.g. aluminium. Ventilated crucibles should preferably be used to avoid changes in pressure during the measurement run and to allow the exchange of gas with the surrounding atmosphere. However, for special purposes, crucibles closed with lids or hermetically sealed crucibles may be required so that they will withstand the overpressure arising during the measurement run.

When using special high-pressure or glass crucibles, their relatively high mass and poor thermal conductivity shall be taken into account. Recalibration of the instrument may be required.

NOTE 2 When using high-pressure or hermetically closed crucibles, measurements are not necessarily performed at constant pressure. Hence, the constant-pressure requirement for measuring enthalpies or c_p may not be fulfilled.

5.3 Balance, capable of measuring the specimen mass with a resolution of ±0,01 mg and an accuracy of ±0,1 mg or better.

5.4 Calibration materials, covering the temperature range of interest and preferably chosen from the list of recommended calibration materials in Annex C.

5.5 Purge gas, preferably a dry and inert gas (e.g. nitrogen of purity 99,99 % or better), used to avoid oxidative or hydrolytic degradation during testing.

For the investigation of chemical reactions, including oxidation, special reactant gases may be required.

If a gas generator is used to supply gas for purging and environmental control during testing, rather than using a pressurized gas bottle purge, it is recommended that suitable drying and filtering systems be installed.

6 Specimen

The specimen shall be in the liquid or solid state. Solid-state specimens may be in any form which fits into the crucible (e.g. powder, pellets, granules, fibres) or may be cut from bigger pieces to a suitable size. The specimen shall be representative of the sample being examined and shall be prepared and handled with care. Particular care shall be taken to avoid any contamination of the specimen. If the specimen is taken from larger pieces by cutting, care shall be taken to prevent heating, polymer orientation or any other effect that may alter the specimen properties. Operations such as grinding that could cause heating or reorientation and could therefore change the thermal history of the specimen shall be avoided. The method of sampling and specimen preparation shall be stated in the test report.

If the specimen crucible is closed or sealed with a lid, this shall not cause any deformation of the bottom of the crucible. Good thermal contact between the specimen and crucible and between the crucible and holder shall be ensured.

Typical specimen masses are between 2 mg and 40 mg.

NOTE Incorrect specimen preparation can change the thermal properties of the polymers examined. For further information, refer to Annex E.

7 Test conditions and specimen conditioning

7.1 Test conditions

The instrument shall be maintained and operated in an atmosphere suitable for the intended test.

Unless excluded by special requirements for particular test procedures, all calibration and test measurements shall be performed using closed, ventilated crucibles, preferably made of aluminium, to improve reproducibility.

It is recommended that the instrument be protected from air draughts, exposure to direct sunlight and abrupt changes in temperature, pressure or mains voltage.

7.2 Conditioning of specimens

Specimens shall be conditioned prior to the measurement run as specified in the relevant material standard or by a method agreed between the interested parties.

Unless otherwise specified, specimens shall be dried to constant mass before performing measurements. Care shall be taken to choose suitable drying conditions to prevent physical changes, such as ageing or changes in crystallinity of the specimens.

NOTE Depending on the material and its thermal history, the methods of preparation and conditioning of the sample and specimens may be crucial to the values obtained, the consistency of the results and their significance.

8 Calibration

8.1 General

Before commissioning a new instrument or after replacing or modifying essential components or after cleaning the measuring cell by heating to elevated temperatures, the calorimeter shall be calibrated at least with respect to temperature and heat. In addition, heat flow rate calibration may be required for heat capacity measurements. Recalibration of the instrument shall be carried out regularly at the required calibration intervals, e.g. when the instrument is being used as part of a quality assurance system.

NOTE In many cases, the calibration procedures will be built into the instrument control software and thus at least partly automated.

Recalibration of the instrument should preferably be performed each time the test conditions are significantly changed. More frequent checks may be carried out as required.

The calibration can be affected by the following:

— type of calorimeter used and its stability;

— heating and cooling rates;

— type of cooling system used;

— type of purge gas used and its flow rate;

— type of crucible used, the crucible size and the positions of the crucibles in the crucible holder;

— location of the specimen in the specimen crucible;

— mass and particle size of the specimen;

— thermal contact between the specimen crucible and the crucible holder.

The conditions of the actual determination should therefore be defined as precisely as possible and the calibration carried out under these conditions as closely as possible. Computer-controlled DSC instruments may automatically correct for the effects of some of these sources of error.

The calibration shall be carried out using the same type of crucible, made of the same material, and using the same purge gas at the same flow rate as will be used for subsequent measurements.

Calibration specimens shall be heated only slightly above their transition temperatures to prevent reactions between the calibration materials and the crucibles.

Immediately after the measurement run, the specimens should preferably be cooled until the transition back to the initial state has taken place.

For most practical measurements, it will be sufficient to use the calibration procedures specified in 8.2 to 8.5. For more accurate calibrations, the procedures specified in Annexes A and B may be used.

8.2 Calibration materials

Preferably, certified reference materials should be used. The true temperature, T_{cal}, the true heat of transition, ΔQ_{cal}, and the true specific heat, $c_{p,\mathrm{cal}}$, which are used for the calibration shall be those appearing on the certificate accompanying the reference material.

If certified values are not available, the values given in Tables C.1, C.2 and C.3 may be used. Additional calibration materials may be used provided their thermal properties are sufficiently defined. The calibration materials shall not interact with the crucibles or purge gas used (see Annex D).

For each calibration, a fresh calibration specimen shall be used. Any coating of oxide on the surface of the calibration specimen shall be removed, e.g. by freshly cutting the specimen. The position of the specimen in the crucible should preferably be kept the same to improve the repeatability of the results.

To avoid misleading results or damage to the crucible holder, combinations of calibration and crucible materials which are not expected to have any influence on the melting point should preferably be used (see Annex D). Combinations in which the calibration material is expected to dissolve the crucible material should be avoided.

8.3 Temperature calibration

8.3.1 General

This is the establishment of the relationship between the temperature, T_{meas}, indicated by the instrument and the true temperature, T_{cal}, of the transition of the calibration material. The relation $T_{\mathrm{cal}} = T_{\mathrm{meas}} + \Delta T_{\mathrm{corr}}$ is valid, where ΔT_{corr} is a temperature correction.

When using calibration materials other than those listed in Annex C, only first-order transitions, e.g. the melting of pure substances, shall be used for calibration purposes.

NOTE True transition temperatures can be obtained from calibration material certificates, other qualified sources or the literature.

With the calibration materials listed in Annex C, temperature calibration shall be carried out in the heating mode only. However, correctly calibrated instruments that give consistent results in the heating mode will not necessarily give consistent results in the cooling mode because of supercooling of the substance during the transition in question. The symmetry of the temperature scale in the heating and cooling mode can be checked with substances that do not supercool, e.g. liquid crystals.

8.3.2 Procedure

The following procedure describes the minimum requirements for carrying out temperature calibration.

Weigh at least two calibration materials, covering the temperature range required, into crucibles, preferably made of aluminium with an oxidized surface.

After having melted and recrystallized each calibration specimen, carry out a heating run during which the melting peak is recorded. Perform cooling and heating runs at the same rate as will be used for subsequent measurements.

For each melting peak measured, determine the extrapolated peak onset temperature, $T_{\mathrm{ei,m}}$ (see Figure 2), using the interpolated virtual baseline between peak onset and peak end.

For each calibration material, i, obtain the temperature correction, $\Delta T^{i}_{\mathrm{corr}}$ by subtracting the extrapolated peak onset temperature, $T^{i}_{\mathrm{ei,m}}$ from the true transition temperature, T^{i}_{cal} :

$$\Delta T^{i}_{\mathrm{corr}} = T^{i}_{\mathrm{cal}} - T^{i}_{\mathrm{ei,m}} \tag{1}$$

Then correct the temperature scale of the instrument, by linear interpolation of the temperature correction within the temperature range covered by the calibration materials used, in accordance with Formula (2):

$$\Delta T_{corr}(T) = \Delta T^{1}_{\mathrm{corr}} + (\Delta T^{2}_{\mathrm{corr}} - \Delta T^{1}_{\mathrm{corr}}) \times \frac{T - T^{1}_{\mathrm{cal}}}{T^{2}_{\mathrm{cal}} - T^{1}_{\mathrm{cal}}} \tag{2}$$

where

$\Delta T^{1}_{\mathrm{corr}}$, $\Delta T^{2}_{\mathrm{corr}}$	are the temperature corrections for the two calibration materials;
T^{1}_{cal}, T^{2}_{cal}	are the true transition temperatures of the two calibration materials.

In order to keep errors caused by deviation from linearity of the temperature correction versus temperature relationship small, it is recommended that the temperature range covered by the two calibration materials be kept as small as possible. If bigger temperature ranges are required, more than two calibration materials should be used.

NOTE 1 If more than two calibration materials are used, it is possible to use a polynomial interpolation.

NOTE 2 The temperature correction may be performed automatically by some instruments.

This calibration procedure is dependent on the heating rate and has to be performed for each heating rate.

8.3.3 Accuracy of calibration

The accuracy of this temperature calibration procedure is expected to be better than ±0,8 K provided the temperature difference between the calibration materials does not exceed 50 K and there is no deviation from linearity of ΔT_{corr} versus T. Bigger temperature differences and significant deviations from linearity will result in lower accuracy.[11][12]

For a more precise method of temperature calibration taking into account the effect of heating rate, refer to Annex A.

8.4 Heat calibration

8.4.1 General

This procedure establishes the relationship between the heat, ΔQ_{m}, measured by the instrument $\left(\Delta Q_{\mathrm{m}} = \int_{t_1}^{t_2} \frac{\mathrm{d}Q}{\mathrm{d}t}\,\mathrm{d}t\right)$, which is proportional to the area between the DSC curve and the virtual baseline, and the true heat, ΔQ_{tr}, absorbed or released by the specimen as a result of a transition. The relationship $\Delta Q_{\mathrm{tr}} = K_Q(T) \times \Delta Q_{\mathrm{m}}$ is valid, where $K_Q\ (T)$ is a temperature-dependent calibration factor.

For calibration materials, ΔQ_{tr} is equal to ΔQ_{cal}.

8.4.2 Procedure

The following procedure describes the minimum requirements for carrying out heat calibration.

For heat calibration, the same measurements can be made as those made for temperature calibration.

Carry out a heating run with one material, preferably indium.

Draw the linear virtual baseline (see Figure 1) and obtain the specific heat of melting from the area between the DSC curve and the virtual baseline, using Formula (3):

$$\Delta q_{\mathrm{m}} = \frac{1}{m} \times \frac{60}{\beta} \int_{T_{\mathrm{i,m}}}^{T_{\mathrm{f,m}}} \frac{d(\Delta Q)}{\mathrm{d}t} \mathrm{d}T \tag{3}$$

where

Δq_{m} is the specific-heat change, $\Delta Q_{\mathrm{m}}/m$;

m is the mass of the calibration specimen;

β is the heating rate;

$\frac{\mathrm{d}(\Delta Q)}{\mathrm{d}t}$ is the difference in heat flow rate between the DSC curve and the virtual baseline;

T is the temperature of the calibration specimen.

The heat calibration factor, K_Q, is obtained by dividing the true specific heat of the transition of the calibration material, Δq_{cal}, by the measured specific transition heat, Δq_{m}:

$$K_Q = \Delta q_{\mathrm{cal}} / \Delta q_{\mathrm{m}} \tag{4}$$

8.4.3 Accuracy of calibration

The accuracy of this method is not expected to be better than ±2,5 % for indium. Due to the dependence of the calibration factor on the mass and thermal conductivity of the specimen and on heating rate, peak shape and temperature, this may deteriorate to ±10 % and even beyond.[11][12]

For an extended, more precise, method of heat calibration, refer to Annex B.

8.5 Heat flow rate calibration

8.5.1 General

This procedure establishes the relationship between the heat flow rate, $(\mathrm{d}Q/\mathrm{d}t)_\mathrm{m}$, measured by the instrument and the true rate of flow, $(\mathrm{d}Q/\mathrm{d}t)_\mathrm{tr}$, of the heat absorbed by the specimen due to its heat capacity, c_p, the heating rate, β, and the specimen mass, m:

$$(\mathrm{d}Q / \mathrm{d}t)_\mathrm{tr} = \frac{c_p \times \beta \times m}{60} \qquad (5)$$

The relationship $(\mathrm{d}Q / \mathrm{d}t)_{tr} = K_{(\mathrm{d}Q/\mathrm{d}t)}(T) \times (\mathrm{d}Q / \mathrm{d}t)_\mathrm{m}$ is valid, where $K_{(\mathrm{d}Q/\mathrm{d}t)}(T)$ is a temperature-dependent calibration factor.

The heat flow rate calibration shall be carried out for measurements of specific heat and changes in specific heat at the glass transition temperature, T_g.

For calibration materials, $(\mathrm{d}Q/\mathrm{d}t)_\mathrm{tr}$ is equal to $(\mathrm{d}Q/\mathrm{d}t)_\mathrm{cal}$.

8.5.2 Procedure

Heat flow rate calibration can be performed with corundum (synthetic sapphire) or another material which has a well-defined heat capacity in the temperature range of interest. The heat capacity of sapphire is given in Annex C.

Choose the mass of the calibration specimen such that the heat capacity of the calibration specimen matches that of the actual specimen as closely as possible. Use crucibles of the same type and of masses which are as similar as possible for empty runs (carried out with an empty crucible) and calibration specimen measurements.

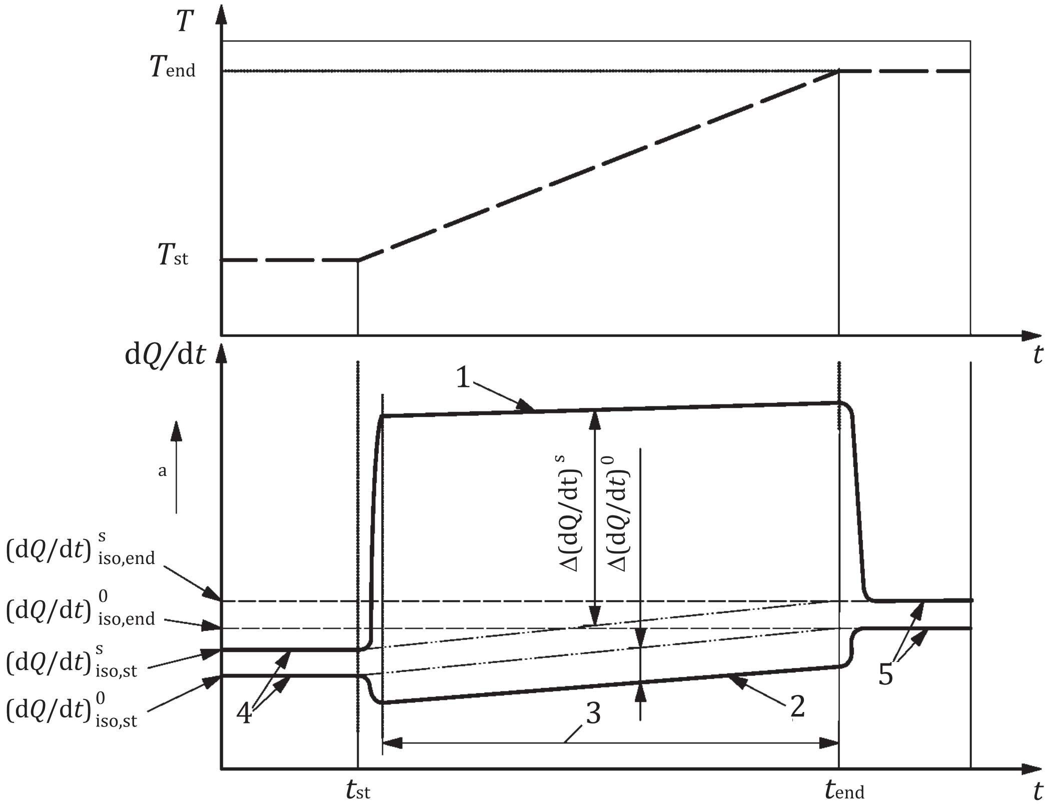
Subject the calibration specimen and the empty crucible to the same temperature programme, which is divided in three segments (see Figure 5):

— isothermal starting lines for calibration specimen measurement, $(\mathrm{d}Q / \mathrm{d}t)^\mathrm{s}_\mathrm{iso,st}$ and the empty run, $(\mathrm{d}Q / \mathrm{d}t)^0_\mathrm{iso,st}$

— a dynamic segment (heating rate preferably 10 K/min, duration preferably between 10 min and 30 min) for calibration specimen measurement, $(\mathrm{d}Q/\mathrm{d}t)^\mathrm{s}$ and the empty run $(\mathrm{d}Q/\mathrm{d}t)^0$;

— isothermal ending lines for calibration specimen measurement, $(\mathrm{d}Q / \mathrm{d}t)^\mathrm{s}_\mathrm{iso,end}$ and the empty run, $(\mathrm{d}Q / \mathrm{d}t)^0_\mathrm{iso,end}$.

The isothermal segments shall be long enough for steady-state conditions to be reached (generally after 2 min to 5 min).



Key

1	calibration specimen run	T	temperature
2	empty run	dQ/dt	heat flow rate
3	quasi-stationary range	t	time
4	isothermal start lines	a	Endothermic direction.
5	isothermal end lines		

Figure 5 — DSC curves for heat flow rate calibration

In the quasi-stationary range of the dynamic segment, the corresponding heat flow rate values measured for the calibration specimen and the empty run are evaluated in accordance with Formula (6) and are monitored against temperature to obtain the calibration function, $K_{(\mathrm{d}Q/\mathrm{d}t)}(T)$:

$$K_{(\mathrm{d}Q/\mathrm{d}t)}(T) =$$

$$\frac{c_p^{\mathrm{cal}}(T)\times\beta\times m_{\mathrm{cal}} + c_p^{\mathrm{cr}}(T)\times\beta\times(m_s - m_r)}{60\times\left\langle\left\{\left(\frac{\mathrm{d}Q}{\mathrm{d}t}\right)^s - \left[\left(\frac{\mathrm{d}Q}{\mathrm{d}t}\right)^s_{\mathrm{iso,st}} + \frac{\left(\frac{\mathrm{d}Q}{\mathrm{d}t}\right)^s_{\mathrm{iso,end}} - \left(\frac{\mathrm{d}Q}{\mathrm{d}t}\right)^s_{\mathrm{iso,st}}}{t_{\mathrm{end}} - t_{\mathrm{st}}}\times\left(t - t_{\mathrm{st}}\right)\right]\right\} - \left\{\left(\frac{\mathrm{d}Q}{\mathrm{d}t}\right)^0 - \left[\left(\frac{\mathrm{d}Q}{\mathrm{d}t}\right)^0_{\mathrm{iso,st}} + \frac{\left(\frac{\mathrm{d}Q}{\mathrm{d}t}\right)^0_{\mathrm{iso,end}} - \left(\frac{\mathrm{d}Q}{\mathrm{d}t}\right)^0_{\mathrm{iso,st}}}{t_{\mathrm{end}} - t_{\mathrm{st}}}\times\left(t - t_{\mathrm{st}}\right)\right]\right\}\right\rangle} \quad (6)$$

where

c_p^{cal}, c_p^{cr} are the specific heat capacities of the calibration and crucible materials, respectively;

β is the heating rate;

m_{cal}, m_{s}, m_{r} are the masses of the calibration specimen, specimen crucible and reference crucible, respectively.

From Figure 5, it can be seen that Formula (6) can be rewritten as

$$K_{(\mathrm{d}Q/\mathrm{d}t)}(T) = \frac{c_p^{\mathrm{cal}}(T) \times \beta \times m_{\mathrm{cal}} + c_p^{\mathrm{cr}}(T) \times \beta \times (m_{\mathrm{s}} - m_{\mathrm{r}})}{60 \times [\Delta(\mathrm{d}Q / \mathrm{d}t)^s - \Delta(\mathrm{d}Q / \mathrm{d}t)^0]} \qquad (7)$$

9 Procedure

9.1 Setting up the apparatus

9.1.1 Switching on

Switch the instrument on at least 1 h prior to any calibration or testing to allow it to reach steady-state conditions.

9.1.2 Purge gas

Unless excluded by special requirements, perform measurements while purging the instrument with inert gas (e.g. N_2, He or Ar). The instrument shall be calibrated with the same purge gas that is to be used for actual measurements.

9.1.3 Experimental conditions

The experimental conditions (e.g. heating rate, specimen mass) used will depend on the thermal effect to be investigated and are described in the appropriate parts of ISO 11357. Other experimental parameters may be used if prescribed in relevant material or product standards or specifications or agreed between the interested parties.

9.1.4 Baseline determination

Place empty crucibles of the same nominal mass at the specimen and reference positions in the crucible holder. Adjust the experimental conditions to those which will be used for the actual measurement run. The recorded DSC curve (i.e. the instrument baseline) should be close to a straight line over the required temperature range. If significant baseline curvature is observed, check the crucible holder for contamination.

NOTE With computer-controlled instruments, any remaining curvature can be corrected for by subtracting the instrument baseline from the DSC curve.

When a reasonably straight line cannot be obtained, record the DSC curve after confirming its repeatability.

9.2 Loading the specimen into the crucible

9.2.1 General

Do not handle sample material or crucibles with bare hands. Use either tweezers or gloves.

9.2.2 Selection of crucibles

Use only clean crucibles of volume and material appropriate for the intended measurements.

Unless excluded by the particular type of test, use closed, ventilated crucibles to obtain quantitative results and to allow sufficient contact with the purge gas. The crucibles shall be such that they will not become deformed during loading and closing so that good thermal contact is ensured between the specimen and the instrument.

Select two identical crucibles, one for the specimen and one (normally empty) as the reference crucible.

9.2.3 Weighing the specimen crucible

Weigh the specimen crucible, together with its lid, to the nearest 0,01 mg.

9.2.4 Loading the specimen

Load the specimen into the specimen crucible. The specimen mass will depend on the thermal effect being investigated and is specified in more detail in the relevant part of ISO 11357.

NOTE In the case of transitions and reactions of filled or reinforced materials, the specimen mass is considered to be the polymer fraction of the material which contributes to such thermal effects.

If necessary, homogenize the sample to be investigated to obtain a representative specimen.

9.2.5 Determination of the mass of the specimen

Weigh the crucible containing the specimen and calculate the mass of the specimen by subtracting the mass of the empty crucible determined in 9.2.3.

The specimen under investigation should preferably not contain volatile substances, which should be eliminated by appropriate conditioning. However, it should be taken into account that conditioning may change the specimen by inducing chemical reactions, removing volatile substances, ageing or changing the morphology or crystallinity. If volatile substances are an important part of the specimen under investigation, gas- and pressure-tight crucibles or a pressure DSC instrument should be used.

9.3 Insertion of crucibles into the instrument

Loading of the specimen and reference crucibles should preferably be carried out at, or slightly above, room temperature (max. 50 °C) to prevent condensation of moisture on or inside the crucibles. Unless crucibles are loaded by an automatic specimen changer, use tweezers or another suitable tool to insert the crucibles in the crucible holder, checking that there is good thermal contact between the crucibles and the crucible holder. Do not use bare hands. After loading the crucibles, close the cover of the crucible holder, if it has one.

9.4 Performing measurements

9.4.1 General

Due to transients which occur on start-up, reliable data cannot be obtained at temperatures near the starting temperature or time. Such transient effects are larger with higher heating or cooling rates.

9.4.2 Scanning mode

9.4.2.1 Preparing the instrument

Programme the instrument and set the experimental parameters to carry out the required thermal cycle(s). Two types of programme can be used: continuous or stepwise heating or cooling.

9.4.2.2 Starting the measurement run

Start the temperature programme and record the heat flow rate data for subsequent evaluation.

Since DSC measurements on polymers are greatly affected by the thermal history and morphology of the specimen, it is recommended that the heating or cooling run be carried out twice. The first run reflects the as-received state and is performed up to the melting or glass transition where the material reaches thermal equilibrium. The second run is carried out after cooling the specimen at a defined rate to erase prior thermal history and thus allows comparison of material properties. The intermediate cooling run reveals information about nucleation and crystallization of the material (see Annex E for further information).

With reactive systems, the first run provides information on the curing process. Depending on the level of cure achieved, subsequent runs reveal information about the material in its cured or partially cured state.

9.4.2.3 Unloading the specimen

After finishing the measurement run, bring the crucible holder back to the loading temperature and take out the crucible containing the specimen.

9.4.2.4 Processing of data

Process the recorded data in accordance with the instrument manufacturer's instructions and the thermal effects under investigation.

9.4.3 Isothermal mode

9.4.3.1 General

Depending on the type of instrument used, two different isothermal procedures are available, with the specimen being introduced at room temperature or at some other specified temperature.

9.4.3.2 Specimen introduced at room temperature

9.4.3.2.1 Loading the instrument

Introduce the crucible containing the specimen and that serving as reference into the crucible holder at, or slightly above, room temperature (max. 50 °C) and bring the instrument to the required starting temperature as rapidly as possible.

9.4.3.2.2 Starting the measurement run

Maintaining the temperature at this value, record the DSC curve as a function of time. Continue the run, with the test conditions unchanged, until at least 5 min after the endothermic or exothermic reaction or transition has finished and a stable baseline is obtained. Record the heat flow rate data for subsequent evaluation.

9.4.3.2.3 Unloading the instrument

Bring the instrument back to the loading temperature and remove the specimen crucible.

9.4.3.2.4 Data processing

Process the recorded data in accordance with the instrument manufacturer's instructions and according to the thermal effects under investigation.

9.4.3.3 Specimen introduced at a temperature other than room temperature

9.4.3.3.1 Preparing the instrument

Set the instrument to the specified measurement temperature and allow it to reach steady-state conditions.

9.4.3.3.2 Loading the specimen and carrying out the measurement run

Introduce the crucible containing the specimen and that serving as reference into the crucible holder at this temperature and immediately start the instrument to record the DSC curve as a function of time. To reduce uncontrolled transient changes in the temperature of the crucible holder, keep the time during which the crucible holder is open as short as possible. Continue the run, with the test conditions unchanged, until at least 5 min after the endothermic or exothermic reaction or transition has finished and a stable baseline is obtained again. Record the heat flow rate data for subsequent evaluation.

9.4.3.3.3 Unloading the specimen

Bring the instrument back to the loading temperature and remove the specimen crucible.

9.4.3.3.4 Data processing

Process the recorded data in accordance with the instrument manufacturer’s instructions and according to the thermal effects under investigation.

9.5 Post-run checks

9.5.1 Check for loss in mass

Reweigh the crucible containing the specimen after the test. If any loss in mass is observed, this could have created an additional thermal effect or perturbed the instrument baseline.

9.5.2 Inspection of specimens

If any unexpected chemical change is suspected, open the specimen crucible and inspect the specimen carefully. Do not use damaged crucibles for any further measurements.

The re-use of crucibles is not recommended. However, in exceptional circumstances, when it has been unambiguously demonstrated that there is no interaction between the specimens and the crucibles, that no residual contamination is left on removal of the specimen and that the crucibles are not damaged, then crucibles may be re-used. Their re-use shall be reported in the test report, however.

9.5.3 Checking of crucibles and crucible holder

Examine the specimen crucible to check for any change of location within the crucible holder, any deformation of the crucible or any overflow of specimen material. If any of these has occurred, repeat the measurement run.

If the crucible holder has been contaminated from specimen overflow or condensed volatile substances, clean it in accordance with the manufacturer’s instructions and recalibrate it.

10 Test report

The test report shall include the following information:

a) a reference to the relevant part of ISO 11357;

b) all information necessary for complete identification of the material examined;

c) the type of DSC instrument used (heat-flux or power-compensated), as well as the instrument model and manufacturer;

d) the type of crucible used, the crucible material and, when necessary, the mass of each crucible;

e) the purge gas used, its purity and the flow rate used;

f) the type of calibration procedure used (simple or extended) and details of the calibration materials used, including source, mass and other properties important for calibration;

g) details of sampling, specimen preparation and conditioning, if applicable;

h) the shape and dimensions of the specimen, if applicable;

i) the mass of the specimen;

j) the thermal history of the sample and the specimen;

k) the temperature programme parameters, including the time and temperature of isothermal steps and the rate of dynamic steps;

l) the change in mass, if any, of the specimen during the test;

m) the test results, including the DSC curves obtained;

n) any additional information, including details of any deviations from the procedure and any operations not specified in the relevant part of ISO 11357 which could have had an influence on the results;

o) the date of the test.

Annex A
(normative)

Extended, high-precision, temperature calibration[12]

The extended temperature calibration shall be used if one or more of the following are required:

- a precision higher than ±0,8 K over a temperature range of 50 K;
- the inclusion of the effect of heating rate in the calibration procedure;
- the inclusion of the influence of specimen mass in the calibration procedure.

Two specimens of each of at least three different calibration materials covering the temperature range required, with masses, m, of approximately 3 mg and 10 mg, shall be weighed into crucibles, preferably made of aluminium with an oxidized surface.

For each heating and cooling rate, β = 1 K/min, 5 K/min, 10 K/min and 20 K/min, the specimen shall be melted and recrystallized and then subjected to a heating run at the same rate, during which the melting peak shall be recorded.

For each peak, determine the extrapolated peak onset temperature, $T_{\mathrm{ei,m}}$ (see Figure A.2), using the interpolated virtual baseline between peak onset and peak end.

For each calibration material and each mass, plot the extrapolated peak onset temperatures against the heating rate and extrapolate the plot in a straight line to the heating rate $\beta = 0$ K/min (see Figure A.1).

Determine the temperature correction, $\Delta T_{\mathrm{corr}}(T_{\mathrm{cal}}, m)$, by subtracting the extrapolated peak onset temperature thus determined, $T_{\mathrm{ei,m}}(\beta = 0)$, from the true transition temperature, T_{cal} (see Figure A.1):

$$\Delta T_{\mathrm{corr}}(T_{\mathrm{cal},} m) = T_{\mathrm{cal}} - T_{\mathrm{ei,m}}(\beta = 0) \tag{A.1}$$

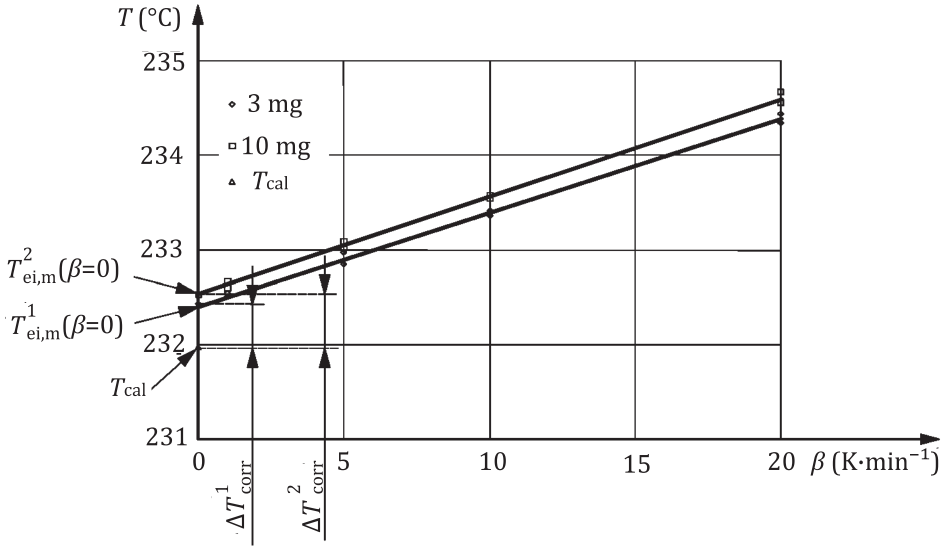
Plot the temperature correction terms determined by this procedure against the extrapolated peak onset temperatures, $T_{\mathrm{ei,m}}(\beta = 0)$, to give the temperature dependence of the temperature calibration (see Figure A.2):

$$\Delta T_{\mathrm{corr}}(T, m) = f[T_{\mathrm{cal}} - T_{\mathrm{ei,m}}(T_{\mathrm{cal}}, m, \beta = 0)] \tag{A.2}$$

NOTE The temperature correction with respect to the heating rate and/or temperature is made automatically by some instruments.

If wider temperature ranges are required, it is preferable to use more than three calibration materials.

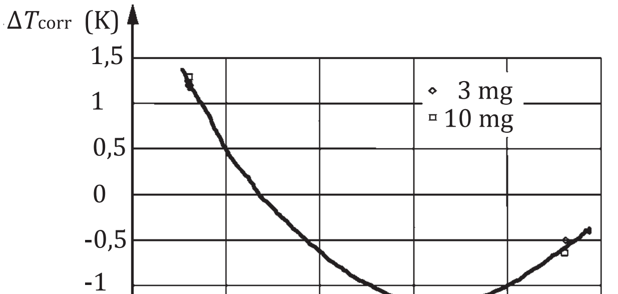
The accuracy of this temperature calibration procedure would be expected to be better than ±0,3 K over a temperature range from 25 °C to 330 °C.[13]



Key

T	temperature
β	heating rate
T_{cal}	true transition temperature of calibration material (tin)
$T_{ei,m}^{1}(\beta = 0), T_{ei,m}^{2}(\beta = 0)$	peak onset temperatures extrapolated to zero heating rate for 3 mg and 10 mg specimen masses, respectively
ΔT_{corr}^{1}, ΔT_{corr}^{2}	temperature corrections for 3 mg and 10 mg specimen masses, respectively

Figure A.1 — Determination of temperature correction from plots of extrapolated peak onset temperature versus heating rate using tin as calibration material



Key

ΔT_{corr}	temperature correction
$T_{ei,m}(\beta = 0)$	peak onset temperature for calibration material extrapolated to zero heating rate

Figure A.2 — Temperature calibration function obtained with gallium, indium and tin

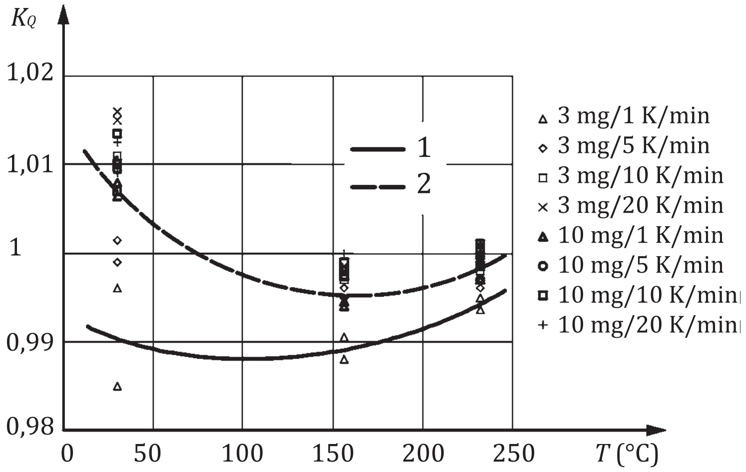
Annex B
(normative)

Extended, high-precision, heat calibration

The extended heat calibration shall be used if one or more of the following are required:

- a precision higher than ±2 %;
- the inclusion of the effect of heating rate in the calibration procedure;
- the inclusion of the influence of specimen mass in the calibration procedure.

For each of the peaks obtained as specified in Annex A, draw a linear virtual baseline (see Figure 1) and determine the heat of melting from the area between the DSC curve and the virtual baseline using Formula (8) (see 8.4.2). Figure B.1 shows a heat calibration function obtained using gallium, indium and tin.



Key

K_Q heat calibration factor, dependent on calibration material, specimen mass and heating rate
T temperature
1 calibration curve for specimen mass of 3 mg and heating rate of 1 K/min
2 calibration curve for specimen mass of 10 mg and heating rate of 1 K/min

Figure B.1 — Heat calibration function determined with gallium, indium and tin

The individual heat calibration factors, K_Q, are obtained by division of the true specific heats of transition, Δq_{cal}, by the measured specific heats of transition, Δq_{m}, of the respective calibration materials:

$$K_Q(T_{\text{cal}}, m, \beta) = \Delta q_{\text{cal}} / \Delta q_m(T_{\text{cal}}, m, \beta) \tag{B.1}$$

where T_{cal} is the true transition temperature of the calibration material.

The heat calibration factors are plotted against temperature to obtain the heat calibration function (see Figure B.1):

$$K_Q(T, m, \beta) = f[\Delta q_{\mathrm{cal}} / \Delta q_m(T_{\mathrm{cal}}, m, \beta)] \tag{B.2}$$

If the dependencies on heating rate and/or mass are not negligible, these will have to be determined separately.

The accuracy of this procedure would be expected to be better than ±0,5 %.[6]

Annex C
(informative)

Recommended calibration materials

Table C.1 — Transition temperature, heat of transition and type of transition for various recommended calibration materials[4][6]

Material	Transition temperature °C	Heat of transition $J \cdot g^{-1}$	Type of transition	Remarks
Cyclopentane	− 155,77	69,60	solid-solid	Measure in a hermetically sealed crucible only. Introduce as a liquid and reweigh to determine the mass.
Cyclopentane	− 135,09	4,91	solid-solid	
Cyclopentane	− 93,43	8,63	solid-liquid	
Water	0,00	—	solid-liquid	Not suitable for heat calibration.
Gallium	29,76	79,88	solid-liquid	Melt reacts with Al. Allow for strong supercooling.
Indium	156,60	28,62	solid-liquid	
Tin	231,93	60,40	solid-liquid	Melt reacts with Al.
Bismuth	(271,40)	53,84	solid-liquid	Melt reacts with Al. Not suitable for temperature calibration.
Lead	327,46	—	solid-liquid	Not suitable for heat calibration.
Zinc	419,53	—	solid-liquid	Not suitable for heat calibration.
Lithium sulfate	578,28	228,1	solid-solid	Anhydrous compound is hygroscopic: weigh in as $Li_2SO_4.H_2O$. Dehydration starts at 110 °C with brisk movement of the particles in the crucible. High water vapour pressure (do not use hermetically sealed crucibles). Reweigh after measurement run to determine the mass.
Aluminium	660,32	398,1	solid-liquid	Melt reacts strongly with Pt.

For other suitable calibration materials, refer to the recommendations of ICTAC1), GEFTA2) and NIST3).

Certified calibration materials can be obtained from national metrological institutes (e.g. LGC, PTB, NIST, LNE, NMIJ), instrument manufacturers or other qualified sources.

Do not re-use calibration materials that have, or might have, reacted with the crucible material.

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1) International Confederation for Thermal Analysis and Calorimetry (ICTAC): http://www.ictac.org

2) Gesellschaft für Thermische Analyse e.V. (GEFTA): http://www.gefta.org

3) National Institute of Standards and Technology (NIST): http://www.nist.gov

Table C.2 — Recommended materials for heat flow rate calibration[5][6]

Material	Temperature range K	Heat capacity, $c_p(T)$ $J{\cdot}g^{-1}{\cdot}K^{-1}$	Uncertainty[5] %	Remarks
Corundum (α-Al_2O_3) (synthetic sapphire)	70 to 300	$\sum_{i=0}^{7} a_i T^i$	0,4 to 0,1	No limitations on crucible material below its melting point.
	290 to 2 250	$\sum_{i=0}^{7} b_i T^i$	0,1 to 0,2	
Copper (Cu)	20 to 97,5	$\sum_{i=0}^{6} c_i T^i$	0,1	Oxygen-free, high-conductivity quality. No limitations on crucible material below its melting point.
	97,5 to 320	$\sum_{i=0}^{4} d_i T^i$	0,1	

T is the temperature, in kelvins.

a, b, c and d are the coefficients of the best-fit polynomials (see Table C.3).

Table C.3 — Coefficients of the best-fit polynomials in Table C.2 for the heat capacity of the heat flow rate calibration materials[5][6]

i	a	b	c	d
0	3,632 45 × 10^{-2}	− 5,811 26 × 10^{-1}	1,437 45 × 10^{-2}	− 1,635 70 × 10^{-1}
1	− 1,114 72 × 10^{-3}	8,259 81 × 10^{-3}	− 1,210 86 × 10^{-3}	7,077 45 × 10^{-3}
2	− 5,386 83 × 10^{-6}	− 1,767 67 × 10^{-5}	− 1,233 05 × 10^{-5}	− 3,789 32 × 10^{-5}
3	5,961 37 × 10^{-7}	2,176 63 × 10^{-8}	4,205 14 × 10^{-6}	9,607 53 × 10^{-8}
4	− 4,929 23 × 10^{-9}	− 1,605 41 × 10^{-11}	− 8,497 38 × 10^{-8}	− 9,361 51 × 10^{-11}
5	1,830 01 × 10^{-11}	7,017 32 × 10^{-15}	6,714 59 × 10^{-10}	
6	− 3,367 54 × 10^{-14}	− 1,676 21 × 10^{-18}	− 1,940 71 × 10^{-12}	
7	2,502 51 × 10^{-17}	1,684 86 × 10^{-22}		

Table C.4 — Specific heat capacity of corundum in the temperature region from 290 K to 550 K (calculated using data from Tables C.2 and C.3)

Temperature K	Heat capacity, $c_p(T)$ $J{\cdot}g^{-1}{\cdot}K^{-1}$
290	0,758 3
300	0,779 4
310	0,799 5
320	0,818 6
330	0,836 8
340	0,854 1
350	0,870 6
360	0,886 3
370	0,901 2
380	0,915 4

Table C.4 *(continued)*

Temperature K	**Heat capacity, $c_p(T)$** $\mathrm{J \cdot g^{-1} \cdot K^{-1}}$
390	0,929 0
400	0,941 9
410	0,954 1
420	0,965 8
430	0,976 9
440	0,987 5
450	0,997 6
460	1,007 2
470	1,016 4
480	1,025 1
490	1,033 5
500	1,041 4
510	1,049 0
520	1,056 3
530	1,063 2
540	1,069 9
550	1,076 2

Annex D
(informative)

Interaction of calibration materials with different crucible materials

The calibration materials recommended in Table C.1 may form mixed phases with some of the crucible materials normally used for DSC. In these cases, there is a risk of a molten calibration specimen dissolving some of the crucible material, which may result in an unpredictable change in melting point and/or damage to the crucible. Table D.1 shows combinations in which interactions may occur, which can be inferred from the respective phase diagrams.

Table D.1 — Interaction of calibration and crucible materials[4]

Crucible material	Calibration material								
	Cyclopentane	**Water**	**Gallium**	**Indium**	**Tin**	**Lead**	**Zinc**	**Lithium sulfate**	**Aluminium**
Corundum, Al_2O_3	o	o	+	+	+	+	+	+	+
Boron nitride, BN	o	o	+	+	+	+	+	+	+
Graphite, C	o	o	+	+	+	+	+	+	+
Silicate glass	+	+	+	+	+	+	?	+	-
Quartz glass, SiO_2	+	+	+	+	+	+	+	+	-
Aluminium, Al	+	•	-	+	-	+	-	+	x
Aluminium, oxidized	+	+	+	+	+	+	+	+	x
Silver, Ag	+	+	-	-	-	-	-	?	-
Gold, Au	+	+	•	•	-	-	-	+	-
Nickel, Ni	+	+	•	•	•	•	•	?	-
Iron, Fe	+	•	•	+	•	+	-	?	-
Stainless steel	+	+	•	+	•	+	-	?	-
Platinum, Pt	+	+	•	•	-	-	-	+	-
Molybdenum, Mo	+	+	•	?	•	?	•	?	?
Tantalum, Ta	+	+	?	+	?	?	?	+	-
Tungsten, W	o	o	•	?	?	•	+	?	•

Key

+	no solubility and no influence on melting point to be expected;
-	melt dissolves crucible material, resulting in greater change in melting point;
•	partial-dissolution processes are possible with negligible change in melting point;
x	crucible melts;
?	interaction unknown;
o	hermetic sealing of crucible may be difficult.

It is strongly recommended that those combinations in Table D.1 marked with a “-” should not be used because dissolution of the crucible cannot only invalidate the calibration but also damage the crucible holder. The combinations marked with a “+” should preferably be used for calibration. A “•” indicates systems in which no significant falsification of the temperature is to be expected, although, in these cases, a certain amount of caution is advisable with respect to the consequences of partial dissolution of the crucible material.

As can be seen from Table D.1, there is at least one crucible material suitable for each of the recommended calibration materials. If necessary, the crucible used can be coated with a protective layer for calibration purposes. Aluminium oxide is ideally suited for this purpose. In the case of the aluminium crucibles normally used, this protective oxide layer can be produced in sufficient thickness by heating to 570 °C in air.

Annex E
(informative)

General recommendations

This test method is suitable for comparative measurements on polymeric materials. However, the results obtained may be influenced by systematic errors such as incorrect calibration, incorrect baseline correction and incorrect specimen preparation and conditioning. It is strongly recommended that suitable polymeric reference materials (similar to those materials routinely analysed) be analysed, for comparative purposes, in parallel with the materials being tested. This allows data obtained from different laboratories, from different instruments, on different dates and using different specimen conditioning and preparation procedures, etc. to be compared.

Except for special cases in which the decomposition of polymers is the subject of investigation, it is not recommended that measurements be continued beyond the decomposition temperature of the polymer sample. This decomposition may lead to the contamination of the crucible holder assembly by materials in open or ventilated crucibles or to the explosion of hermetically sealed crucibles. At worst, the crucible holder assembly may be destroyed. In addition to this, very high temperatures or large temperature-scanning ranges could cause alteration in the linearity of the calibration settings, resulting in erroneous data.

The interpretation of a DSC curve indicating the occurrence of several thermal effects, such as glass transition steps or first-order transition peaks, is fairly straightforward when these effects are clearly separated. Quite often, however, DSC curves will show steps and/or peaks that cannot be separated easily. These types of curve are a result of several reactions and/or transitions which overlap or occur simultaneously. In these cases, the only thermal properties that can be determined without using sophisticated curve separation procedures are the overall heat of reaction and/or transition, the onset temperature and extrapolated onset temperature of the first reaction or transition (bearing in mind that, very often, these onset temperatures are poorly defined in the case of polymers having an extremely broad melting range of up to 150 K) and the extrapolated end temperature and end temperature of the last reaction or transition, as well as several peak temperatures. It is not always possible to identify all of these individual reactions and/or transitions by DSC alone. In some cases, it may be helpful to adjust the heating and/or cooling rates to enhance the separation of these phenomena. However, care should be exercised as the heating and cooling rates can have a significant effect on the characteristic temperature(s) observed at the subsequent heating or cooling rate.

For some polymers, the DSC curve can have several peaks during the first heating run while there is only one peak during the second heating run. Normally, a cooling run performed at the same rate (e.g. 10 K/min or 20 K/min) as that used for heating precedes the second heating scan. The information obtained in the first heating run may be indicative of the thermal history of the polymer (such as processing and specimen conditioning and preparation). Therefore, it is advisable when analysing polymers to carry out three DSC runs: first heating, then cooling and finally second heating, preferably at the same rate. Using this procedure in conjunction with a record of the initial mass of the specimen in the crucible and the masses of the specimen in the crucible before and after the second heating scan can aid identification of the various peaks observed. To obtain information on the thermal properties of the sample material without being influenced by its thermal history, the results of the cooling and second heating scan should be used. With respect to the solid-liquid phase transition, this means that the cooling run will indicate nucleation and the temperature or kinetics of crystallization while the second heating will reflect the material-specific melting properties of the polymer. Of course, the glass transition characteristics can be estimated as well without being perturbed by thermal history.

In the event of gas evolution (due to decomposition, solvent evaporation, etc.) during the heating of a specimen, the pressure generated inside a hermetically sealed crucible can deform the crucible. This results in disturbance of the heat transfer between the specimen and the measuring system. To avoid such disturbances, a punched (perforated) lid or a special pressure-tight crucible can be used.

To investigate chemical reactions induced by exposure to visible or UV light, special photo-DSC instruments are available.

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