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Plastics — Differential scanning calorimetry (DSC) —

Part 4: Determination of specific heat capacity

Plastiques — Analyse calorimétrique différentielle (DSC) — Partie 4: Détermination de la capacité thermique massique

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Foreword

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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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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 third edition cancels and replaces the second edition (ISO 11357-4:2014), which has been technically revised. The main changes compared to the previous edition are as follows:

— the measurement procedure has been updated;

— reference data of α-alumina 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.

Plastics — Differential scanning calorimetry (DSC) —

Part 4: Determination of specific heat capacity

1 Scope

This document specifies methods for determining the specific heat capacity of plastics by differential scanning calorimetry.

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 11357-1, *Plastics — Differential scanning calorimetry (DSC) — Part 1: General principles*

ISO 80000-1, *Quantities and units — Part 1: General*

3 Terms and definitions

For the purposes of this document, the terms and definitions given in ISO 472, ISO 11357-1 and the following apply.

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

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

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

3.1
calibration material
material of known specific heat capacity

Note 1 to entry: Usually, α-alumina (such as synthetic sapphire) of 99,9 % or higher purity is used as the calibration material.

3.2
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

Note 1 to entry: It is given by the following formula:

$$c_p = m^{-1} \cdot C_p = m^{-1} \cdot \left(\frac{dQ}{dT} \right)_p$$

where

c_p is the specific heat capacity and is expressed in kilojoules per kilogram per K ($kJ \cdot kg^{-1} \cdot K^{-1}$) or in joules per gram per K ($J \cdot g^{-1} \cdot K^{-1}$); subscript *p* indicates an isobaric process;

m is the mass of material, expressed in kilogram (kg) or gram (g);

C_p is the total heat capacity and is expressed in kilojoules per K ($kJ \cdot K^{-1}$) or in joules per K ($J \cdot K^{-1}$); subscript *p* indicates an isobaric process;

$\left(\frac{dQ}{dT}\right)_p$ is the quantity of heat d*Q* necessary to raise the temperature of the material by d*T*, expressed in kilojoules per K ($kJ \cdot K^{-1}$) or in joules per K ($J \cdot K^{-1}$), measured at constant pressure.

This formula is valid in a temperature range where a material shows no first-order phase transition.

The quotient $\left(\frac{dQ}{dT}\right)$ can be obtained by dividing the heat flow rate by the heating rate:

$$(dQ/dT)=\frac{(dQ/dt)}{(dT/dt)}$$

where

(dQ/dt) is the heat flow rate, expressed in kilojoules per second ($kJ \cdot s^{-1}$) or in joules per second ($J \cdot s^{-1}$) or in watts (W);

(dT/dt) is the heating rate, expressed in kelvins (K) per second (s) ($K \cdot s^{-1}$).

Note 2 to entry: At phase transitions, there is a discontinuity in the heat capacity. Part of the heat is consumed to produce a material state of higher energy and it is not all used in raising the temperature. For this reason, the specific heat can only be determined properly outside regions of phase transitions.

4 Principle

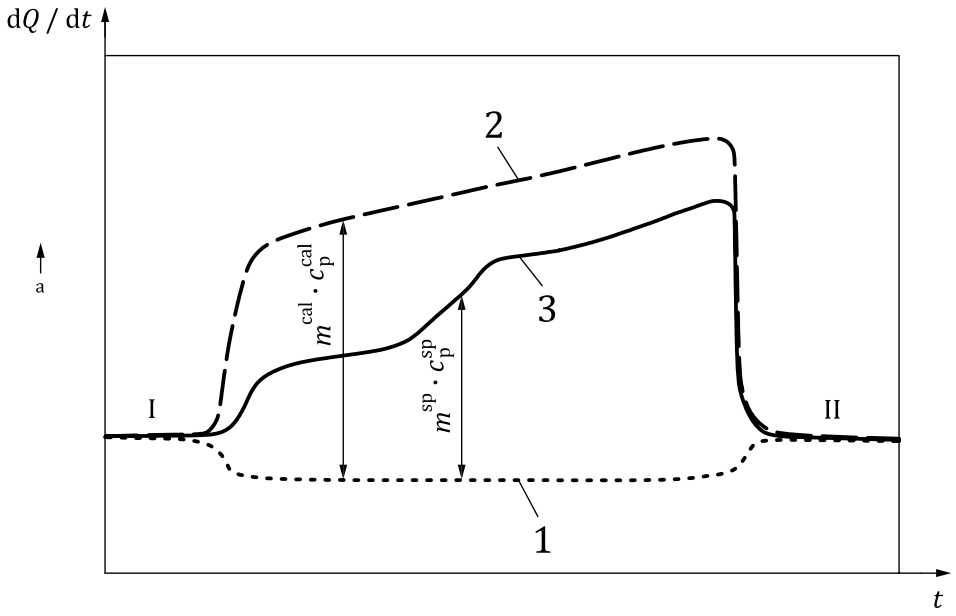
4.1 General

Each measurement consists of three runs at the same scanning rate (see Figure 1):

a) a blank run (empty crucibles in sample and reference holders);

b) a calibration run (calibration material in sample holder crucible and empty crucible in reference holder);

c) a specimen run (specimen in sample holder crucible and empty crucible in reference holder).



Key

dQ/dt	heat flow rate
t	time
1	blank run
2	calibration run
3	specimen run
I	isothermal baseline at start temperature, T_s
II	isothermal baseline at end temperature T_f
a	Endothermic direction.

Figure 1 — Schematic drawing of typical DSC curves for specific heat capacity measurement (blank, calibration and specimen runs) after baseline adjustment

4.2 Continuous-scanning method

Based on the DSC principle (see ISO 11357-1) and the definition of specific heat capacity at constant pressure given in 3.2, the following relations shown as Formulae (1) and (2) can be obtained:

$$m^{sp} \cdot c_p^{sp} \propto P_{sp} - P_{bl} \tag{1}$$

$$m^{cal} \cdot c_p^{cal} \propto P_{cal} - P_{bl} \tag{2}$$

where

P is the heat flow rate (dQ/dt);

sp is the specimen;

bl is an empty crucible (blank run);

cal is the calibration material.

See Figure 1.

When P_{sp}, P_{cal} and P_{bl} are measured, c_p^{sp} can be calculated using Formula (4), since the values of c_p^{cal}, m^{sp} and m^{cal} are known:

$$\frac{m^{sp} \cdot c_p^{sp}}{m^{cal} \cdot c_p^{cal}} = \frac{P_{sp} - P_{bl}}{P_{cal} - P_{bl}} \tag{3}$$

$$c_p^{sp} = c_p^{cal} \cdot \frac{m^{cal}\left(P_{sp} - P_{bl}\right)}{m^{sp}\left(P_{cal} - P_{bl}\right)} \tag{4}$$

4.3 Stepwise-scanning method

In the stepwise-scanning method, the total temperature range to be scanned is divided into small intervals and a complete determination consisting of the three runs mentioned in 4.1 is performed for each temperature interval. Upon integration of the heat flow rate curve, the total heat ΔQ consumed in the interval can be obtained. Dividing ΔQ by the temperature interval ΔT and the mass of the specimen gives the specific heat (see 3.2):

$$m^{sp} \cdot c_p^{sp} \propto \left(\frac{\Delta Q^{sp}}{\Delta T}\right)_p - \left(\frac{\Delta Q^{bl}}{\Delta T}\right)_p \tag{5}$$

$$m^{cal} \cdot c_p^{cal} \propto \left(\frac{\Delta Q^{cal}}{\Delta T}\right)_p - \left(\frac{\Delta Q^{bl}}{\Delta T}\right)_p \tag{6}$$

Keeping the temperature intervals ΔT constant, combining Formula (5) and Formula (6) results in:

$$c_p^{sp} = c_p^{cal} \cdot \frac{m^{cal}}{m^{sp}} \cdot \frac{\Delta Q^{sp} - \Delta Q^{bl}}{\Delta Q^{cal} - \Delta Q^{bl}} \tag{7}$$

5 Apparatus

5.1 DSC apparatus. See ISO 11357-1.

5.2 Crucibles. See ISO 11357-1.

The crucibles for the test specimen and the reference specimen (calibration material) shall be of the same shape and material and their masses shall not differ by more than 0,1 mg.

NOTE The same blank run and calibration run can be used for several measurements, if the instrument is sufficiently stable and the difference in mass between the calibration material crucible and the empty crucible is corrected for. An adequate correction can be obtained by adding the term $c_{p,\,\text{crucible}}(T)\beta\Delta m$ to the heat flow rate of the calibration run, where $c_{p,\text{crucible}}(T)$ is the specific heat capacity of the calibration crucible as a function of temperature, β is the heating rate and Δm is the difference in mass between the calibration crucible and the empty crucible. The same procedure can also be used for correcting differences in mass between the specimen run and the blank run.

5.3 Analytical balance. See ISO 11357-1.

6 Test specimen

See ISO 11357-1.

7 Test conditions and specimen conditioning

See ISO 11357-1.

8 Procedure

8.1 Selection of crucibles

Prepare three crucibles and their lids and weigh the crucibles together with their lids. The total mass shall not differ by more than 0,1 mg (see 5.2). In other respects, such as material, size, crucible type (open or sealed), the crucibles shall be identical.

NOTE It is also possible to use the same crucible in the sample holder for blank run, calibration run, and specimen run if the lid is just laid upon the crucible for blank run and calibration run. For the specimen run, the crucible can be hermetically sealed.

8.2 Setting up the apparatus and adjustment of isothermal baselines

8.2.1 Place a pair of empty crucibles with lids in the DSC sample and reference holders.

8.2.2 If using a continuous-scan programme:

a) Set the start and end temperatures (T_s and T_f). The start temperature T_s should be at least 30 K lower than that at which data are first required.

When more precise results are required over a wide temperature range, the overall range may be divided into two (or more) smaller ranges, each 50 K to 100 K wide. The start temperature T_s of the second range should be 30 K lower than the end temperature T_f of the first temperature range to ensure sufficient overlap.

b) Set the scanning rate.

c) Set the dwell time of the isothermal stages I and II (see Figure 1) and allow the respective isothermal baselines to stabilize. This dwell time will usually be between 2 min and 10 min.

NOTE Some calorimeters, such as those of the Calvet type, can require up to 30 min before the baseline stabilizes.

8.2.3 If using a stepwise-scan programme:

When the specific heat capacities of the samples do not significantly depend on the temperature, the stepwise-scanning method may be used in which the integration of the heat flow over small temperature intervals gives a set of individual specific heat values for the temperature intervals considered. Attention shall be paid to the following points.

a) The dwell time of the isothermal stages shall be sufficiently long to obtain a stable baseline.

b) This method shall not be used over a temperature range in which first-order phase transitions occur.

The stepwise scan is performed as follows.

— Set the start and end temperatures (T_s and T_f).

— Set the temperature increment preferably to 5 K or 10 K.

— Set the temperature-scanning rate to 5 K·min^{-1} or 10 K·min^{-1}.

— Set the dwell time of the isothermal stages, usually to between 2 min and 10 min.

8.2.4 Set the sensitivity of the heat flow rate in order to obtain an ordinate span of at least 80 % of full scale (see Figure 1).

8.2.5 Adjust the apparatus so that the isothermal baselines before and after the heating stage are at the same ordinate level.

Check that adjustment of the baselines of the respective DSC curves results in the same ordinate level. If the baseline reproducibility is poor, readjust the apparatus and repeat the determination.

NOTE Other reasons for poor baseline reproducibility can be contamination of the sample crucible, the position of the lid, the stability of the purge gas flow rate, sample decomposition, sample evaporation, chemical reaction between crucible and sample, etc.

8.2.6 Execute the temperature programme set as described in 8.2.2 or 8.2.3. Figure 2 shows a typical DSC curve obtained in the continuous-scanning mode whereas Figure 3 shows a DSC curve obtained in the stepwise-scanning mode.

8.3 Measurement of specific heat capacity of calibration material

Using an analytical balance, weigh a calibration material, such as *α*-alumina (synthetic sapphire) of 99,9 % or higher purity, into one of the crucibles prepared in 8.1. Put the crucible containing the calibration material, with the lid, in the sample holder and carry out the same measurement(s) as described for the blank run(s) in 8.2.

NOTE Small differences in the masses of the crucibles used for the specimen, calibration and blank runs can be corrected for as indicated in the Note to 5.2.

The heat capacity of the calibration material should match that of the specimen to be analysed as closely as possible in order to minimize systematic errors.

The nominal values of the specific heat capacity of *α*-alumina at various temperatures are given in Annex A, Table A.1.