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Plastics — Temperature modulated DSC —

Part 1: General principles

Plastiques — DSC à température modulée —

Partie 1: Principes généraux

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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*.

A list of all parts in the ISO 19935 series can be found on the ISO website.

Any feedback or questions on this document should be directed to the user's national standards body. A complete listing of these bodies can be found at www.iso.org/members.html.

Introduction

The ISO 19935 series specifies temperature modulated differential scanning calorimetry (DSC) methods for the thermal analysis of polymers such as thermoplastics, thermosets and elastomers.

It is designed for observing and quantifying various phenomena or properties of the abovementioned materials such as

— physical transitions (glass transition, phase transitions like melting, crystallization, and cold crystallization, etc.);

— chemical reactions (cross-linking and curing of elastomers and thermosets, etc.);

— heat capacity;

— separation of overlapping thermal transitions.

This document describes the realization of several standardized thermoanalytical test methods which can be used for the determination of comparable data needed for data sheets or databases as well as for research purposes, but it can also be applied to quality assurance or to routine checks of raw materials and finished products, if desired. The procedures mentioned in this document apply as long as special product standards or standards describing special atmospheres for conditioning of samples do not require alternate provisions.

For scientific investigations or resolution of special analytical problems, all technical capabilities of the instruments beyond the provisions of this document may be used.

Plastics — Temperature modulated DSC —

Part 1: General principles

1 Scope

This document establishes general principles of temperature modulated differential scanning calorimetry (DSC) such as description of the principle and the apparatus, sampling, calibration and general aspects of the procedure and test report common to all parts of the ISO 19335 series.

NOTE Details on performing specific methods are intended to be given in the future parts of the ISO 19335 series.

2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 472, *Plastics — Vocabulary*

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

ISO 80000-5, *Quantities and units — Part 5: Thermodynamics*

3 Terms and definitions

For the purposes of this document, the terms and definitions given in ISO 472, ISO 11357-1 and ISO 80000-5 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/

4 Calculation of heat flow rate and heat capacity

4.1 Temperature modulation, *T(t)*

A periodic temperature profile superimposed to a linear temperature change or constant temperature, is given by Formula (1):

$$T(t) = T_0 + \beta_0 \cdot t + T_A \cdot f(t) \quad (1)$$

where

t is the time;

T_0 is a start temperature;

β_0 is the underlying heating or cooling rate;

T_A is the amplitude of sample temperature profile;

$f(t)$ is the periodic function of the temperature profile.

The periodic temperature profile can have any waveform. Multi-frequency temperature modulation can be used in one and the same measurement.

4.2 Heating rate

The heating rate is not constant as in the case of conventional differential scanning calorimetry (DSC), which follows from Formula (1):

$$\frac{dT(t)}{dt} = \beta_0 + T_A \cdot \frac{df(t)}{dt} \tag{2}$$

If the temperature profile is a sinusoidal function with angular frequency, ω [see Formula (3)]:

$$f(t) = sin(\omega t) \tag{3}$$

Formula (2) is derived as shown in Formula (4):

$$\frac{dT(t)}{dt} = \beta_0 + T_A \cdot \omega \cdot \cos(\omega t) \tag{4}$$

4.3 Heat flow rate $\Phi(t)$ and heat capacity

4.3.1 General

For a temperature perturbation that consists of an underlying part $\Phi_{underlying}$, a periodic part $\Phi_{periodic}$, and an additional endothermic or exothermic excess heat exchange part $\Phi_{ex.}$, the heat flow rate $\Phi(T, t)$ can be expressed as Formula (5):

$$\Phi(T,t) = \Phi_{underlying} + \Phi_{periodic} + \Phi_{ex.} \tag{5}$$

assuming the pure thermodynamic heat capacity is as shown in Formula (6):

$$\Phi(T,t) = C_p(T) \cdot \frac{dT(t)}{dt} + \Phi_{ex.} \tag{6}$$

$$= C_p \beta_0 + C_p \cdot \frac{T_A}{K(\omega)} \cdot \frac{df(t)}{dt} + \Phi_{ex.}$$

where

C_p is the heat capacity;

$K(\omega)$ is the frequency-dependent calibration function of the heat capacity (see 7.1).

The different cases are distinguished in 4.3.2 to 4.3.4.

Formulae (5) and (6) are enabled only for slow modulation with $\omega\tau << 1$, where τ is the time constant of the instrument. For higher frequencies, the calibration factor $K(\omega)$ [see 7.1, Formula (26)] has to be used.

4.3.2 Heat capacity with no processes

In this case, Formula (6) applies with $\Phi_{ex.} = 0$, if the temperature profile is a sinusoidal function, then Formula (4) yields:

$$\Phi(T,t) = C_p \beta_0 + C_p \cdot \frac{T_A}{K(\omega)} \cdot \omega \cdot \cos(\omega t) \tag{7}$$

Formula (7) means that the measured heat flow rate is the sum of two components, the first term is referred to as the underlying, $\Phi_{underlying}$, and the second one is the periodic, $\Phi_{periodic}$. The average within one period by integration derives $\Phi_{underlying}$ as Formula (8):

$$\Phi_{underlying} = \int_{t-t_p/2}^{t+t_p/2} \Phi(T,t)\,dt = C_p \cdot \beta_0 \tag{8}$$

If the underlying part is subtracted from the measured heat flow rate, the periodic part is given as:

$$\widetilde{\Phi}(T,t) = \Phi(T,t) - \Phi_{underlying}(T,t) = C_p \cdot T_A \cdot \omega \cdot \cos(\omega t) = \Phi \cdot \cos(\omega t) \tag{9}$$

From the amplitude of the periodic part, Φ_A, the heat capacity of the sample is:

$$C_p = \frac{\Phi_A}{T_A \cdot \omega} \tag{10}$$

The specific heat capacity, c_p:

$$c_p = \frac{C_p}{m} = \frac{\Phi_A}{m \cdot T_A \cdot \omega} \tag{11}$$

where m is the mass of the sample, called “specific heat capacity”.

NOTE True C_p can be found either by calibration procedure using the calibration factor $K(\omega)$ [see 7.1, Formula (26)].

$$C_p = \frac{\Phi_A}{T_A \cdot \omega} \cdot K(\omega) \tag{12}$$

$$c_p = \frac{\Phi_A}{m \cdot T_A \cdot \omega} \cdot K(\omega)$$

or calculated following the manufacturer’s instructions.

Formulae (7) to (11) are valid for a sinusoidal temperature modulation. There are different types of temperature modulation functions and evaluation procedures:

a) stepwise temperature changes with isothermal segments;

b) single frequency modulations;

c) use of non-sinusoidal modulation waveforms, such as square, triangle, etc.;

d) multi-frequency modulation.

The procedure in Formulae (7) to (11) is categorized under type b). Similar formulae can be derived for other waveforms, too. The generalized theory of temperature modulated DSC is described in Annex A and in the related References [1] to [7].

4.3.3 Heat capacity with additional processes

In this case, additional processes with endothermic or exothermic latent heat exchange are taking place, Formula (7) is extended with the excess heat flow rate shown in Formula (13):

$$\Phi(T,t) = C_p \cdot \beta_0 + C_p \cdot T_A \cdot \omega \cdot \cos(\omega t) + \Phi_{ex.}(T,t) \tag{13}$$

Subtracting the underlying part from the total signal yields the periodic part:

$$\Phi(T,t) = C_p \cdot T_A \cdot \omega \cdot \cos(\omega t) + \frac{\partial \Phi_{ex.}(T_u,t)}{\partial T} \cdot T_A \cdot \sin(\omega t) \tag{14}$$

where $T_u = T_0 + \beta_0 t$ and $\Phi_{ex.}$ can be substituted by the first approximation of the Taylor series. Formula (14) can be written as Formula (15):

$$\Phi(T,t) = \Phi_A \cdot \cos(\omega t + \delta) \tag{15}$$

where

$$\Phi_A = \sqrt{\left(C_p(T) \cdot T_A \cdot \omega\right)^2 + \left(T_A \frac{\partial \Phi_{ex.}}{\partial T}(T_u,t)\right)^2};$$

$$\delta = tan^{-1} \frac{\frac{\partial \Phi_{ex.}}{\partial T}(T_u,t)}{C_p(T) \cdot \omega}.$$

From the amplitude, an "apparent" heat capacity $C_p^{app.}$ can be calculated in a similar manner as in Formula (10):

$$C_p^{app.} = \sqrt{\left[C_p(T)\right]^2 + \left(\frac{1}{\omega} \frac{\partial \Phi_{ex.}}{\partial T}(T_u,t)\right)^2} \tag{16}$$

Formula (16) is understood as the absolute value of a complex heat capacity which is given either as real and imaginary parts or as magnitude and phase angle in the following relations (see Formulae (17) and (18):

$$C_p^* = C_p' + iC_p'' = \left|C_p^*\right| \cdot e^{i\delta} = \left|C_p^*\right| \cdot cos\delta + i \cdot \left|C_p^*\right| \cdot sin\delta \tag{17}$$

$$\left|C_{\mathrm{p}}^{*}\right|=\sqrt{C_{\mathrm{p}}^{'2}+C_{\mathrm{p}}^{''2}}\text{, and }\tan\delta=\frac{C_{\mathrm{p}}^{''}}{C_{\mathrm{p}}^{'}} \tag{18}$$

In the case with additional endothermic or exothermic latent heat exchange, the real and imaginary parts of the complex heat capacity are as shown in Formula (19):

$$C_{\mathrm{p}}^{'}=C_{\mathrm{p}}\text{ and }C_{\mathrm{p}}^{''}=\frac{1}{\omega}\frac{\partial\Phi_{\mathrm{ex.}}}{\partial T}\left(T_{\mathrm{u}},t\right) \tag{19}$$

4.3.4 Time dependent heat capacity

In this case, the relaxation processes like vitrification or devitrification are considered. Time dependent heat capacity means a non-equilibrium state of a system of the sample. Formula (6) is not valid anymore and is replaced by the convolution product of the time dependent heat capacity and the heating rate given by Formula (20):

$$\Phi\left(T,t\right)=\frac{d}{dt}\int_{-\infty}^{\infty}\left(C_{\mathrm{p}}\left(T,t-t'\right)\cdot\frac{\partial T\left(t'\right)}{\partial t}\right)dt' \tag{20}$$

The convolution product in time domain is transformed into a common product in the frequency domain via Fourier transform, $\tilde{F}$, [see Formula (21)]:

$$\tilde{F}\left[\Phi\left(t\right)\right]=\tilde{F}\left[C_{\mathrm{p}}\left(T,t\right)\right]\cdot\tilde{F}\left[\dot{T}\left(t\right)\right] \tag{21}$$

which is equivalent to a product of two complex function in Fourier space as shown in Formula (22):

$$\Phi^{*}\left(\omega\right)=C_{\mathrm{p}}^{*}\left(\omega\right)\cdot\dot{T}^{*}\left(\omega\right) \tag{22}$$

5 Principles

5.1 General

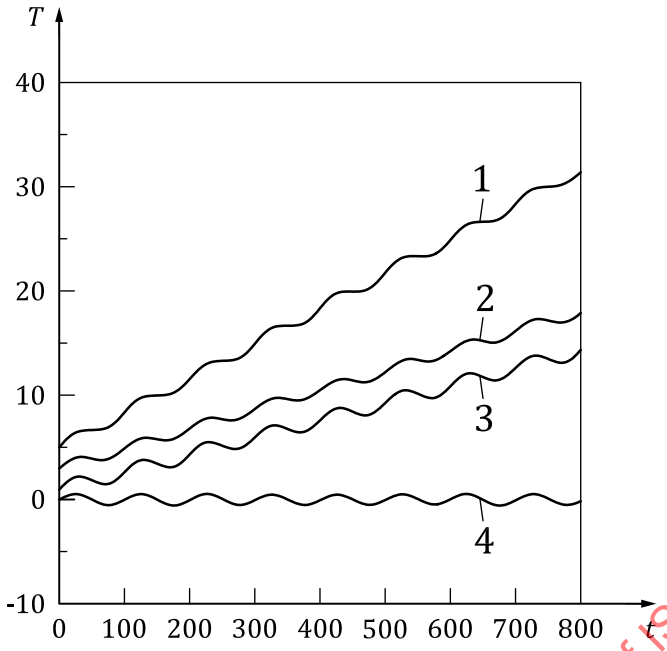
The difference between the heat flow rate into a specimen and that into a reference is measured as a function of temperature and/or time while the specimen and the reference are subjected to the same controlled temperature modulation under a specified atmosphere.

Depending on the design of instrumentation, the calibration procedures of the modulated part of the apparent heat capacity are required.

5.2 Mode of temperature modulation

5.2.1 Variable heating rate of periodic modulation

The simplest modulation type is a fixed frequency periodic temperature change. This can be done in sinusoidal waveform [see 4.2, Formula (3)] or alternative waveforms such as square, triangle, etc. Different modes of temperature modulation are distinguished depending on the magnitude of β_0, T_{A}, and ω as shown in Figure 1.



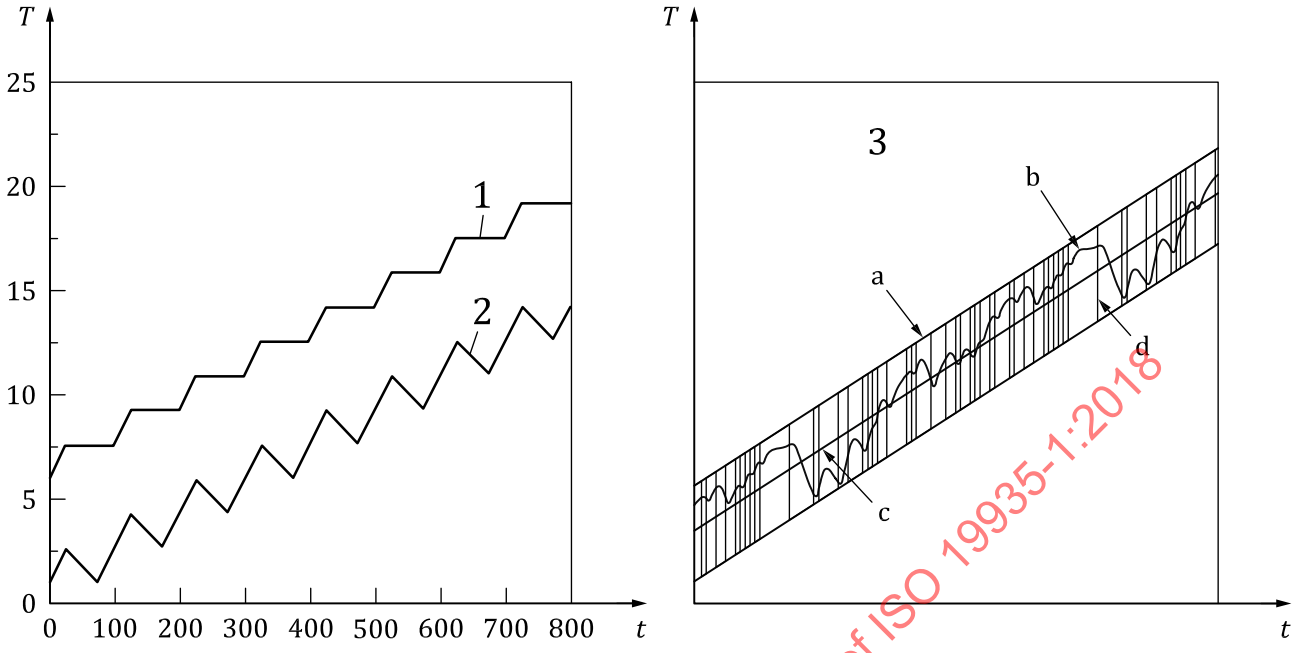
Key

1 heating only $T_A \cdot \omega < \beta_0$
2 heating iso $T_A \cdot \omega = \beta_0$
3 heating cooling $T_A \cdot \omega > \beta_0$
4 quasi-isothermal $\beta_0 = 0$
T temperature in °C
t time in s

Figure 1 — Temperature modulated modes of operation with variable heating rate

5.2.2 Variable temperature modulated mode

Special temperature modulated mode such as a step-scan or a saw tooth or multi-frequency modulation mode can be operated (see Figure 2).



a) Step-scan and saw tooth modulation

b) Multi-frequency modulation

Key

1 step scan
2 saw tooth
3 multifrequency
T temperature in °C
t time in s

a Pulse height.
b Cell temperature.
c Underlying temperature.
d Setpoint temperature.

Figure 2 — Special mode of temperature modulation

5.3 Heat capacity determined with the temperature modulation — Complex heat capacity

From the amplitude of the periodic part, the specific heat capacity of the sample is given in three different cases.

a) If no additional processes occur, the heat capacity is given as $C_p = \frac{\Phi_A}{T_A \cdot \omega} \cdot K(\omega)$, where the calibration factor $K(\omega)$ is defined in 7.1, Formula (26).

b) If additional processes occur, the complex heat capacity is introduced as $C_p^* = C_p' + iC_p'' = \left|C_p^*\right| \cdot e^{i\delta}$.

NOTE Adapted from Formula (17).

c) If the time dependent heat capacity $C_p(t)$ in the relaxation processes is given from $C_p^*(\omega)$ in the Fourier space, then it is $\Phi^*(\omega) = C_p^*(\omega) \cdot \dot{T}^*(\omega)$

NOTE Adapted from Formula (22).

5.4 Reversing and non-reversing heat capacity

Even in the case of process occurring in the sample, an apparent specific heat capacity is defined as:

$$c_{\mathrm{p,reversing}}(T)=\frac{\Phi_{\mathrm{A}}(T)}{m\cdot T_{\mathrm{A}}\cdot\omega}$$

which is called the reversing specific heat capacity and is taken from Formula (11).

The reversing heat flow rate can be calculated as Formula (23):

$$\Phi_{\mathrm{rev.}}(T)=c_{\mathrm{p,reversing}}(T)\cdot m\cdot\beta_0 \tag{23}$$

The non-reversing heat flow rate is calculated as Formulae (24) and (25):

$$\Phi_{\mathrm{non-rev.}}(T)=\Phi_{\mathrm{underlying}}(T)-\Phi_{\mathrm{rev.}} \tag{24}$$

$$c_{\mathrm{p,non-reversing}}(T)=c_{\mathrm{p,underlying}}(T)-c_{\mathrm{p,reversing}}(T) \tag{25}$$

where

$$c_{\mathrm{p,underlying}}(T)=\frac{\Phi_{\mathrm{underlying}}(T)}{m\cdot\beta_0}$$ adapted from Formula (8);

$$c_{\mathrm{p,non-rev.}}(T)=\frac{\Phi_{\mathrm{non-rev.}}(T)}{m\cdot\beta_0}.$$

For temperature ranges without processes, the reversing heat flow shall be equal to the total heat flow, and the non-reversing heat flow shall be zero.

5.5 Advantage of the temperature modulation applied to DSC

Temperature modulated DSC is distinguished in the following measurement procedures and analytical processes.

a) Measurement of the specific heat c_{p} under consideration of the coefficient $K(\omega)$ and a measurement based on sapphire (the sapphire measurement is only necessary for specific heat calculations).

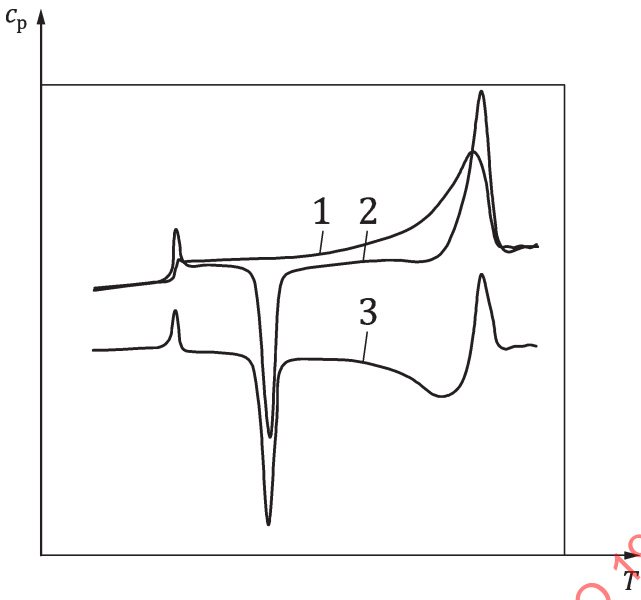
b) Separation of sensible and latent heat flow.

c) Determination of glass transitions including frequency dependence.

d) Quasi-isothermal measurement of heat capacity.

NOTE Typical results of specific heat capacity of PET and PS measured with temperature modulated DSC are shown in Figure 3 and Figure 4 in relation with the above topics. The details are intended to be given in the future parts of the ISO 19935 series.

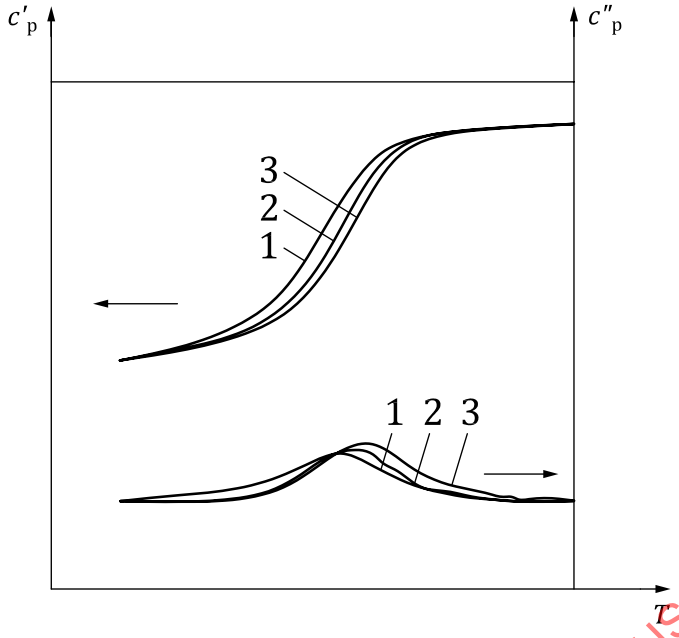
The use of multi-frequency modulation methods allows simultaneous measurement of sample properties as a function of time and temperature over a large frequency range and thus provides frequency-dependent heat capacity values based on one single measurement. This enables quick and easy differentiation between frequency-dependent effects (e.g. glass transitions) and frequency-independent effects (e.g. cold crystallization) as shown in Figure 5 as well as the determination of the quasi-static heat capacity without running multiple temperature modulation scans.



Key

1 reversing c_p
2 total (apparent) c_p
3 non-reversing c_p
c_p specific heat capacity in $J \cdot g^{-1} \cdot K^{-1}$
T temperature in °C

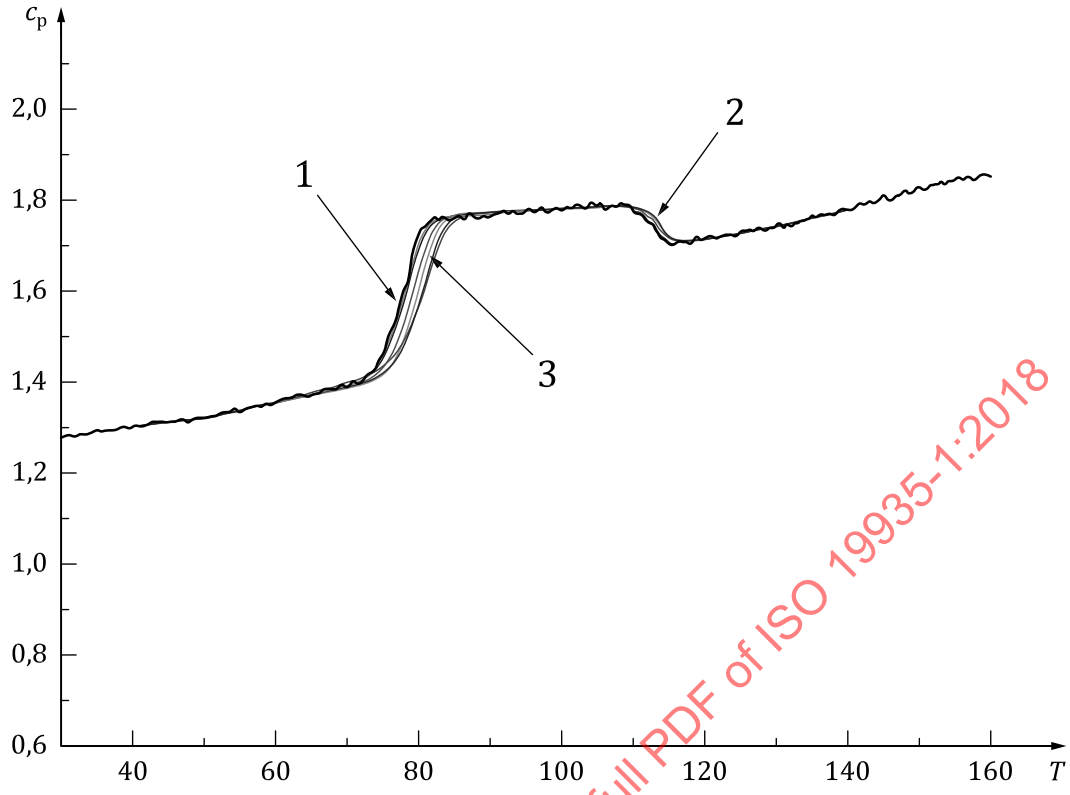
Figure 3 — Total, reversing and non-reversing c_p of amorphous PET



Key

1	10 mHz
2	20 mHz
3	30,3 mHz
c'_p and c''_p	specific heat capacity in $J \cdot g^{-1} \cdot K^{-1}$
T	temperature in °C

Figure 4 — Real and imaginary c_p of PS



Key

1 glass transition
2 cold crystallization
3 frequency change from 0 mHz to 70 mHz
c_p specific heat capacity in $J \cdot g^{-1} \cdot K^{-1}$
T temperature in °C

Figure 5 — Frequency dependence of glass transition and frequency independence of cold crystallization detected in amorphous PET by using multi-frequency modulation in one single measurement

6 Apparatus and materials

6.1 General

Apparatus, crucibles, balance, calibration materials, purge gas, test specimens, and specimen conditioning for the temperature modulated differential scanning calorimeter shall be in accordance with ISO 11357-1, following the requirements for DSC measurement.

6.2 Temperature control of modulated differential scanning calorimeter

The temperature modulated DSC shall have the capability to allow temperature control by varying temperature periodically, or by a step, or by an input of pulse sequence with an amplitude up to 1,5 K and a frequency down to 10 mHz, superimposed on the underlying rate.

7 Calibration

7.1 General

In addition to the normal calibration of temperature and heat (which should always be carried out) as well as of heat flow rate in accordance with ISO 11357-1 (if c_p determination is required), the frequency dependence of the heat capacity shall be taken into account for temperature modulated DSC experiments. The calibration factor $K(\omega)$ can either be derived from the heat flow rate calibration (e.g. by using sapphire) or can be calculated according to manufacturer's instruction. The calibration factor $K(\omega)$ is introduced by Formula (26).

$$C_{\mathrm{p,true}} = K(\omega) \cdot C_{\mathrm{p,meas.}} \tag{26}$$

where

$C_{\mathrm{p,true}}$ is the true heat capacity;

$C_{\mathrm{p,meas}}$ is the measured heat capacity.

7.2 Calibration of modulation amplitude

The calibration factor by means of a substance with known heat capacity such as sapphire is led by Formula (27):

$$K(\omega) = \frac{\left|C_{\mathrm{p,cal.-sap.}}\right|}{\left|C_{\mathrm{p,meas.-sap.}}\right|} \tag{27}$$

where

$C_{\mathrm{p,cal.-sap.}}$ is the heat capacity of sapphire in the literature;

$C_{\mathrm{p,meas.-sap.}}$ is the measured heat capacity of sapphire at frequency ω and temperature T.

NOTE Specific heat of sapphire is the same for all frequencies used in the temperature modulated DSC measurements.

7.3 Calibration of phase

The phase is strongly influenced by heat transfer of the device as well as the sample itself. The phase shift is not only a function of frequency but also of the thermal resistance and heat capacity. The complex transfer function assuming the simple RC element in the electrical analogy gives the phase shift δ as Formula (28):

$$\delta = tan^{-1}\left(\omega \cdot R_{\mathrm{th}} \cdot C_{\mathrm{p}}\right) \tag{28}$$

where R_{th} and C_{p} are the thermal resistance and the heat capacity of the assuming heat conducting networks, respectively[6].

8 Procedure

8.1 General

The procedures of temperature modulated DSC (setting up the apparatus, loading the specimen into the crucibles, insertion of crucibles into the instrument, performing measurements, and removal of crucibles) shall be in accordance with ISO 11357-1.

8.2 Experimental conditions

The experimental conditions specified to temperature modulated DSC (e.g. amplitude of the modulated heat flow, amplitude of modulated temperature, the waveform and the frequency of the modulation superimposed on the underlying rate) to be used depend on the thermal effect to be investigated and are described in the appropriate parts of the ISO 19935 series.

8.3 Interpretation of results

Heat flow rate, heat capacity, and specific heat capacity in different processes are determined based on the definitions and procedures described in Clauses 4 and 5.

9 Test report

The test report shall include the following information:

a) a reference to this document, i.e. ISO 19935-1:2018;

b) type and complete identification of specimen;

c) type (heat flux or power compensated), manufacturer and model of DSC instrument used;

d) material, type and mass of crucible used;

e) type, purity and flow rate of purge gas used;

f) type of calibration procedure (simplified or extended), calibration materials used, including source, mass and other properties important for calibration;

g) details of sampling, preparation of specimen and conditioning procedures, if applicable;

h) shape and dimensions of specimen, if applicable;

i) mass of specimen;

j) thermal histories of sample and specimen;

k) temperature program parameters, including time and temperature of isothermal steps and rate of dynamic steps, frequency, amplitude and waveform of the modulation;

l) change of mass of specimen over duration of test, if any;

m) test results including DSC curves;

n) date of test;

o) any additional information or operating details not specified in this document which may be important for assessment of the results.