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

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Foreword

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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.

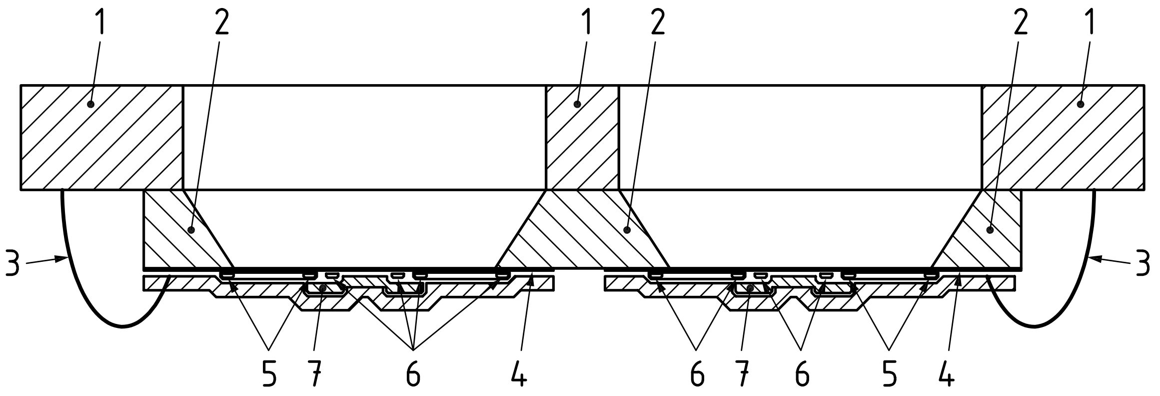
3.6
addenda heat capacity
additional heat capacity contribution of the sensor not related to the specimen

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

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;

