

**Recommendation for Temperature Calibration of Fast Scanning
Calorimeters (FSCs) for Sample Mass and Scan Rate;
Text in English**

Empfehlung für die Temperaturkalibrierung von Fast Scanning Calorimeters (FSCs)
für Probenmasse und Scanrate;
Text in Englisch

Recommandations pour l'étalonnage de la température des Calorimètres à Balayage
Rapide de la masse de l'échantillon et la vitesse de balayage;
Texte en anglais

Zur Erstellung einer DIN SPEC können verschiedene Verfahrensweisen herangezogen werden:
Das vorliegende Dokument wurde nach den Verfahrensregeln einer PAS erstellt.

Gesamtumfang 37 Seiten

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Foreword

This DIN Specification on differential scanning calorimetry, which has been developed by a standardization group using the PAS procedure, deals with high to very high scan rates and low to very low sample masses respectively, and is complementary to the International Standard ISO 11357 which is dealing with low scan rates.

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The work is an outcome of the NaPolyNet project of the 7th Framework Programme of the European Commission and was partially financed by NaPolyNet funds (EU-FP7 CSA NMP-2007-2.1-3).

DIN Deutsches Institut für Normung e.V., Berlin
March 21st, 2011

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Introduction

Thermal history – especially cooling and heating in combination with isothermal stays – and sample/product treatment can change the behavior of materials drastically, influencing end properties. Experimentally it has been a challenging and very demanding job to realize fast, controlled cooling and heating at constant rates higher than the typical rates of Standard DSC, which are centred on approximately 10 °C/min. In the past decade this challenge has been met through instrumental breakthroughs resulting in various Fast Scanning Calorimeters (FSCs), including commercial ones. This progress necessitates a dedicated protocol for temperature calibration of FSCs.

To address this need for extending existing temperature calibration protocols, the present Recommendation is firstly intended to inform the user about various types of FSCs and to compare their performances. To the opinion of the authors, FSC opens a new world with respect to the analysis of substances, materials and products thereof. Undoubtedly it will lead to new concepts in domains like metastability, kinetics, reorganization, crystallization, melting, real-life conditions, and processing conditions.

Secondly, one should be aware that instrumentation facilitating different scan rates has consequences with respect to the way of performing measurements, especially because of the influence of scan rate and sample mass on sensitivity, resolution, thermal lag etc.

Thirdly, because the impact is different for different FSCs, a need arises of a general applicable temperature calibration protocol, covering the issues mentioned and supporting measurements of good quality resulting in trustable and comparable results.

In order to meet the abovementioned requirements an international standardization group has been formed with the aim to provide the users of FSCs with a recommendation covering: *Temperature Calibration of FSCs for Sample Mass and Scan Rate*.

1 Scope

This specification describes a protocol of temperature calibration procedures for Fast Scanning Calorimeters for *high to very high scan rates* and *low to very low sample masses*, respectively, thus complementing ISO 11357.

Procedures are given for both an extensive temperature calibration as well as a rather quick temperature calibration of FSCs in the heating and the cooling modes for various scan rates and concomitant adjusted sample masses.

Thus, the specification also facilitates making the right choices to minimize the thermal lag arising at increasing scan rates before performing a measurement.

2 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 11357-1, *Plastics — Differential scanning calorimetry (DSC) — Part 1: General principles* (2009); in the present specification, terms and definitions used in ISO 11357-1 are accounted for.

3 Abbreviations and Units

3.1 Abbreviations

FSC	Fast Scanning Calorimetry/- Calorimeter
DSC	Differential Scanning Calorimetry/- Calorimeter
HPer DSC/ HyperDSC	High Performance Differential Scanning Calorimetry/- Calorimeter
RHC	Rapid Heat Cool differential scanning calorimeter
UFSC	Ultra Fast Scanning Calorimetry/- Calorimeter
MEMS	Micro-Electro-Mechanical Systems
ICTAC	International Confederation for Thermal Analysis and Calorimetry
GEFTA	Gesellschaft für Thermische Analyse e. V.
NIST	National Institute of Standards and Technology, Gaithersburg and Boulder, USA
PTB	Physikalisch-Technische Bundesanstalt, Braunschweig, Germany
In	indium
Ad	adamantane
Sn	tin
Pb	lead
HP-53	4-(4-pentyl cyclohexyl)-benzoic acid-4-propyl-phenylester
BCH-52	4'-ethyl-4(4propylcyclohexyl)-biphenyl
M-24	4-cyano-4'-octyloxybiphenyl
m	sample mass
T	temperature
T_{ei}	extrapolated onset temperature
$T_{ei,ref}$	extrapolated onset temperature for reference value of primary standards
t	time
β	scan rate
β_{min}	minimal scan rate
β_{max}	maximal scan rate
SD	standard deviation
CF	Correction Factor
$CF_{T_{ei}}$	Correction Factor for the extrapolated onset temperature

3.2 Units

Scan rate: °C/min or K/min; °C/s or K/s

Heat flow rate: mW

Specific heat flow: J/g°C and J/gK

$T/^{\circ}\text{C} = T/\text{K} - 273.15$

3.3 Convention

Heating and cooling curves are plotted upwards and downwards respectively.

4 Fast Scanning Calorimetry (FSC)

4.1 General

FSCs have received a great deal of attention in recent years. The reason that FSC is becoming increasingly popular is because, firstly, in practice, some physical and chemical processes occur at much higher scan rates than realizable using Standard DSC; and, secondly, most nano-structures in materials and substances, including polymers and pharmaceuticals, are in metastable states. Thermal history – specifically cooling and heating rates – and sample/product treatment can change their behavior drastically, leading to deviating end properties. Phenomena related to metastability of nano-structured crystallites and superstructures (if present) are well known to polymer scientists; daily they encounter supercooling, amorphization, ‘hot’ crystallization, cold crystallization, recrystallization (after melting), annealing, reorganization etc.

One of the breakthroughs in the past decennium with respect to the development of FSC was the realization of High Performance DSC [1, 2, 3, 4]. (HPer; the term ‘High Performance’ was meant as a general name for DSCs that realize higher scan rates than those attainable by Standard DSC, and show quantitative operation). It has been promoted commercially since then by PerkinElmer (coining the name ‘HyperDSC’, operating at scan rates up to 750 °C/min [5]) and recently also by TA Instruments (project RHC, a rapid-scanning DSC operating at scan rates up to 2 000 °C/min [6]). One of the great benefits of these calorimeters based on DSC technology, see Table 1, is that they can mimic temperature-time ramps as occurring in practice, and specifically most of the cooling rates used in processing. A further advantage is the increased sensitivity, enabling measurement of low heat flow rate signals as related to small transitions and to minute amounts of material.

Another break-through was the (further) development of extremely fast-operating chip-calorimeters, see Table 1, based on MEMS technology, as described in various publications (see e.g. [7, 8] and references therein). So far the results by the chip calorimeter have been obtained by specific equipment located at universities, like the instruments of the Polymer Physics Group at the Universität Rostock [9]. Continuous development and fine-tuning in this exciting field of research has been taken place over the years and with it the interest and demand with respect to FSC increased within and outside the thermal analysis community. This is confirmed by the recent development of a commercially available FSC: the Mettler-Toledo Flash DSC 1 [10, 11]. To avoid the concomitantly strong increase of the thermal lag with increasing scan rate, the sample mass is decreased accordingly.

Due to these developments, the scan rate operating window of existing commercial DSCs is extended to more than 8 orders in magnitude in total, and even 12 orders with specialized instrumentation [12]. In this way research groups have access to a huge range of scan rates as constituted by (for example) Calvet calorimetry, Standard DSC, HPer DSC and (Ultra-)FSC.

In order to support this rapidly-growing field, and to facilitate a trouble-free utilization, an adequate and quick temperature calibration of FSCs in the heating and cooling mode should be possible. In addition, the symmetry of an instrument used with respect to the cooling and the heating modes has to be checked.

4.2 DSCs

Table 1 — Representation of some characteristics of calorimeters based on DSC technology discussed in this specification, for empty cells, high scan rates and at the conditions given

DSC	scan rate in °C/min		achievable temperature at constant rate in °C		purge gas in ml/min	Source Figure
	heating	cooling*	heating up to	cooling down to*		
HyperDSC Pyris 1	350	200	350	75	He-Ne 25	**
	350	200	350	0	He 25	**
	350	200	350	125	N2 25	**
HyperDSC Diamond	350	200	350	50	He-Ne 25	A1
	300	200	300	-20	He 25	A3
	300	200	300	185	N2 25	A2/A3
RHC	1 500/1 000	—	240/350	—	Ne 10	A4
	1 500/1 000	1 000/500	175/275	100/-20	He 10	A4
* Cooling rate is determined by the cooling device, type of heat flow and rate, environmental conditions etc.						
** The graph is not included in this document.						

4.3 Chip Calorimeters

Table 2^a — Representation of some characteristics of calorimeters based on MEMS technology discussed in this specification, for empty cells, high scan rates and at the conditions given

FSC	scan rate in °C/s		achievable temperature at constant rate in °C		purge gas in ml/min	Source Figure
	heating	cooling*	heating up to	cooling down to*		
Flash DSC 1	20 000	5 000	410	40	N2 20	A6
	20 000	5 000	410	140**	N2 20	A6
	20 000	5 000	200	-25	He 20	***
UFSC Rostock	2 000 000	500 000	700	30	Air 0	A5
	2 000 000	10 000	700	-180	Air 0	A5
^a Sample mass is difficult or impossible to measure directly. Usually it is estimated from the particle size or by comparing the heat capacity measured away from transitions (e.g. in the melt) with the known specific heat capacity obtained from literature or obtained from an independent measurement [9].						
* Cooling rate is determined by the cooling device, type of heat flow and rate, environmental conditions etc.						
** No use of cooling accessory.						
*** The graph is not included in this document.						

5 Temperature Calibration Protocol

5.1 FSC Performance (Annex A)

Prior to any measurement using an FSC, a performance check of the instrument is *recommended*, especially with respect to its scan rate capabilities, resulting in “windows to operate” depending on the measurement settings and samples (scan rate, sample mass etc.) and environment (cooling accessory, purge gas etc.).

In this report, a window to operate means the temperature range in which the desired “sample” heating or cooling rate is constant. The achieved or “sample” heating or cooling rates are calculated by taking the derivative of the “sample” temperature (if available, as approximated by an as-close-to-the-sample-as-possible temperature sensor) as a function of that sample temperature [2, 3, 13, 20 and Annex A]. A temperature limit of a window to operate is reached when the “sample” scan rate is not constant anymore. A choice of performance checks of various types of FSCs is presented in Annex A. As will be obvious, the ‘windows to operate’ differ strongly for various calorimeters, e.g., for a Calvet calorimeter, a Standard DSC, a HPer DSC and a (Ultra-)FSC.

5.2 Primary Temperature Calibration (Annex B)

The primary temperature calibration as described in this paragraph is *required*. Calibration procedures for Standard DSCs [14, 15, 22, 23] with respect to temperature, heat and heat flow rate have been recommended by GEFTA and ICTAC [18, 22], and also by international standardization organizations like ASTM and ISO (see, e.g., ISO 11357-1 and -3) [15, 21]. Usually such a procedure complies with the one implemented by the instrument provider. However, FSC experiments are typically performed using various and sometimes very different (low and high) scan (heating and cooling) rates and sample masses. Therefore, in order to adapt an existing calibration procedure for temperature calibration of FSCs, it has to be extended appreciably.

The calibration in case of the extended temperature calibration procedure is the result of the following corrections:

- 1) a correction of the temperature as measured by the sensor towards its value in the limit of zero heating rate [16];
- 2) and a correction for the thermal lag [17, 18, 19]. The thermal lag usually has two origins:
 - a) one is due to the scan rate and
 - b) the other is dependent on the sample size (or mass) and geometry.

It is recommended to use the protocol in order to optimize experimental conditions – especially to minimize thermal lag – before starting a measurement.

A correct way to perform temperature calibration for FSCs starts with a standard calibration over a wide temperature range using primary standards, see Tables in references [20, 21, 22], which standards are selected on the basis of their phase transition temperatures situated in the temperature range of interest. It is advised to vary the heating rates as relevant for the FSC used and to confirm that the temperature range of measurement fits into the window-to-operate in which the scan rates should be constant. Examples are presented in Annex B. An extrapolation procedure towards zero is required to determine the extrapolated onset (T_{ei}) values of the standards which values are incorporated in the calibration file.

One should be aware of other parameters influencing repeatability/reproducibility of the heat flow rate, like the type of purge gas used; its flow rate, pressure, and stability; and sample related topics like the contact between sample and the chip or the sample container, the type, the homogeneity, shape, stability, chemical reactivity of the sample etc. The sample mass has to be chosen on one hand as low as possible to avoid a too high thermal lag at the highest scan rate, and on the other hand to be high enough to avoid noise becoming dominant, while it should be representative of the artifact being studied. Also careful attention must be paid to the position of the sample.

5.3 Check of the Primary Temperature Calibration

It is *recommended* to check/validate the primary temperature calibration procedure by measuring a (fresh) calibration sample, either the same primary standard or (preferred) another primary standard, see Tables in references [20, 21, 22]. The T_{ei} value(s) has/have to be determined and compared with the calibration data taking into account the (scan rate) dependent uncertainty(ies).

5.4 Temperature Calibration with Respect to Sample Mass and Scan Rate (Annex C)

A temperature calibration according to sample mass and scan rate is crucial and is *required* as described in this paragraph.

- 1) *Sample mass*: a primary standard – e.g. indium – has to be used, and one sample will do. Depending on the type of FSC used, optimal sample masses differing 2 orders of magnitude have to be used in combination with different scan rates, see Tables 1 and 2 for examples. A recommended way to calibrate is to use (at least) three samples: one having an optimal mass and two samples having lower and higher sample masses.
- 2) *Scan rate*: in selecting a suitable set of scan rates for each type of FSC, more than five scan rates – minimum (β_{min}), maximum (β_{max}) and at least three rates (β) in between – have to be chosen. The maximum scan rate of the instrument is known or has to be determined. The lowest scan rate has to be taken with $\beta_{min} \leq 1/10 \beta_{max}$. The “sample” scan rate should be taken if present.

The experimental data are to be fitted by means of one of the following formulas:

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

For some FSCs, formula (1) can be simplified to:

$$T_{ei}(\beta, m) = a_0 + a_1\beta m \quad (2)$$

The fit can encompass the whole set of data or part of the set as a whole. The following steps have to be taken (Annex C):

- 1) Perform the fit of the data according to the formulas 1 or 2; determine all parameters. It is *recommended* to calculate the standard deviation on the fitted parameters and to calculate the error limits of formula (1) or (2).
- 2) The result(s) of the fit should be shifted with a constant value. This constant value, C , is a correction factor for the extrapolated (to $\beta = 0$) onset temperature being defined on the basis of the reference value of the primary temperature standard $C = T_{ei,ref} - a_0$. Finally all starting values for zero scan rate will be equal to the $T_{ei,ref}$ value.
- 3) Calculate the Correction Factor for the extrapolated onset temperature $CF_{T_{ei}}$, defined as:

$$CF_{T_{ei}} = T_{ei,ref} - T_{ei}(\beta, m) \quad (3)$$

In addition, based on the formula for the Correction Factor (3) a correction matrix for the extrapolated onset temperature is calculated based on the fitting by formulas (1) or (2).

5.5 Check of the Temperature Calibration for Sample Mass and Scan Rate (Annex C)

It is *recommended* to check/validate the sample mass and scan rate calibration procedure by measuring a (fresh) calibration sample, either the same primary standard or (preferred) another primary standard, see Tables in [20, 21, 22]. The T_{ei} values of only one particular sample mass and some heating rates (at least five) have to be determined and compared with the calibration data taking into account the (scan rate) dependent uncertainty(ies).

5.6 Symmetry (Annex D)

It is *required* to investigate the symmetry of the instrument used as described in this paragraph. In literature [11, 20, 22, 23] the symmetries of the HPer DSC and various types of DSCs concerning heating and cooling have been verified using liquid crystal secondary temperature standards. If the furnaces or chips reveal "symmetrical" behavior with respect to the extrapolated onset temperatures, it means that the Correction Factors found in the heating mode also apply for the cooling mode, apart from their sign. If not, a correction matrix in cooling has to be built in addition to the one established in heating.

Three liquid crystals have been reported in literature for checking the symmetry of the FSCs: 4-cyano-4'-octyloxybiphenyl (M-24), 4-(4-pentyl cyclohexyl)-benzoic acid-4-propyl-phenylester (HP-53), and 4'-ethyl-4(4-propylcyclohexyl)-biphenyl (BCH-52) by way of the peak temperatures. These substances are secondary temperature reference materials provided by Merck®²⁾ for testing the accuracy of DSC's according to ISO 9001, and traceable to standard reference materials from NIST (National Institute of Standards and Technology, Gaithersburg and Boulder, USA) and PTB (Physikalisch-Technische Bundesanstalt, Braunschweig, Germany).

For the measuring procedure for FSCs, it is now *recommended* to use the *extrapolated onset temperature* (instead of the peak temperature being more vulnerable to thermal lag as caused by scan rate) of the smectic B to nematic (SmB — N) transition of BCH-52 to check the symmetry by way of the following steps:

- 1) determine the T_{ei} of the SmB – N transition as a function of heating and cooling of a sample having a mass typical for the selected FSC and for the application(s) in mind. The results should be mirrored two times according to Figure 1;
 - a) mirror the T_{ei} values obtained during cooling with respect to the zero scan rate axis (Mirror 1 in Figure 1);
 - b) mirror these new values a second time with respect to the average temperature value of both intersection lines with the zero scan rate axis (Mirror 2 in Figure 1);
- 2) it is *recommended* to compare the deviations of these values with the error limits of formula (1) or (2) applied for the fitting of the experimental data for the primary standard. On this basis the acceptance or rejection of symmetry of the FSC is to be decided. In case of rejection one should establish an additional Correction Factor matrix for cooling.

Alternatively, one can:

- 1) determine the average temperature at 0 °C/s (the average as defined in step b);
- 2) rotate the T_{ei} values obtained during cooling with respect to the average value by 180°.

In Figure 1 and in Annex D examples of the procedure given are presented for the SmB - N transition of BCH-52 as a function of scan rate using a Flash DSC 1.

2) The three certified liquid crystals as produced by Merck KGoA are provided as a calibration kit by Mettler-Toledo, see S. Neuenfeld, Mettler-Toledo UserCom 2/2007, 9–10

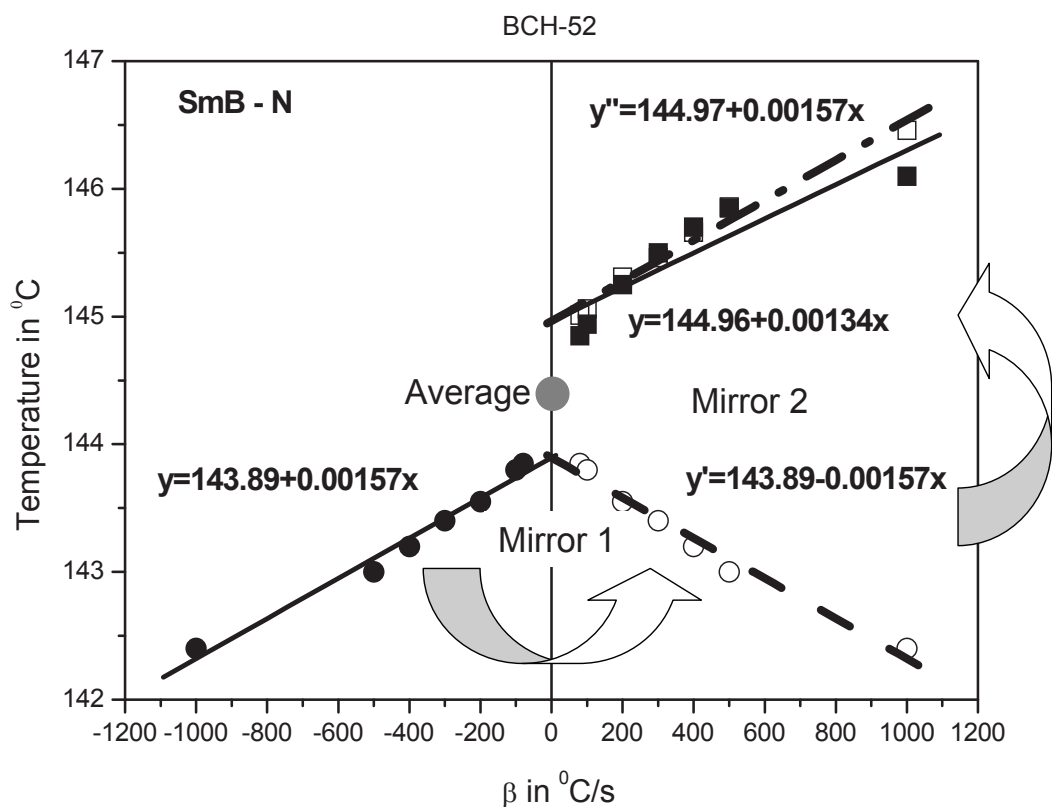


Figure 1 — The procedure to check the symmetry of an instrument using extrapolated onset temperatures of the SmB – N transition of BCH-52 obtained from various cooling and heating measurements

6 Calibration Protocol Flow Chart

