INTERNATIONAL STANDARD

ISO 23976

First edition
2021-02

Plastics — Fast differential scanning calorimetry (FSC) — Chip calorimetry

Plastiques — Calorimétrie différentielle à balayage rapide (FSC) — Calorimétrie à balayage ultra-rapide

Reference number
ISO 23976:2021(E)

COPYRIGHT PROTECTED DOCUMENT

ISO copyright office
CP 401 • Ch. de Blandonnet 8
CH-1214 Vernier, Geneva
Phone: +41 22 749 01 11
Email: copyright@iso.org
Website: www.iso.org

Published in Switzerland

Contents

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).

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights. Details of any patent rights identified during the development of the document will be in the Introduction and/or on the ISO list of patent declarations received (see www.iso.org/patents).

Any trade name used in this document is information given for the convenience of users and does not constitute an endorsement.

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*.

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.

Introduction

The development of fast scanning calorimetry (FSC) based on chip sensors with very high sensitivity using ultrathin SiN membranes was initially driven by the objective to measure thermal properties of very small amounts of sample such as thin films at very high scan rates in the order of magnitude of 10^4 K/s[1]. Shortly after, a differential scanning sensor was also introduced[2]. These quasi-adiabatic calorimeters could be used in heating mode only. The extension of sensors to fast cooling applications was achieved upon operating at non-adiabatic conditions by using gas as thermally inert cooling agent. To avoid the concomitantly strong increase of thermal lag with increasing scan rate, the sample mass is decreased accordingly. Thus, reduction of specimens and heating elements to very small size enabled sufficient temperature control upon fast cooling, see References [3] to [7]. Due to these developments, the scan rate operating window of existing commercial DSCs is extended to more than 7 orders in magnitude.

A break-through was the development of extremely fast-operating chip-calorimeters, see Table 1, based on Micro-Electromechanical-Systems (MEMS) technology, as described in various publications (see, for example, References [8], [9] and [10]). Until recently, results using chip calorimeters have been obtained by specific equipment located at universities[11],[12], however, dedicated research has also led to the development of commercially available FSC instrumentation.

For MEMS-sensor technology, power compensation-based twin-sensor microchip calorimeters, commonly known as fast scanning calorimetry (FSC), and its capabilities have received a great deal of attention in recent years[8]. The reason that FSC has become increasingly popular is because, firstly, in practice, some physical and chemical processes and processing techniques occur at much higher rates than achievable using conventional DSC. Secondly, most nano-structures in materials and substances, including polymers and pharmaceuticals, are in metastable states and these can be studied by FSC. Finally, FSC is facilitated by the world-wide availability of the first commercial FSC instrument[8],[13],[14], followed by an advanced instrument achieving even higher scan rates and higher temperatures[15].

Thermal history – specifically cooling and heating rates – and sample/product treatment can change the material behaviour drastically, leading to strongly deviating end properties. The significantly extended range of achievable scan rates, increased instrument sensitivity and reduced time constant of MEMS-sensors has resulted in strongly increased capabilities of studying the influence of thermal history.

This document describes characteristic features of commercially available non-adiabatic FSCs, calibration procedures and performance of measurements that deviate significantly from those of conventional DSC outlined in the ISO 11357 series. See Reference [16].

Table 1 — Typical characteristics of some chip calorimeters

FSC	Scan rate K/s		Achievable temperature at constant rate °C		Purge gas	
	heating	cooling[a]	heating up to	cooling down to[a]	type	ml/min
Commercial instrument [13],[14],[15],[17]	20 000	5 000	410	40	N_2	20
	20 000	5 000	410	140[b]	N_2	20
	20 000	5 000	200	-25	He	20
Commercial instrument 2[15]	50 000	20 000	950	100	N_2	20
	50 000	20 000	950	250[b]	N_2	20
University instrument [8],[11],[12],[16]	1 000 000	1 000 000	1 000	30	He	0
	1 000 000	1 000 000	1 000	-180	He	0

[a] Cooling rate is determined by the cooling device (temperature difference to base temperature), magnitude of heat flow rate, environmental conditions such as thermal conductivity of purge gas, etc.

[b] Without cooling accessory.

Plastics — Fast differential scanning calorimetry (FSC) — Chip calorimetry

1 Scope

This document specifies the characteristics of non-adiabatic fast differential scanning calorimeters, also covered by the general abbreviation FSC having an open specimen geometry in which specimens are placed directly onto active measurement areas of chip sensors based on Micro-Electro-Mechanical Systems (MEMS) membrane technology, without encapsulation in closed crucibles and ovens.

Due to the open specimen geometry, this document is applicable to very small specimens having masses of not greater than 1 µg only. The occurrence of high temperature gradients during measurements can be prevented by keeping specimen thicknesses as small as possible.

The use of very low specimen masses enables achievement of very high scanning rates in the order of several thousand K/s, both in heating and cooling mode whereby lower specimen masses and thicknesses allow higher heating and cooling rates. Typically, low scanning rates of FSC overlap with high scanning rates of conventional DSC covered by ISO 11357-1, thus enabling connection to conventional DSC results.

NOTE 1 Due to the sensor layout FSC is also called chip calorimetry.

NOTE 2 FSC stands for Fast Scanning Calorimetry but also for Fast Scanning Calorimeter. In practice from the context the choice can be made quite easily.

FSC is suitable for thermal analysis of fast kinetic effects of polymers, polymer blends and composites, 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);
- elastomers (with or without fillers, fibres or reinforcements).

This document specifies methods for qualitative and quantitative analysis of fast physical and chemical processes showing changes in heat flow rate. This includes measurement of characteristic temperatures as well as caloric values of both, solid and liquid materials.

This document is particularly applicable for the observation of fast kinetics of thermal effects such as:

- physical transitions (glass transition, phase transitions such as melting and crystallization, polymorphic transitions, etc.);
- metastability and related processes like reorganization, (re)crystallization, annealing, ageing, amorphization;
- chemical reactions (hydration, oxidation, polymerisation, crosslinking and curing of elastomers and thermosets, decomposition, etc.);
- isothermal measurements of fast crystallising systems or chemical reactions.

It is also applicable for the determination of heat capacity and related changes of thermodynamic functions.

FSC provides a technique to analyse material behaviour at similarly high heating or cooling rates used in industrial polymer processing.

FSC can also enable separation of overlapping thermal effects with different kinetics such as:

- melting and decomposition: higher heating rates can shift decomposition to higher temperatures and allow unperturbed measurement of melting;
- glass transition and cold crystallisation of polymers: higher heating rates can suppress cold crystallisation resulting in unperturbed measurement of glass transition as a function of cooling / heating rates;
- reorganisation of amorphous or semi-crystalline polymers upon cooling and heating: depending on the cooling rate used specimens with different crystallinities can be generated and their reorganisation upon heating analysed using different scanning rates.

This document establishes general aspects of FSC, such as the principle and the apparatus, sampling, calibration and general aspects of the procedure and test report.

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

ISO 11357-2, *Plastics — Differential scanning calorimetry (DSC) — Part 2: Determination of glass transition temperature and step height*

ISO 11357-3, *Plastics — Differential scanning calorimetry (DSC) — Part 3: Determination of temperature and enthalpy of melting and crystallization*

ISO 11357-4, *Plastics — Differential scanning calorimetry (DSC) — Part 4: Determination of specific heat capacity*

ISO 11357-5, *Plastics — Differential scanning calorimetry (DSC) — Part 5: Determination of characteristic reaction-curve temperatures and times, enthalpy of reaction and degree of conversion*

3 Terms and definitions

For the purposes of this document, the terms and definitions given in 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

chip sensor

symmetric power-compensated sample holder having low *addenda heat capacity* (3.6) in the order of nJ/K based on a silicon nitride membrane with a thickness in the µm range

Note 1 to entry: Electronic components for heater and temperature sensor are attached to the membrane. The sample holder has separate areas for sample and reference specimen onto which specimens are placed directly and openly in a purge gas environment without encapsulation in crucibles.

3.2
chip calorimetry
non-adiabatic technique in which the difference between the heat flow rate into the *sample* (3.3) and reference side of a symmetric *chip sensor* (3.1) with open specimen geometry is derived as a function of temperature or time

Note 1 to entry: The temperature difference between sample and reference side of the sensor, both subjected to the same temperature program, is regulated to almost zero by increasing or decreasing the heating power on both sides of the sensor while maintaining the controlled temperature program in a specified atmosphere.

Note 2 to entry: The required differential power is measured as a function of temperature or time. Chip calorimetry enables direct measurement of caloric values and characteristic temperatures.

Note 3 to entry: Information on graphical representation of results can be found in ISO 11357-1.

3.3
sample
small portion of a material taken from a larger quantity of material and intended to be representative of the whole or to represent a particular section of a manufactured part, such as the skin

3.4
specimen
test piece taken from the *sample* (3.3) placed on the sample area of the *chip sensor* (3.1) and analysed

3.5
reference
comparative specimen placed on the reference area of the *chip sensor* (3.1)

Note 1 to entry: The reference area of the chip sensor is usually left empty.

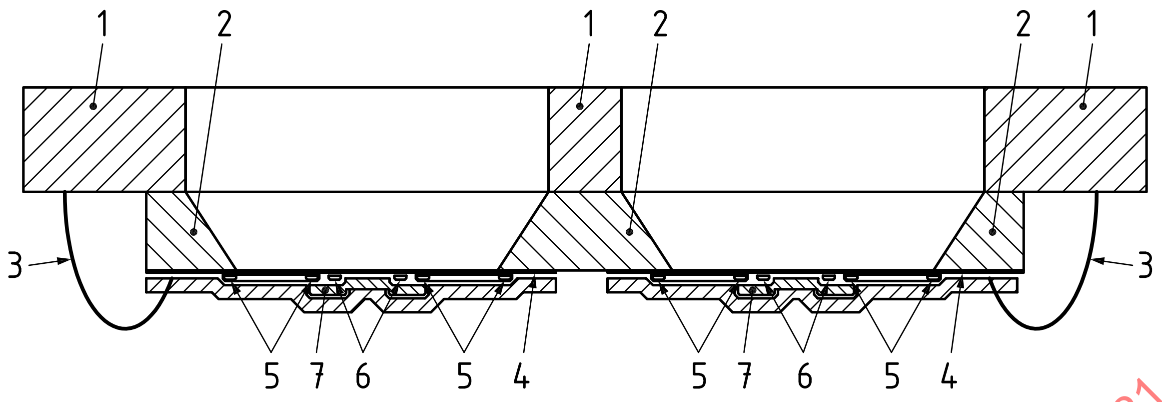
3.6
addenda heat capacity
additional heat capacity contribution of the sensor not related to the specimen

4 Principle

Very small amounts (typically in the order of 10 ng and not more than 1 µg) of sample and, if applicable, reference material are placed directly on the corresponding active areas of the chip sensor. The difference between the heat flow rate into the specimen and that into the reference is measured as a function of temperature and/or time while specimen and reference are subjected to the same temperature-controlled programme under a specified atmosphere.

NOTE Suitable heating and cooling rates can vary depending on the characteristics of particular chip sensors.

Due to the open sample geometry of fast scanning calorimetry the limitation of sample masses to above indicated values is important to prevent significant temperature gradients in sample and, if applicable, reference specimens. Figure 1 shows a schematic picture of a typical chip sensor which consists of two identical siliconnitride/-oxide membranes having lateral dimensions in the mm range or smaller and a thickness in the µm range or smaller coated with a thin metal layer for improved temperature distribution that are mounted in a ceramic plate. The sensor layout is symmetrical where both sides, sample and reference, have identical separate thermal resistance heaters. The temperature is measured by means of thermocouples arranged symmetrically around the measurement areas of the sample and reference side, of the chip sensor, respectively. The measurement principle is power-compensation DSC, i.e. individual heaters are used for sample and reference area. The difference in electrical power required to maintain both the sample position and the reference position at the same temperature is recorded against temperature or time, while each position is subjected to the same temperature-controlled programme. This enables direct measurement of characteristic temperatures and caloric values of thermal effects.



Key

1	ceramic plate
2	silicon frame
3	bonding wire
4	siliconnitride/-oxide membrane
5	thermocouple
6	resistance heater
7	metal plate for improved temperature homogeneity

Figure 1 — Example of chip sensor layout[15]

5 Apparatus

5.1 Chip calorimeter

The instrument shall have the following features:

- chip sensor with designated active areas for placement of sample and reference, for measurements of liquid samples specifically designed sensors may be used;
- capability of generating constant heating and cooling rates up to 1 000 K/s or higher, the upper scanning rate limit shall be sufficiently high for intended measurements;
- capability to maintain the test temperature constant to within ±0,5 K or less for at least 60 min;
- capability to perform step heating or step cooling measurements;

  NOTE 1 Normally, this is achieved by a suitable combination of linear heating or cooling steps and constant temperature steps.

- capability to provide a controlled static or purging gas environment of the sample holder. When using continuous purging of the sample holder, the purge gas flow shall be laminar and the flow rate controllable to within ±10 %;

  NOTE 2 The actual gas flow rate depends on the design of the instrument used and the purpose of measurement.

- capability of generating a temperature range in line with the experimental requirements;
- capability of achieving a heat flow rate range and sensitivity adapted to the designated sample size range of the chip sensor;

  NOTE 3 For a chip sensor designed for specimen masses between 10 ng and 1 µg, typical values of max. heat flow rate signal and sensitivity are approximately 20 mW and 1 µW, respectively.

- an adequate time constant of the sensor to achieve sufficiently high heating and cooling rates;
- a recording device capable of automatically recording the measured curve of heat flow rate against temperature and/or time;

- suitable software for evaluation and interpretation of results.

5.2 Microscope

The instrument shall be equipped with a microscope with sufficient magnification for preparation and correct positioning of sample and, if applicable, reference in the active sensor area, respectively.

For removable chip sensors, preparation and positioning may be done outside of the instrument and the sensor(s) with attached specimen(s) installed in the instrument prior to measurements.

5.3 Tools for sample preparation

Depending on the properties of the material to be analysed and the desired sample size the following tools are recommended for sample preparation:

- a pair of tweezers for holding and moving samples;
- microtome for cutting samples to desired thickness;
- abrasive material for preparation of sample powder;
- glass support slides and knife for cutting samples;
- hair or thin soft wire to position specimens on the sensor area;
- silicone oil, graphite, grease or other suitable contact media for improved thermal contact or wetting.

Other tools may be used as appropriate for particular sample preparation requirements.

5.4 Calibration materials

Calibration materials shall be in accordance with ISO 11357-1.

Stable substances may be archived for later use for additional experiments, as the typical repeatability of measurements using removable commercially available chip sensors is excellent.

Also, volatile organic compounds may be used if they are easily removable from the sensor without any residues and do no interact with the membrane.

5.5 Measuring atmosphere

Measuring atmosphere shall be in accordance with ISO 11357-1.

Normally, nitrogen is used as purge gas. It shows a balanced behaviour in heating and cooling mode and for most samples and experimental conditions nitrogen is sufficiently inert.

Higher cooling rates can be achieved with purge gas of high thermal conductivity such as Helium. However, due to higher thermal loss the maximum temperature at the same purge gas flow rate will be significantly reduced compared to nitrogen. The achievable temperature may be increased using reduced flow rates[14].

The flow rate should be optimized in order to prevent contamination with oxygen on the one hand and maintain laminar flow on the other hand. Alternatively, static atmosphere may be used.

6 Specimens

The specimen shall be in the liquid or solid state. Solid-state specimens may be in any form suitable for the chip sensor area or may be cut from bigger pieces to a suitable size. The specimen thickness shall be kept as low as possible in order to prevent the occurrence of high temperature gradients during measurements.

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.

Contact media, such as silicone oil, may be used to improve the thermal contact between specimen and sensor. Care shall be taken to prevent adverse effects of the contact medium to test results.

Specimen thicknesses and masses shall be adapted to test conditions and instrument, or chip sensor used.

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.

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 can be crucial to the values obtained, the consistency of the results and their significance.

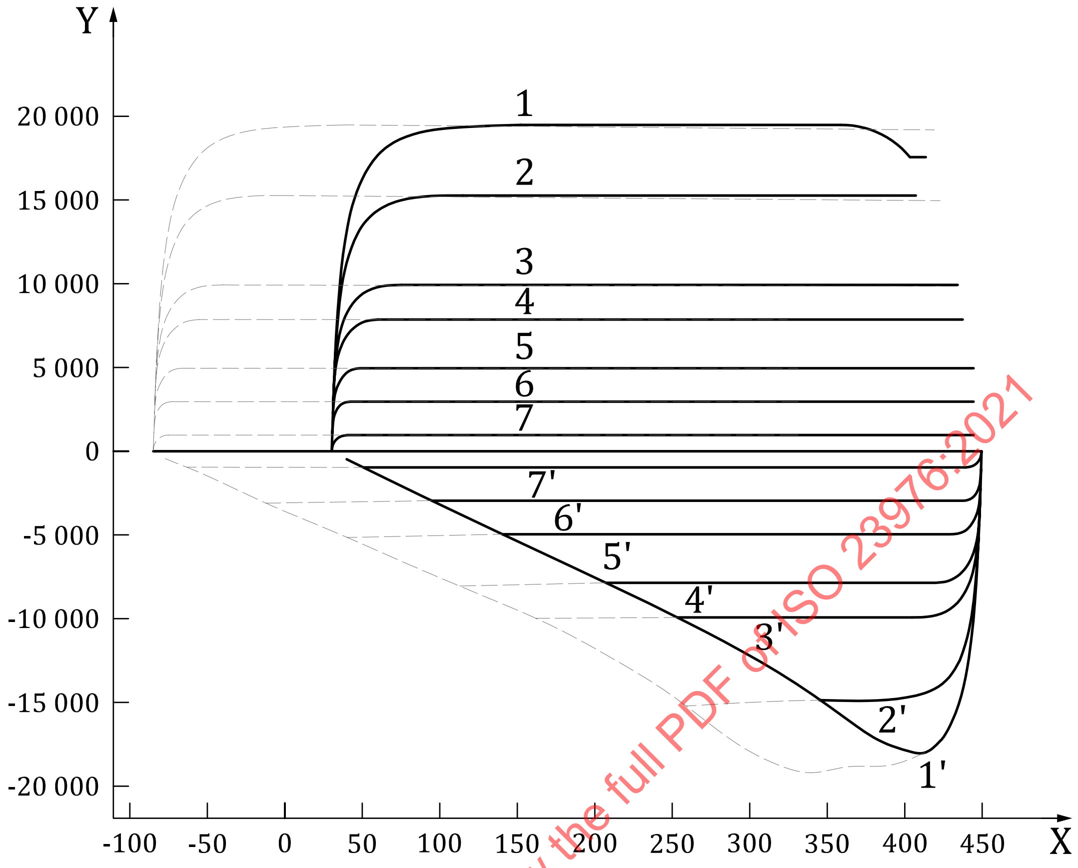
8 Calibration

8.1 Chip calorimeter performance

Prior to any measurement a performance check of the instrument with empty sensor shall be done with respect to its scan rate capabilities depending on heating and cooling mode and environment (cooling accessory, purge gas type and flow rate). This performance check shall be repeated each time the testing environment conditions are changed.

For this performance check, the achieved heating or cooling rates are obtained by plotting the derivative of the achieved sample temperature as a function of achieved temperature as shown in Figure 2 and Figure 3. The instrument shall be used for measurements only within temperature ranges and scan rates where the achieved heating and cooling rates are constant.

Environmental gases with higher thermal conductivity, such as helium, provide higher cooling rates or extended temperature ranges in cooling, but may limit the upper temperature limit upon heating (see Figure 2 and Figure 3). They may also show a higher sensitivity to purge gas flow rate changes[14].

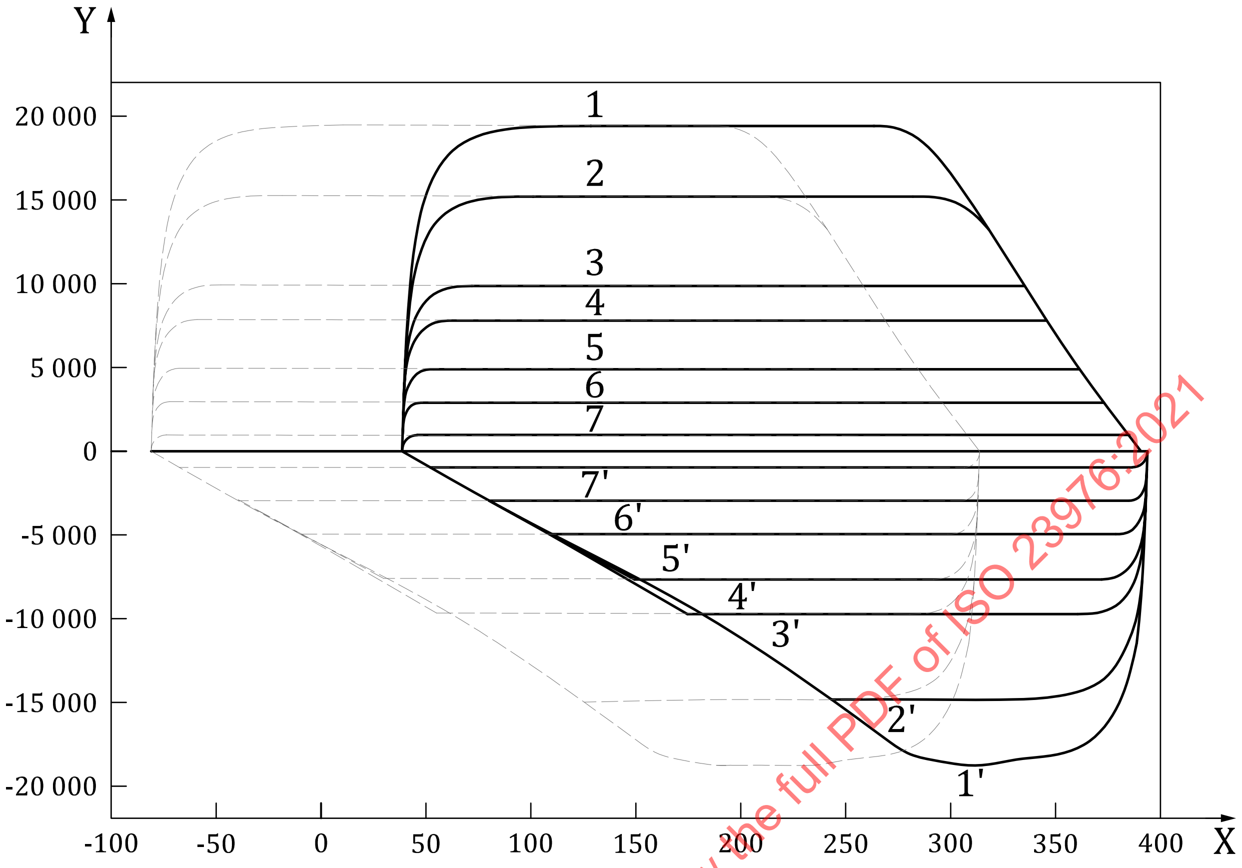


Key

Y	achieved scan rate in K/s	5, 5′	±5 000 K/s
X	programmed temperature in °C	6, 6′	±3 000 K/s
1, 1′	±20 000 K/s	7, 7′	±1 000 K/s
2, 2′	±15 000 K/s	——	without cooling accessory
3, 3′	±10 000 K/s	- - - -	with IntraCooler set to -95 °C
4, 4′	±8 000 K/s		

NOTE Measured using a commercial FSC instrument at scan rates from 20 000 K/s to 1 000 K/s with empty sensor.

Figure 2 — Achieved scan rates vs. sample temperature purged with 20 ml/min N_2 [14]



Key

Y	achieved scan rate in K/s
X	programmed temperature in °C
1, 1′	±20 000 K/s
2, 2′	±15 000 K/s
3, 3′	±10 000 K/s
4, 4′	±8 000 K/s
5, 5′	±5 000 K/s
6, 6′	±3 000 K/s
7, 7′	±1 000 K/s
———	without cooling accessory
– – – –	with IntraCooler set to -95 °C

NOTE Measured using the same instrument and scan rates as in Figure 2 with empty sensor.

Figure 3 — Achieved scan rates vs. temperature purged with 20 ml/min He[14]

8.2 Temperature calibration[14],[17]

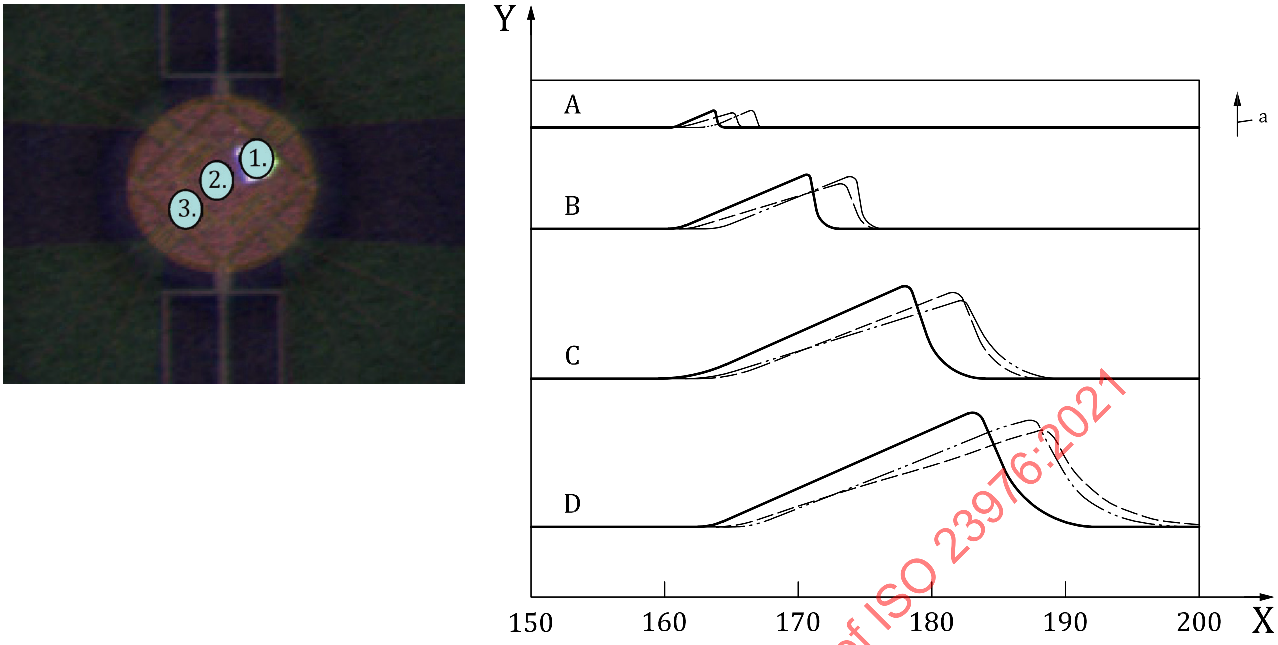
8.2.1 General

A certified or otherwise acknowledged calibration material shall be selected. Suitable calibration materials can be found in ISO 11357-1, but also other calibration materials may be used as appropriate.

The calibration sample shall be placed as close as possible to the centre of the active area of the sample holder to prevent significant shift or broadening of transition peaks[18], as shown in Figure 4[14].

A sufficient number of calibration materials shall be used to cover the temperature range required for measurements.

The temperature calibration shall be done for each purge gas separately. If required, the influence of the purge gas flow rate (e.g. for He) shall be taken into account.



a) Sample positions

b) Melting curves

Key

Y	heat flow rate
X	temperature in °C
A	10 K/s
B	100 K/s
C	300 K/s
D	500 K/s
—..—	side position (1.)
——	centre position (2.)
— — —	opposite side position (3.)
a	Endothermic direction.

Figure 4 — Melting curves obtained at different heating rates with a sample of 1 µg of indium placed at different positions of the active area of the sample holder[14]

The temperature calibration of the sensor shall establish the following three corrections:

- correction for thermal lag due to scan rate;
- correction for thermal lag due to sample mass;
- correction of the measured temperature extrapolated to zero heating rate indicated by the instrument towards the true transition temperature of the calibration material.

In addition, the influence of static temperature gradients caused by low thermal conductivity of specimens or bad thermal contact to the sensor should be taken into account. This can not only cause significant temperature lag at higher scanning rates but can also yield constant temperature offset[19],[20].

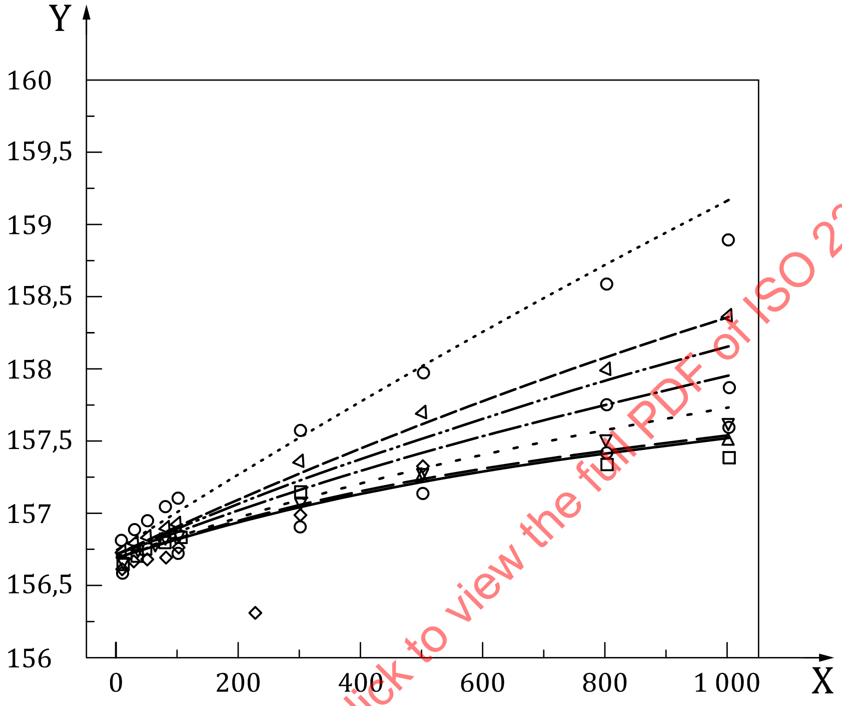
As specimens cannot be easily removed from chip sensors, temperature calibration is generally not done on the very same chip sensor used for measurements but on similar sensors coming from the same production batch. This problem can be eliminated by using volatile calibration substances that can be removed from the sensor without residues.

8.2.2 Correction for thermal lag due to scan rate

For the scan rate correction, a suitable range of scan rates shall be selected for the type of chip calorimeter or sensor used. Calibration runs shall be done at a minimum of five scan rates: the minimum rate β_{min}, the maximum scan rate β_{max} and at least three rates evenly spread in between. The minimum and maximum heating rates shall be selected to cover the scan rate range required for measurements.

8.2.3 Correction for thermal lag due to sample mass

Depending on the type of chip calorimeter or sensor, suitable masses differing by at least two orders of magnitude shall be selected for each scan rate run specified in 8.2.2. At least three sample masses shall be used: one having an optimal mass for the type of instrument or sensor used and two samples having lower and higher mass, respectively.



Key

Y measured extrapolated peak onset temperature in °C

X heating rate in K/s

m sample mass

.... *m* = 2,508 µg

– – – – *m* = 1,997 µg

—..— *m* = 1,567 µg

—.— *m* = 0,408 µg

- - - - *m* = 0,285 µg

— — *m* = 0,103 µg

——— *m* = 0,016 µg

Figure 5 — Extrapolated peak onset temperatures of indium as a function of heating rate and sample mass[14],[17]

An example of extrapolated peak onset temperatures of indium extrapolated to zero heating rate at different sample masses is shown in Figure 5.

8.2.4 Correction of measured temperature extrapolated to zero heating rate

The measured extrapolated peak onset temperatures, obtained by the intersection point of the baseline, i.e. that lower temperature part of the curve that represents the non-transition part of the measurement, with that part of the curve that shows the steepest slope and thus represents the measured transition. These extrapolated peak onset temperatures shall be fitted by Formula (1):

$$T_{\mathrm{ei,p}}(\beta,m)=a_0+a_1\cdot\beta^{a_2}+a_3\cdot\beta\cdot m^{a_4} \tag{1}$$

For some types of chip calorimeters or sensors, Formula (1) can be simplified to:

$$T_{\mathrm{ei,p}}(\beta,m)=a_0+a_1\cdot\beta\cdot m \tag{2}$$

where

$T_{\mathrm{ei,p}}(\beta,m)$	is the extrapolated peak onset temperature extrapolated to zero heating rate and dependent on sample mass;
β	is the heating rate in K/s;
m	is the is the sample mass;
a_0,a_1,a_2,a_3,a_4	are the fitting parameters of Formulae (1) or (2).

The selection of the formula to be used for fitting shall be justified based on the correlation factor.

The peak onset temperatures extrapolated to zero heating rate $T_{\mathrm{ei,p}}(\beta,m)$ shall be shifted by a correction factor $C_{T_{\mathrm{ei}}}$ obtained by comparison with the true transition temperature T_{cal} of the calibration material, shown as Formula (3):

$$T_{\mathrm{cal}}=T_{\mathrm{ei,p}}(\beta,m)+C_{T_{\mathrm{ei}}} \tag{3}$$

Following this procedure, all corrected temperatures extrapolated to zero scan rate will be equal to the true transition temperature, T_{cal}.

In addition, a correction matrix for the extrapolated peak onset temperature $T_{\mathrm{ei,p}}(\beta,m)$ may be calculated based on the fitting by Formula (1) or Formula (2) and the correction factor $C_{T_{\mathrm{ei}}}$ as shown in Table 2.

Table 2 — Correction matrix for the extrapolated onset temperatures of indium as a function of heating rate and sample mass[14],[17]

$C_{T_{\mathrm{ei}}}$ K							
β	**Mass** µg						
K/s	0,05	0,1	0,5	1	1,5	2	4
0	0,0	0,0	0,0	0,0	0,0	0,0	0,0
1	0,0	0,0	0,0	0,0	0,0	0,0	0,0
10	0,0	0,0	0,0	0,0	0,0	0,0	0,0
30	0,0	0,0	0,0	0,0	-0,1	-0,1	-0,1
50	-0,1	-0,1	-0,1	-0,1	-0,1	-0,1	-0,1
80	-0,1	-0,1	-0,1	-0,1	-0,1	-0,1	-0,2
100	-0,1	-0,1	-0,2	-0,2	-0,2	-0,2	-0,2
200	-0,2	-0,2	-0,2	-0,2	-0,2	-0,3	-0,3

Table 2 *(continued)*

$C_{T_{\text{ei}}}$ K							
β	**Mass** µg						
300	-0,2	-0,2	-0,2	-0,3	-0,3	-0,3	-0,4
400	-0,4	-0,5	-0,5	-0,6	-0,6	-0,7	-0,9
500	-0,6	-0,6	-0,7	-0,8	-0,9	-1,0	-1,4
800	-0,8	-0,8	-1,0	-1,2	-1,3	-1,5	-2,1
1 000	-0,9	-1,0	-1,2	-1,4	-1,6	-1,8	-2,6

8.3 Symmetry of temperature calibration[14],[17],[21]

8.3.1 General

The symmetry of temperature calibration between heating and cooling of the chip sensor shall be verified within the scan rates of interest. Symmetrical behaviour of the chip sensor with respect to extrapolated peak onset temperatures means that the correction factors established in heating mode in 8.2 apply for cooling mode, too, with opposite sign. If such verification is not achieved, separate correction factors and a separate correction factor matrix shall be obtained for cooling.

Three liquid crystals have been reported in literature for checking the symmetry of fast scanning calorimeters1):

- 4-cyano-4’-octyloxybiphenyl (8OCB or M-24);
- 4-(4-pentyl cyclohexyl)-benzoicacid-4-propyl-phenylester (HP-53);
- 4’-ethyl-4(4-propylcyclohexyl)-biphenyl (BCH-52).

Calibration symmetry measurements shall be done based on extrapolated peak onset temperatures or peak temperatures, whatever can be determined more accurately, of liquid crystal transitions. The transition peaks shall be continuous and symmetric and shall not show multiple peaks within the scan rate range required for measurements in both, heating and cooling mode. In order to prevent structural reorganisation during heating calibration samples may need to be conditioned to achieve full crystallisation and sufficiently stable crystals[21].

8.3.2 Procedure

The sample used for checking the symmetry of temperature calibration shall have a mass typical for the selected type of chip calorimeter or sensor, and the intended application.

The extrapolated peak onset temperatures T_{ei} or peak maximum temperatures T_{p} shall be determined as a function of heating and cooling rate covering the scan rate range required for measurements. Temperatures or temperature differences vs. known transition temperatures shall be plotted as a function of cooling and heating rate. The respective slope as well as the intersection point with the zero scan rate line shall be determined, as shown in Figure 6.

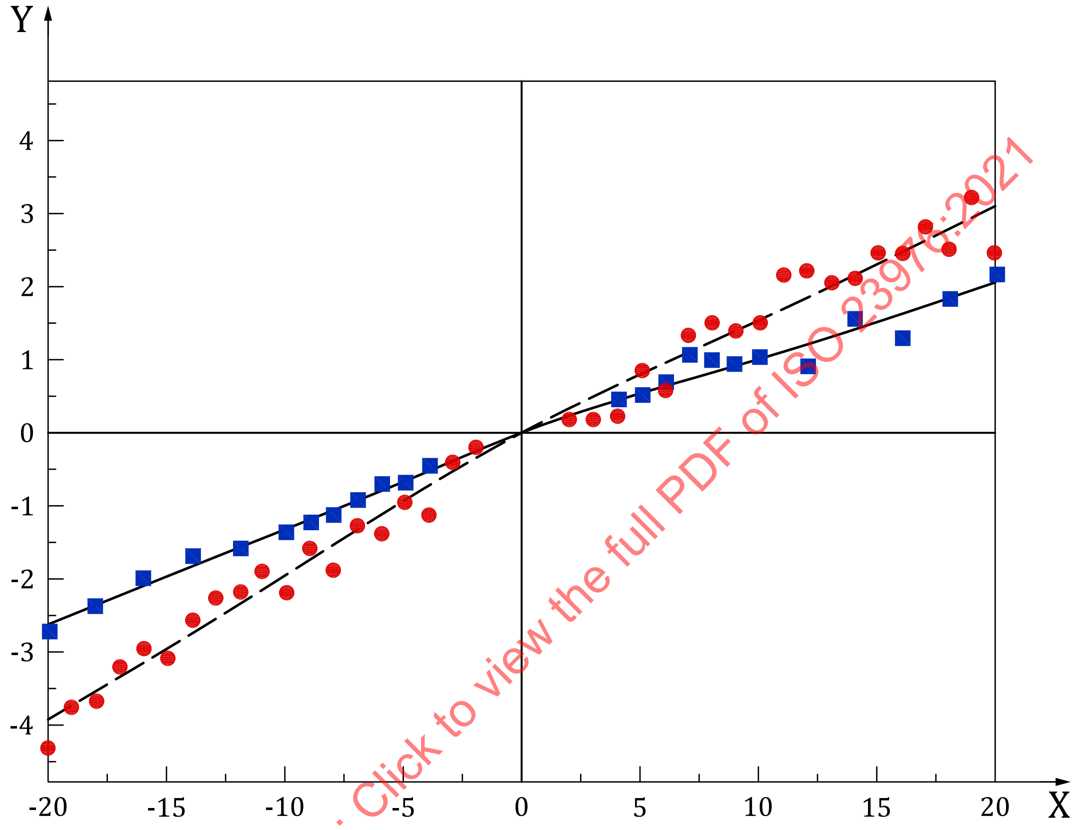
The slopes obtained upon cooling and heating shall be comparable and the intersection point with the zero scan rate line shall match the known transition temperature.

---

1) These substances are secondary temperature reference materials provided by Merck® (com/www.merckgroup.de), and traceable to standard reference materials from National Institute of Standards and Technology (NIST), Gaithersburg and Boulder, USA) and PTB (Physikalisch-Technische Bundesanstalt, Braunschweig, Germany). They are recommended by the Gesellschaft für Thermische Analyse (GEFTA) for temperature calibration and symmetry verification[22].

As the thermal lag is expected to increase with increasing sample mass, the slope will become larger for larger samples, as shown in Figure 6, too.

In case of significant deviations, the chip sensor is not sufficiently symmetrical, and a separate correction factor matrix shall be established for cooling using a similar procedure as specified in 8.2.2 for heating. For this purpose, a calibration material shall be selected that does not show significant undercooling.



Key

Y temperature difference ΔT vs. known transition temperature in K

X scan rate in 10^3 K/s

■ sample mass 20 ng

● sample mass 100 ng

NOTE Measured in cooling and heating mode using peak temperatures of the N-I transition of 8OCB.

Figure 6 — Example of checking the symmetry of temperature calibration[21]

8.4 Calibration of heat and heat flow rate

Due to the impossibility of direct determination of specimen mass, heat and heat flow rate cannot be calibrated directly but only after having determined the specimen mass using one of the methods specified in 12.2 to 12.5.

9 Specimen measurement procedure

9.1 Preparation of apparatus

9.1.1 Starting the instrument

The instrument, including, if applicable, any cooling equipment, shall be switched on at least 1 h prior to any measurement and 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 and flow rate that shall be used for actual measurements.

9.1.3 Preparation of sensor

If applicable, the sensor shall be fixed on the sensor support and any settling or conditioning procedures shall be run that are required for the particular instrument or sensor used.

The experimental conditions shall be set as desired for the actual measurement run and a DSC curve recorded without any specimens on the sensor. This empty sensor curve may then be subtracted from measurements with sample loaded sensor(s), resulting in a reasonable 'apparent' heat flow rate curve for each sample. If significant curvature or slope is obtained, the sensor shall be checked for any contamination, and repeatability of the empty sensor measurement shall be ascertained.

If applicable, a blank correction curve (with sample) may be run in accordance with 9.1.4.

9.1.4 Blank correction for heat loss[23]

The measured heat flow rate in fast scanning DSC can be estimated by Formula (4)

$$\frac{dQ}{dt} = m \cdot \left(c_p + \frac{d\alpha}{dT} \cdot \Delta h \right) \cdot \beta + \Phi_1 \tag{4}$$

where

$\frac{dQ}{dt}$ is the measured heat flow rate;

m is the sample mass;

c_p is the specific heat capacity;

α is the conversion of transformation;

T is the temperature;

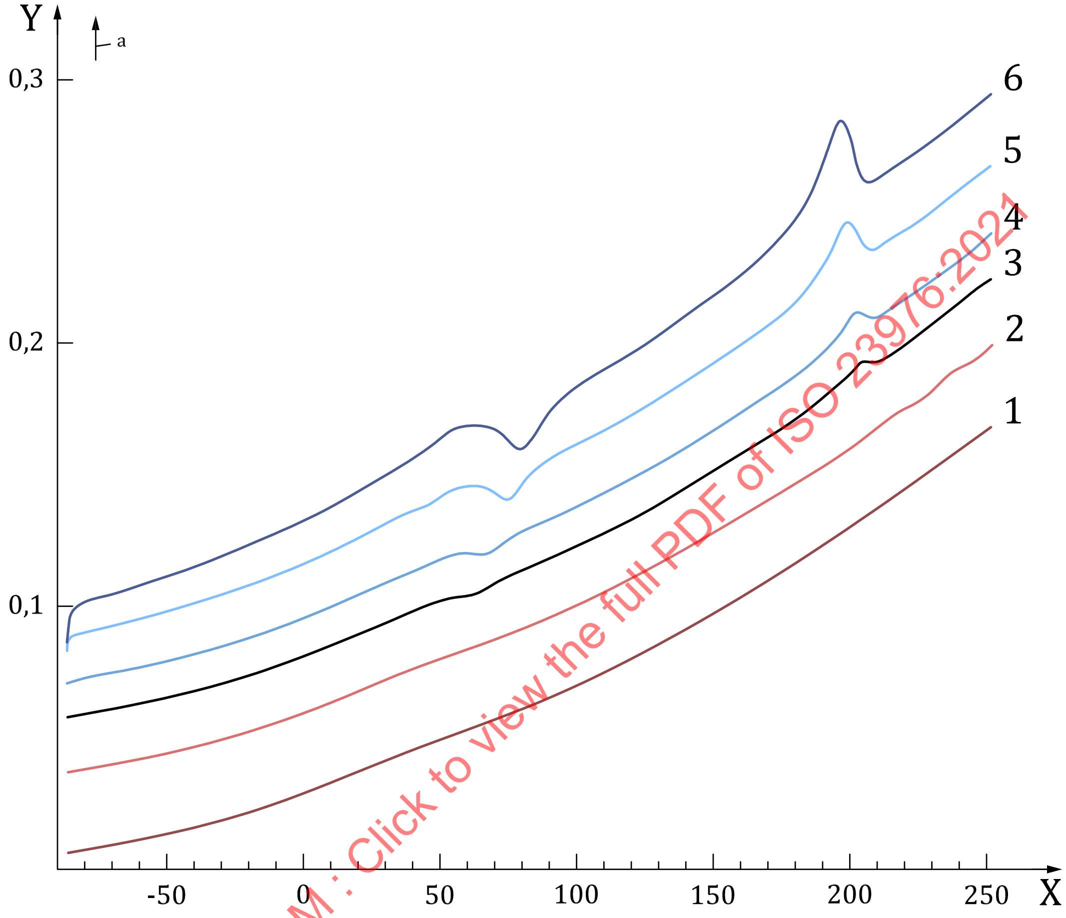
Δh is the specific enthalpy of transformation;

β is the scan rate;

Φ_1 is the non-compensated heat loss.

According to Formula (4), the sample component of the measured heat flow rate increases strongly with the scan rate while heat losses are almost rate-independent. Therefore, heat losses can be neglected at high scan rates and the measured heat flow is nearly identical to the sample heat flow. At sufficiently low heating rates, the sample contribution becomes negligible and the measured heat flow corresponds to the heat loss.

Blank correction in order to correct for non-compensated heat losses may be done by measuring the heat flow rate of a sample-loaded sensor with an empty reference area at a scan rate of at least 100 times lower than the lowest rate for acquisition of measurements. At such low scan rates significant noise may disturb the measured FSC curve and the measured heat flow rate curve may need to be smoothened. The blank curve obtained at low scan rate may be subtracted from all measured curves (see Figure 7).



Key

Y	heat flow rate in mW		1	blank curve, measured at 1 K/s and smoothened
X	temperature in °C		2	1 K/s
a	Endothermal direction.		3	10 K/s
			4	20 K/s
			5	50 K/s
			6	100 K/s

Figure 7 — Heating runs of amorphous PBT at different heating rates[23]

9.2 Placement of specimens on the sensor

Specimens in form of thin films or fine powders may be placed directly on a glass slide. Larger polymer parts or pellets shall be sliced to thin films using a suitable microtome. Samples shall be cut to size on the glass slide and then moved as close as possible onto the centre of the active area of the sensor using sample preparation devices selected from those listed in 5.3. Due to the small size of specimens this shall be done using a microscope.

Samples may also be prepared by evaporation or other suitable deposition techniques.

To prevent generation of adverse static temperature gradients, it is recommended that the specimen thickness does not exceed 10 µm at 1 000 K/s scan rate. For higher scan rates, even lower specimen thickness should be used and for lower scan rates thicker specimens may be acceptable.

NOTE Advices for detection and correction of static temperature gradients in the specimen can be found in the References [19], [20] and [23].

If the specimen is thicker than intended, it may be pre-melted and spread on the heating area of the sensor using a very thin copper wire or a hair that is sufficiently stable at applicable temperatures.

Generally, for higher scanning rates and higher sensitivity of the instrument or sensor lower thicknesses and specimen masses are required.

Specimen and reference shall be placed on the sensor at, or slightly above, room temperature (max. 50 °C) to prevent condensation of moisture.

Thin wires or hairs may be used to position specimen and reference correctly inside the active sensor area, respectively. If specimen positioning is difficult due to electrostatic effects wetting the hair with water or oil or using a different type of hair may be useful.

Preferably, specimens should be heated prior to measurements in order to improve the thermal contact to the sensor. For most semi-crystalline polymers it is sufficient to melt the specimens for approx. 30 K above the melting temperature. Some materials with very high melt viscosity may need to be left a few seconds in the melt to enable sufficient specimen flow.

The use of contact mediums such as silicone oil or graphite may be useful in following cases:

- improvement of thermal contact between sensor and specimen;
- reduction of mechanical stresses within specimens or between specimens and sensor;
- facilitation of positioning or removal of specimens on or from sensor;
- measurement of specimens in the as-received state.

9.3 Performance of measurements

9.3.1 General

Due to transients, which may occur on start-up, reliable data cannot be obtained at temperatures near the starting temperature or time. Therefore, the starting temperature shall be set adequately below the lowest temperature thermal effect in heating mode and adequately above the highest temperature thermal effect in cooling mode.

Similar to conventional DSC also FSC measurements on polymers can be greatly affected by the thermal history and morphology of the specimen. Therefore, it is recommended that the heating run is carried out twice. The first run reflects the as-received state and is performed to temperatures well above the melting or glass transition range where the material reaches thermal equilibrium within the timescale of the isothermal segment and prior thermal history is erased. The second run is carried out after cooling the specimen at a defined temperature program to generate a specified thermal history and thus allows comparison of material properties. The intermediate cooling run reveals information about nucleation and crystallization of the material.

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.

For isothermal measurements, the instrument shall be brought to the required test temperature as fast as possible to avoid phase transitions, (re)crystallization, (re)melting, annealing, enthalpy relaxation, ageing etc. during cooling or heating to the isothermal temperature chosen.

9.3.2 Running the instrument

The instrument shall be programmed, and the experimental parameters set to carry out the required combination of thermal cycle(s) and/or isothermal run(s).

The temperature programme shall be started, and the heat flow rate data recorded vs. temperature or time, as appropriate. Cycle(s) and/or run(s) shall be continued until transitions have finished and a stable heat flow rate is obtained within an adequate experimental timescale.

After termination of measurements correct positioning of specimen and reference, if applicable, shall be re-checked and measurements shall be repeated if specimen or reference have spread within the active sensor area or (partly) moved outside the active sensor area. Photographic documentation of the specimen before and after measurements is recommended.

NOTE In the molten state unnoticed processes can take place like demixing (which can be checked e.g. with microscopy), degradation (which can be checked using a more sensitive characterisation method like infrared spectroscopy), while in the glassy state ageing and enthalpy relaxation can occur.

9.3.3 Reuse of chip sensor

Chip sensors shall be reused only if complete removal of specimens can be achieved. This shall be checked by a repeated measurement of the heat flow rate curve a specified in 9.1.4.

9.3.4 Evaluation of results

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

Perform evaluation of results as agreed between parties involved.

10 Investigation of physical-chemical effects

10.1 General

As direct weighing in of the very small specimens required for FSC is not possible, the determination of specimen mass shall be done using one of the procedures specified in Clause 12.

10.2 First Order phase transitions

Except for the determination of specimen mass investigations of first order phase transitions such as melting, crystallisation, polymorphic transitions, etc. shall be done in accordance with ISO 11357-3.

Due to very high scan rates and low time constants of chip sensors FSC enables isothermal measurements of fast starting crystallisation effects as well as separation of melting or crystallisation peaks lying closely to each other.

NOTE At adequately high scan rates reorganisation or crystallisation effects can deviate significantly compared to conventional DSC or can be suppressed completely.

10.3 Chemical reactions

Except for the determination of specimen mass investigations of chemical reactions shall be done in accordance with ISO 11357-5.

The use of high heating rates in combination with low time constants of chip sensors enables observation also of fast starting reactions from the beginning.

10.4 Glass transitions

Except for the determination of specimen mass investigations of glass transitions shall be done in accordance with ISO 11357-2.

Due to the wide range of available scan rates spanning several decades extended measurements of the time dependence of glass transitions are achievable.

11 Determination of heat capacity[24]

Prior to determination of specific heat, the specimen shall be heated to the desired upper limit temperature and the heat flow rate curves of controlled cooling and subsequent second heating shall be used for the measurement of specific heat.

The heat capacity shall be determined from heat flow rate curves measured from heating and cooling runs at the same scan rate selected within the optimal range of scan rates for the particular instrument. A symmetry line correction shall be done to account for differential heat losses during heating and cooling scans. For this approach, it is assumed that the heat losses are only temperature dependent[3],[5],[11],[12]. In addition, they are assumed to be the same for heating and cooling, and independent of any transition in the specimen. For temperature ranges outside any transition the distance between the symmetry line and the measured heat flow rate at cooling and heating is then a measure of specimen plus addenda heat capacity of the sensor.

As a result of this symmetry line correction heating and cooling scans are placed symmetrically with respect to the abscissa, i.e. the temperature axis. The symmetry line shall be obtained as shown in Figure 8 using the following procedure[24].

The heat flow rate curves measured in heating and cooling mode outside any transition region shall be fitted in first order. The fitted lines shall be used to construct the symmetry line by calculating the arithmetic average of the fitted heating and cooling heat flow rate data. This will result in one or more linear sections of the symmetry line depending on the number of transitions in the temperature range of interest. Symmetry lines within transitions shall be fitted in third order, interpolating through the transition region to connect adjacent sections of the symmetry line. Thereafter heating and cooling heat flow rates are corrected by subtracting the symmetry line. Empty sensor heating and cooling scans measured at the same rate, shall be separately corrected for their symmetry line using the same procedure to take care of the addenda heat capacity of the sensor. The resulting corrected empty sensor heat flow rates shall be subtracted from the corrected specimen heat flow rates.

NOTE 1 Typically, the addenda heat capacity of the sensor is small compared to the specimen heat capacity for chip sensors prepared from the same wafer.

NOTE 2 Uncertainties regarding addenda heat capacity resulting from changes in the temperature distribution in the sensor due to the presence of the specimen are assumed negligible. Also, possible artefacts on the loss curve arising from changes in the specimen itself or thermal contact to the sensor are not considered. For more detailed information on additional interference factors and their influence and possible corrections, see Reference [12].

NOTE 3 If heat capacity is only needed for specimen mass determination, half of the distance between heating and cooling curves outside any transition can be used. Determination of the symmetry line is then not needed[25].

The finally obtained heat flow rate curves corrected for symmetry and addenda heat capacity of the sensor are converted to heat capacity using Formula (5):

$$C_p = \frac{\left(\frac{dQ}{dt}\right)}{\beta} \tag{5}$$

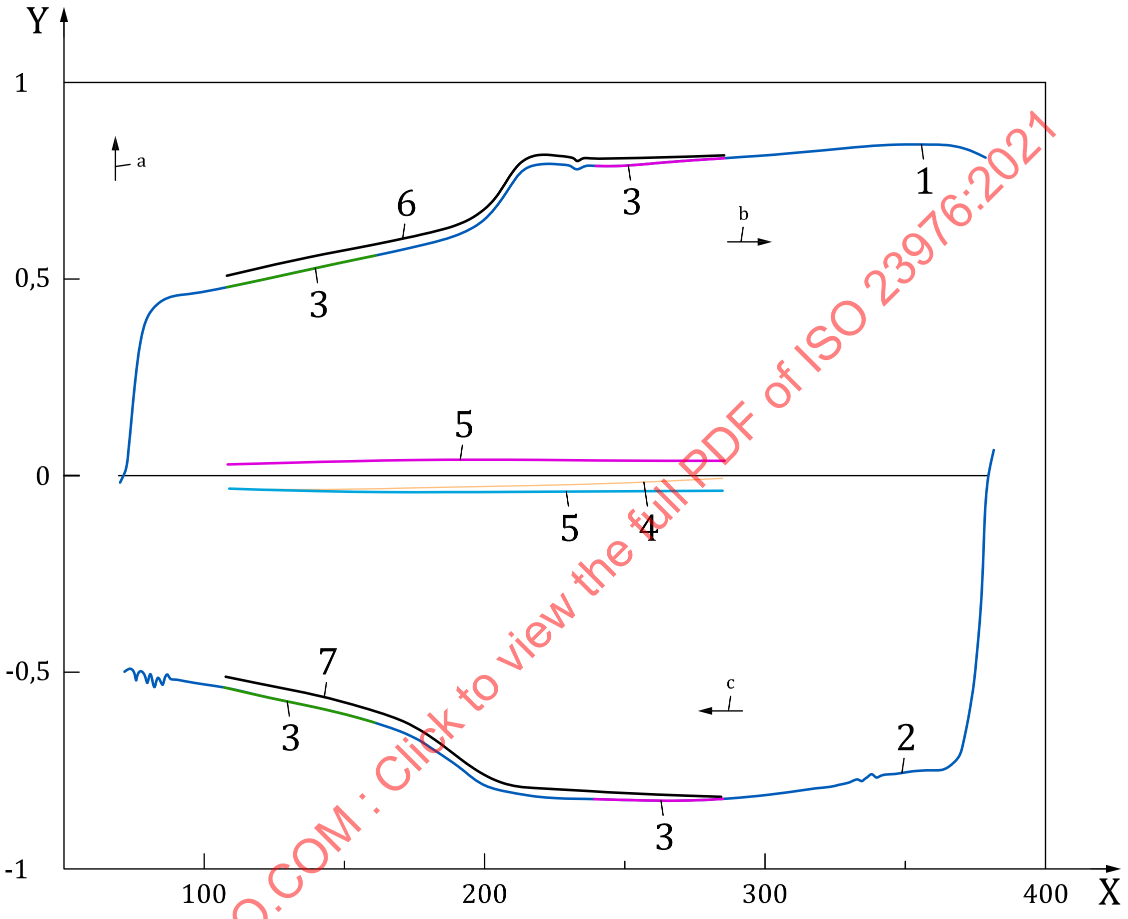
where

C_p is the heat capacity, in units of J/K;

$\left(\dfrac{dQ}{dt}\right)$ is the heat flow rate, in units of W;

β is the scan rate, in units of K/s.

The resulting heat capacity curves in heating and cooling mode are shown in Figure 9.

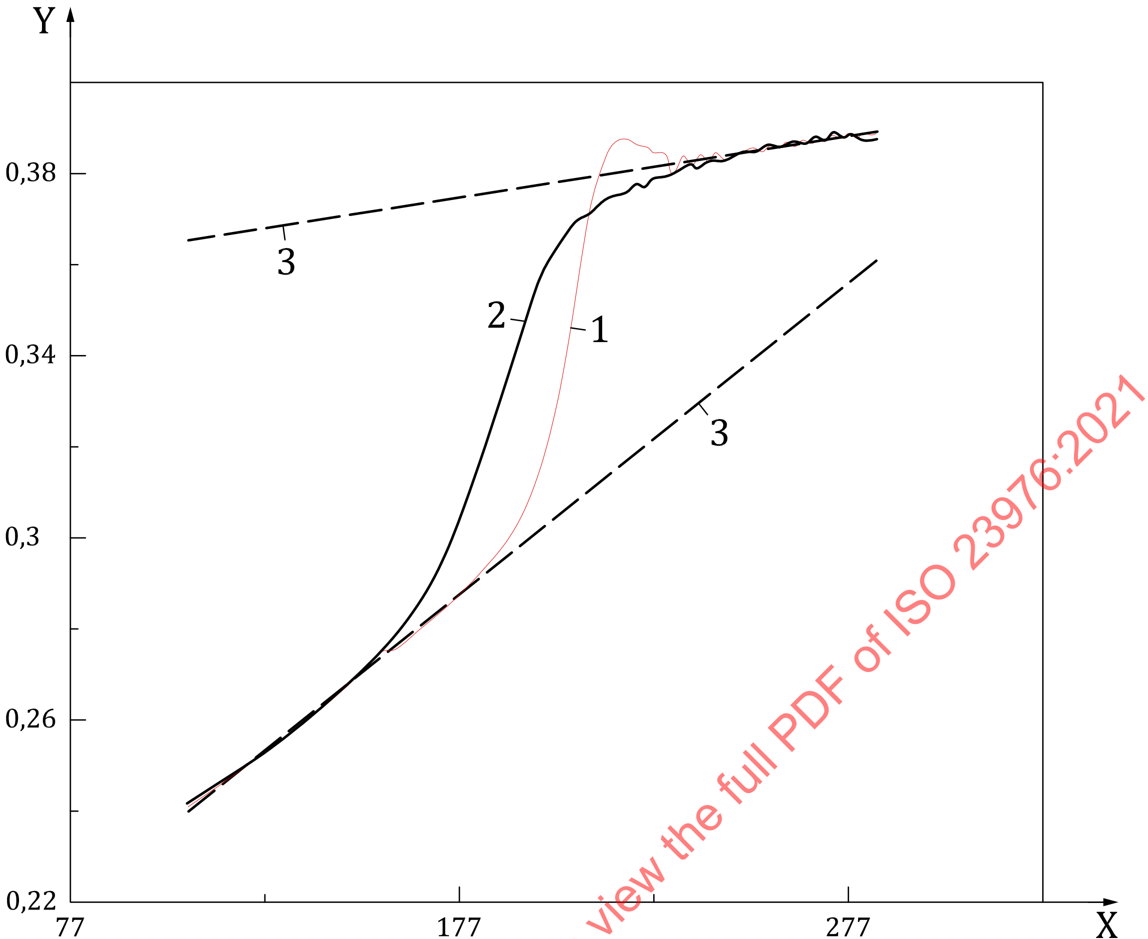


Key

Y heat flow rate, in mW
X temperature, in °C
1 measured heat flow rate curve in heating (blue)
2 measured heat flow rate curve in cooling (blue)
3 regions used for determination of symmetry line via first order fit (heavy green and magenta)
4 specimen symmetry line (orange)
5 empty sensor heat flow rate for heating (thin magenta) and cooling (cyan)
6 corrected sample heat flow after specimen and empty sensor symmetry line subtraction in heating
7 corrected sample heat flow after specimen and empty sensor symmetry line subtraction in cooling
[a] Endotherm direction.
[b] Heating.
[c] Cooling.

NOTE Measured with a commercial FSC instrument using a scan rate of ±20 000 K/s.

Figure 8 — Symmetry line correction applied to heat flow rate data of silk fibroin protein [24]



Key

Y heat capacity, in μJ/K

X temperature, in °C

1 corrected heat capacity in heating (red)

2 corrected heat capacity in cooling (black)

3 extrapolated lines from low and high temperature tangents (dashed)

NOTE Calculated from data of Figure 8.

Figure 9 — Corrected heat capacities of silk fibroin protein[24]

12 Determination of specimen mass[14],[23]

12.1 General

As the very low specimen masses to be used for FSC measurements cannot be measured directly by means of a balance, indirect methods for the determination of the specimen mass are required. In this document, mass determination methods are established based on:

— specific heat capacity of material;

— specific heat capacity change at glass transition;

— specific heat of fusion;

— specimen dimensions at known density.