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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 main task of technical committees is to prepare International Standards. Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

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ISO 11357-4 was prepared by Technical Committee ISO/TC 61, *Plastics*, Subcommittee SC 5, *Physical-chemical properties*.

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*

— *Part 3: Determination of temperature and enthalpy of melting and crystallization*

— *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*

— *Part 7: Determination of crystallization kinetics*

Plastics — Differential scanning calorimetry (DSC) —

Part 4: Determination of specific heat capacity

1 Scope

This part of ISO 11357 specifies methods for determining the specific heat capacity of plastics by differential scanning calorimetry.

2 Normative references

The following referenced documents are indispensable for the application 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 11357-1:1997, *Plastics — Differential scanning calorimetry (DSC) — Part 1: General principles*

ISO 31-0:1992, *Quantities and units — Part 0: General principles*

3 Terms and definitions

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

3.1
calibration material
material of known specific heat capacity

NOTE 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 It is given by the following equation:

$$c_p = m^{-1}C_p = m^{-1}(\mathrm{d}Q/\mathrm{d}T)_p \quad (1)$$

where

m is the mass of material;

C_p is the heat capacity;

$\mathrm{d}Q$ is the quantity of heat necessary to raise the temperature of the material by $\mathrm{d}T$;

subscript p indicates an isobaric process;

c_p is expressed in kilojoules per kilogram per K ($kJ \cdot kg^{-1} \cdot K^{-1}$) or in joules per gram per K ($J \cdot g^{-1} \cdot K^{-1}$).

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

$$(dQ/dT) = (dt/dT) \times (dQ/dt) = (\text{heating rate})^{-1} \times (\text{heat flow rate}) \quad (2)$$

NOTE 2 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

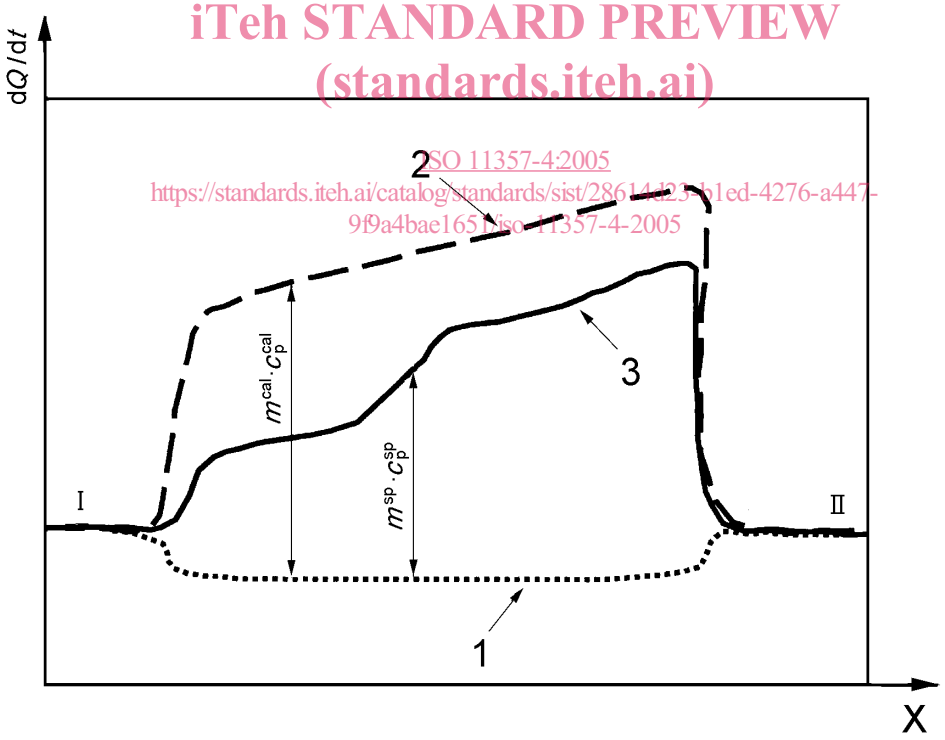
4.1 General

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

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

2) a calibration run (calibration material in sample holder pan and empty pan in reference holder);

3) a specimen run (specimen in sample holder pan and empty pan in reference holder).



Key

X temperature T or time t
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

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 given in 3.2, the following relations can be obtained:

$$m^{\mathrm{sp}} \cdot c_{\mathrm{p}}^{\mathrm{sp}} \propto P_{\text{specimen run}} - P_{\text{blank run}} \tag{3}$$

$$m^{\mathrm{cal}} \cdot c_{\mathrm{p}}^{\mathrm{cal}} \propto P_{\text{calibration run}} - P_{\text{blank run}} \tag{4}$$

where

P is the heat flow rate ($\mathrm{d}Q/\mathrm{d}t$);

superscripts sp and cal represent specimen and calibration material, respectively (see Figure 1).

When $P_{\text{specimen run}}$, $P_{\text{calibration run}}$ and $P_{\text{blank run}}$ are measured, $c_{\mathrm{p}}^{\mathrm{sp}}$ can be calculated using Equation (6), since the values of $c_{\mathrm{p}}^{\mathrm{cal}}$, m^{sp} and m^{cal} are known:

$$\frac{m^{\mathrm{sp}} \cdot c_{\mathrm{p}}^{\mathrm{sp}}}{m^{\mathrm{cal}} \cdot c_{\mathrm{p}}^{\mathrm{cal}}} = \frac{P_{\text{specimen run}} - P_{\text{blank run}}}{P_{\text{calibration run}} - P_{\text{blank run}}} \tag{5}$$

$$c_{\mathrm{p}}^{\mathrm{sp}} = c_{\mathrm{p}}^{\mathrm{cal}} \cdot \frac{m^{\mathrm{cal}}\left(P_{\text{specimen run}} - P_{\text{blank run}}\right)}{m^{\mathrm{sp}}\left(P_{\text{calibration run}} - P_{\text{blank run}}\right)} \tag{6}$$

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 Equation (1)]:

$$m^{\mathrm{sp}} \cdot c_{\mathrm{p}}^{\mathrm{sp}} \propto \left(\frac{\Delta Q}{\Delta T}^{\mathrm{sp}}\right)_{\mathrm{p}} - \left(\frac{\Delta Q}{\Delta T}^{\mathrm{blank}}\right)_{\mathrm{p}} \tag{7}$$

$$m^{\mathrm{cal}} \cdot c_{\mathrm{p}}^{\mathrm{cal}} \propto \left(\frac{\Delta Q}{\Delta T}^{\mathrm{cal}}\right)_{\mathrm{p}} - \left(\frac{\Delta Q}{\Delta T}^{\mathrm{blank}}\right)_{\mathrm{p}} \tag{8}$$

Keeping the temperature intervals ΔT constant, combining Equations (7) and (8) results in:

$$c_{\mathrm{p}}^{\mathrm{sp}} = c_{\mathrm{p}}^{\mathrm{cal}} \cdot \frac{m^{\mathrm{cal}}}{m^{\mathrm{sp}}} \cdot \frac{\Delta Q^{\mathrm{sp}} - \Delta Q^{\mathrm{blank}}}{\Delta Q^{\mathrm{cal}} - \Delta Q^{\mathrm{blank}}} \tag{9}$$

5 Apparatus

5.1 DSC apparatus

See ISO 11357-1:1997, Subclause 5.1.

5.2 Pans

See ISO 11357-1:1997, Subclause 5.2.

The pans 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 pan and the empty pan is corrected for. An adequate correction can be obtained by adding the term $c_{p,pan}(T)\beta\Delta m$ to the heat flow rate of the calibration run, where $c_{p,pan}(T)$ is the specific heat capacity of the calibration pan as a function of temperature, β is the heating rate and Δm is the difference in mass between the calibration pan and the empty pan. 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 11357-1:1997, Subclause 5.3.

6 Test specimen

See ISO 11357-1:1997, Clause 6.

7 Test conditions and specimen conditioning

See ISO 11357-1:1997, Clause 7.

8 Procedure

8.1 Selection of pans

Prepare three pans and their lids and weigh the pans 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, pan type (open or sealed), the pans shall be identical.

8.2 Setting up the apparatus and adjustment of isothermal baselines

8.2.1 Place a pair of empty pans 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 is first required.

NOTE 1 When more precise results are required over a wide temperature range, the overall range can 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 time interval between the isothermal stages I and II (see Figure 1) and allow the respective isothermal baselines to stabilize. This interval will usually be between 2 min and 10 min.

NOTE 2 Some calorimeters, e.g. those of the Calvet type, may need 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 can 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 time interval between 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:

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

2) Set the temperature increment preferably to 5 K to 10 K.

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

4) Set the time interval between 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.

If microcomputer-based systems are used, the isothermal baselines can be adjusted to the same ordinate level after the data has been acquired. However, it is strongly recommended that baseline adjustment is done before any measurements are made in order to improve the accuracy of the results. If a conventional pen recorder is used, proper apparatus adjustment is crucial to minimize differences in isothermal baseline 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 pan, the position of the lid, the stability of the purge gas flow rate, sample decomposition, sample evaporation, chemical reaction between pan 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 pans prepared in 8.1. Put the pan containing the calibration material, with the lid, in the sample holder and perform a DSC run.

NOTE 1 Small differences in the masses of the pans used for the specimen, calibration and blank runs can be corrected for as indicated in the Note to 5.2.

NOTE 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.

For the blank run, use another of the empty pans prepared in 8.1. Carry out the same measurement(s) as described in 8.2. The nominal values of the specific heat capacity of α-alumina at various temperatures are given in Table A.1.