INTERNATIONAL STANDARD

ISO 11357-1

Fourth edition
2023-02

Plastics — Differential scanning calorimetry (DSC) —

Part 1: General principles

Plastiques — Analyse calorimétrique différentielle (DSC) —

Partie 1: Principes généraux

Reference number
ISO 11357-1:2023(E)

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Published in Switzerland

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Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular, the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

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For an explanation of the voluntary nature of standards, the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the World Trade Organization (WTO) principles in the Technical Barriers to Trade (TBT), see www.iso.org/iso/foreword.html.

This document was prepared by Technical Committee ISO/TC 61, *Plastics*, Subcommittee SC 5, *Physical-chemical properties*., in collaboration with the European Committee for Standardization (CEN) Technical Committee CEN/TC 249, *Plastics,* in accordance with the Agreement on technical cooperation between ISO and CEN (Vienna Agreement).

This fourth edition cancels and replaces the third edition (ISO 11357-1:2016), which has been technically revised.

The main changes compared to the previous edition are as follows:

— the examples of materials given for temperature and enthalpy calibration have been updated;

— the data of sapphire to be used for calibration of heat flow rate have been updated.

A list of all parts in the ISO 11357 series can be found on the ISO website.

Any feedback or questions on this document should be directed to the user's national standards body. A complete listing of these bodies can be found at www.iso.org/members.html.

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Introduction

The ISO 11357 series 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.

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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 determine applicable regulatory requirements.

1 Scope

The ISO 11357 series 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).

The ISO 11357 series is applicable 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 document 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 parts.

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

2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements of this document. 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, ISO 80000-5 and the following apply.

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ISO and IEC maintain terminology databases for use in standardization at the following addresses:

— ISO Online browsing platform: available at https://www.iso.org/obp

— IEC Electropedia: available at https://www.electropedia.org/

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. Suitable reference materials are thermally inactive over the temperature and time range of interest and have heat capacities 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:

$$Q = \int \frac{dQ}{dt} dt$$

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:

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

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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 ($J \cdot g^{-1}$) or joules per amount of material in moles ($J \cdot mol^{-1}$);

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

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:

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

or

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

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 ($K \cdot min^{-1}$);

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

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

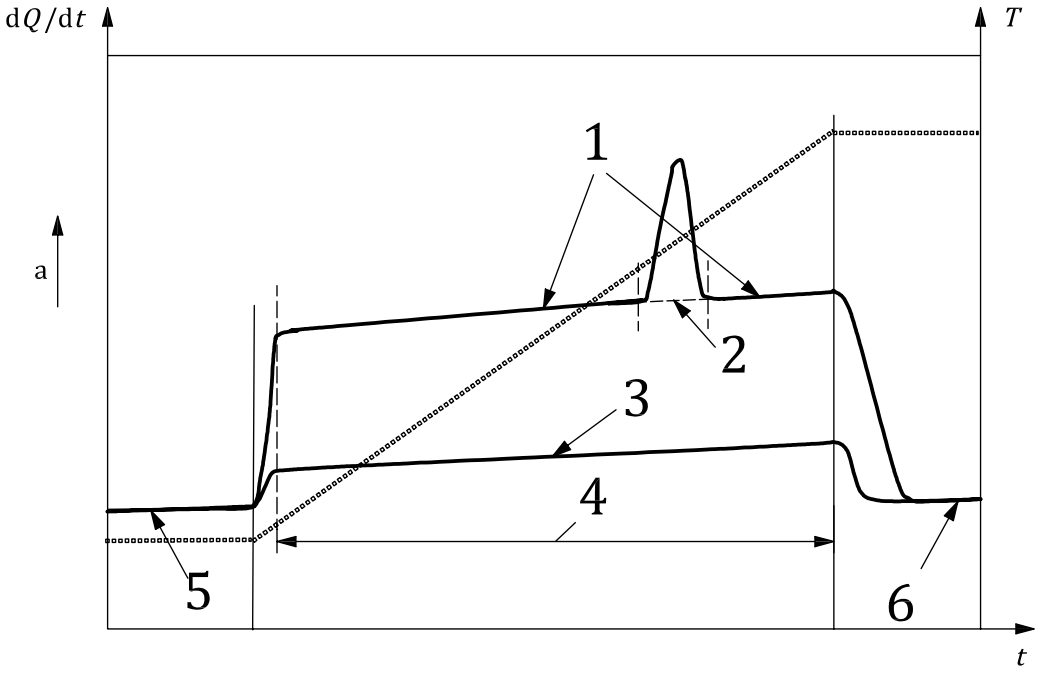
Note 2 to entry: When analysing polymers, ensure that the measured specific heat capacity does not include any heat change due to a chemical reaction or a physical transition.

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).

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Key

dQ/dt	heat flow rate	2	virtual baseline
T	temperature	3	instrument baseline
t	time	4	quasi-stationary range
———	dQ/dt vs. t	5	isothermal start baseline
·····	T vs. t	6	isothermal end baseline
1	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).

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3.7.3
virtual baseline
imaginary line drawn along the peak width 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, i.e., the peak baseline, (see Figure 2) 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 can 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)

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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) with optional use of any SI prefix, 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;

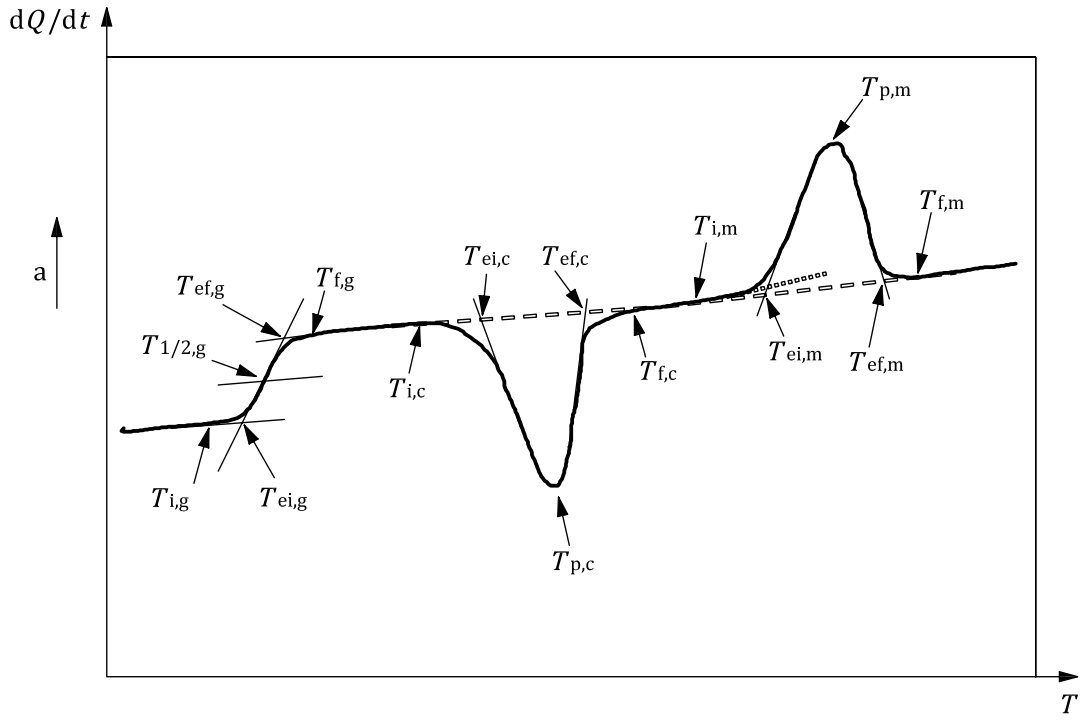
— the temperature at the specimen position.

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*.

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Key

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

Characteristic temperatures if temperature is used as abscissa scale (similarly, characteristic times apply if time is used as abscissa scale)

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 of the step height;
—	peak temperature	T_p	greatest distance between curve and virtual baseline during an endothermic or exothermic peak, i.e., peak height;
—	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)

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