INTERNATIONAL STANDARD

ISO 19935-2

First edition
2020-09

Plastics — Temperature modulated DSC —

Part 2: Measurement of specific heat capacity c_p

Plastiques — DSC à température modulée —

Partie 2: Mesurage précis de la chaleur spécifique c_p

Reference number
ISO 19935-2:2020(E)

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Published in Switzerland

Contents

Page

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

This document describes the realization of standardized thermoanalytical test methods which can be used for the determination of specific heat capacity data needed for data sheets or databases as well as for research purposes. 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 regulations.

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

Plastics — Temperature modulated DSC —

Part 2: Measurement of specific heat capacity c_p

1 Scope

This document establishes a method for measurement of specific heat capacity, c_p, using temperature modulated differential scanning calorimetry.

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 19935-1, *Plastics — Temperature modulated 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, ISO 19935-1 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 Symbols and abbreviated terms

4.1 Temperature modulation, *T(t)*

According to ISO 19935-1.

4.2 Scanning rate

According to ISO 19935-1.

4.3 Heat flow rate, Φ(t)

According to ISO 19935-1.

5 Principles of determination of specific heat capacity with temperature modulated DSC

5.1 General

The use of temperature modulated DSC is advantageous for the measurement of specific heat capacity not only outside the region of a transition, because it does not require a stable baseline to achieve high accuracy. The measurement of specific heat capacity is only based on the amplitude of the modulated heat flow rate signal.

5.2 Specific heat capacity with no processes

According to ISO 19935-1.

5.3 Reversing and non-reversing specific heat capacity

According to ISO 19935-1.

5.4 Step scan method

In the step scan method, the isothermal line is called iso-kinetic (iso-K) base line. Specific heat capacity, c_p, can be determined by integrating the heat flow rate Φ(t) in one cycle as Formula (1):

$$c_p = \frac{1}{m\Delta T}\int_{t_0}^{t_e}\Phi(t)\,dt \tag{1}$$

where

m is the mass of the sample;

ΔT is a temperature step;

t_e, t_0 is a time interval in one period.

5.5 Multiple frequencies

Assuming the linear response theory, the input of multiple frequencies or random pulses as a modulated heat source are analysed with the procedures in the ISO 19935-1. An example is shown in Annex D.

6 Apparatus and materials

6.1 General

Use the apparatus according to ISO 19935-1.

6.2 Temperature control of the modulated differential scanning calorimeter

Specifications of temperature control required for temperature modulated DSC are added as follows.

a) Capability to vary temperature periodically, or stepwise, or by an input of a pulse sequence with an amplitude, typically in the range of (±0,1 to 2,0) K, and a frequency, typically down to 10 mHz, superimposed on the underlying rate, typically less than 3 K/min.

b) Depending on the relation of the underlying scanning rate β_0 to the amplitude of sample temperature profile $T_A\omega$ (where ω the angular frequency) four cases of scanning rates are distinguished.

   1) Quasi–isothermal mode, $\beta_0 = 0$. If $\beta_0 = 0$, heat capacity can be measured as function of time, e.g. during chemical reactions like curing or during crystallization. All other calorimetric methods measure heat capacity as function of temperature only.

   2) For other modes, such as $T_A\omega > \beta_0$, $T_A\omega < \beta_0$, and $T_A\omega = \beta_0$, refer to ISO 19935-1.

c) Any mode of temperature modulation specified in ISO 19935-1 can be used.

7 Calibration

7.1 General

According to ISO 19935-1.

7.2 Calibration of modulation amplitude

According to ISO 19935-1.

7.3 Calibration of phase

According to ISO 19935-1.

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.

The experimental conditions specified for temperature modulated DSC (for example, amplitude of the modulated heat flow rate, amplitude of modulated temperature, and the frequency of the modulation superimposed on the underlying rate) to be used depend on the magnitude of the specific heat capacity to be determined.

8.2 Calculation of the specific heat capacity

Specific heat capacity is calculated as Formula (2):

$$c_{\mathrm{p}} = \frac{\Phi_A}{m \cdot T_{\mathrm{A}} \cdot \omega} \cdot \mathrm{K}(\omega) \tag{2}$$

where

c_{p} is the specific heat capacity of the specimen, in $\mathrm{Jg^{-1}K^{-1}}$;

T_{A} is the amplitude of sample temperature profile, in K;

Φ_{A} is the amplitude of the periodic part of the modulated heat flow rate, in mW;

m is the mass of the specimen, in mg;

ω is the angular frequency of the modulated temperature, in rad/s; $\omega = 2\pi f$, where f is the frequency in Hz;

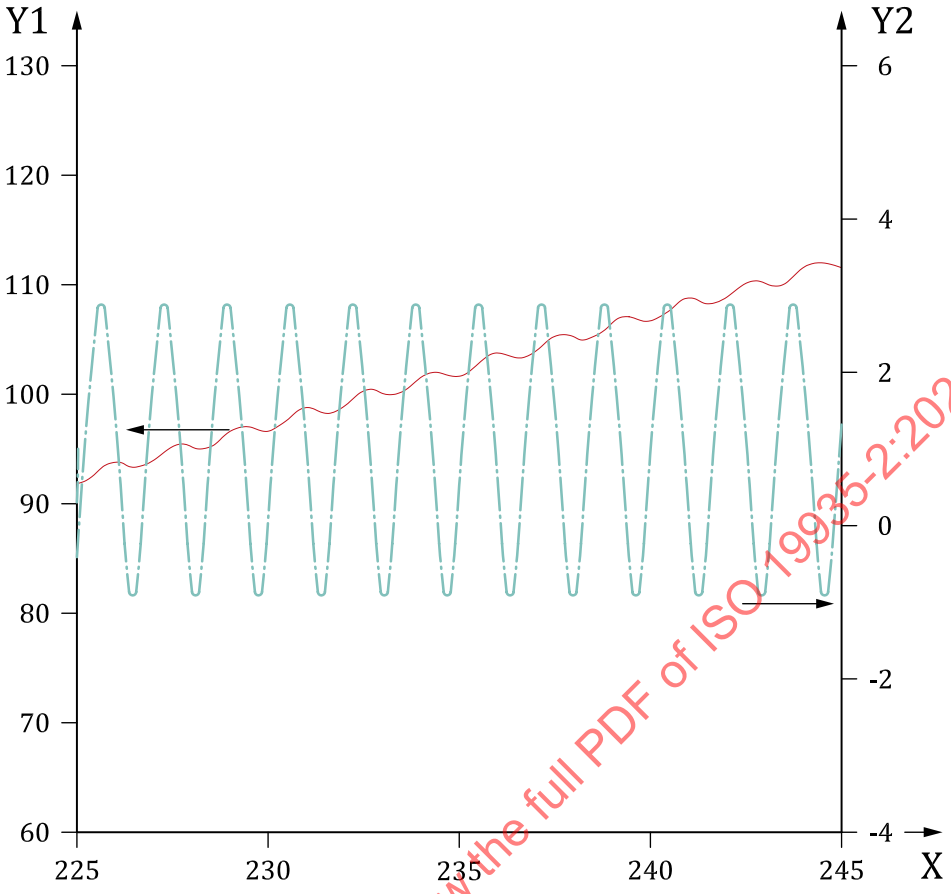
$K(\omega)$ is the calibration constant calculated according to the definition in ISO 19953-1. For precise measurements, ω shall be low (typically ω < 60 mrad/s), so that K(ω) becomes independent on ω.

For the case of step scan mode, Formula (1) shall be used to calculate c_{p}.

8.3 Examples of the results

8.3.1 Modulated heat flow rate and scanning rate of modulation

Figure 1 shows a typical example of modulated temperature and scanning rate (of modulation) derived by a derivative of modulated temperature of a sinusoidal waveform for the heat flux DSC plotted vs time. The scanning rate of modulation is measured as a sinusoidal wave.



Key

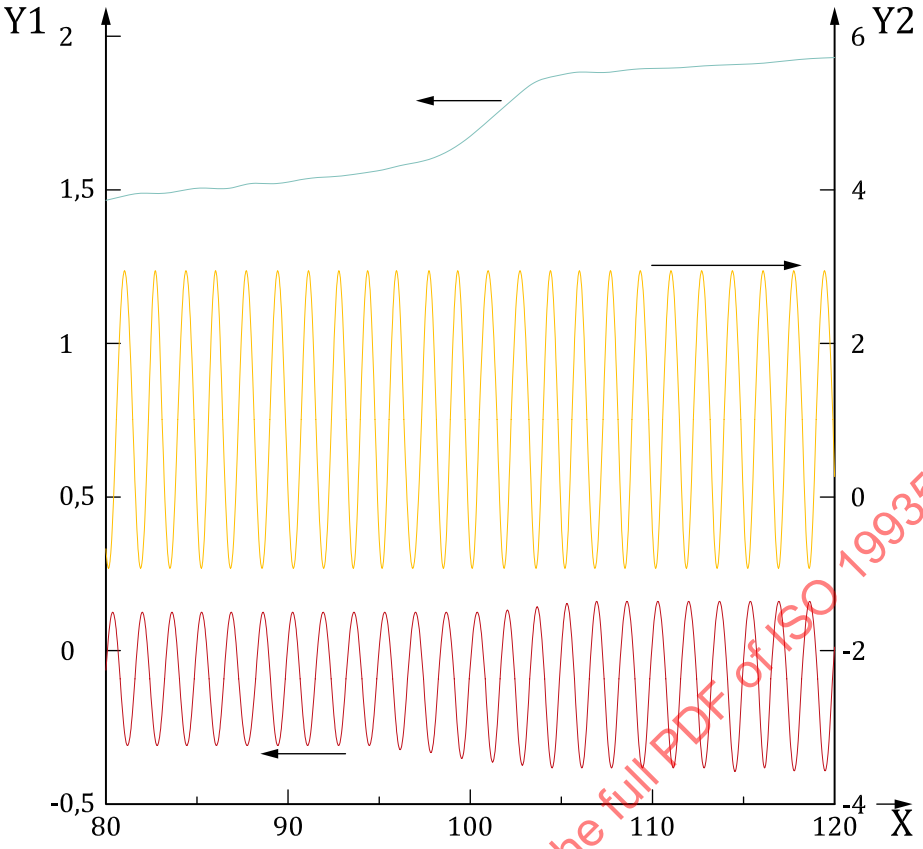
X	t/min
Y1	modulated temperature / K
Y2	derivative of the modulated temperature /K min^{-1}
———	modulated temperature T/ K
—·—·—	derivative modulated temperature / K min^{-1} (scanning rate)

NOTE Measured at an underlying scanning rate of 1,0 K/min, with a modulation frequency of 10 mHz and a modulation amplitude of ± 0,5 K of an input of sinusoidal waveform.

Figure 1 — Modulated temperature and (modulated) scanning rate (derivative of modulated temperature) of polystyrene (PS)

8.3.2 Determination of specific heat capacity

In Figure 2, the modulated heat flow rate and the scanning rate of modulation are plotted vs temperature. The specific heat capacity c_p is determined using these data (the modulated heat flow rate and the scanning rate of modulation) according to Formula (2).



Key

X	T / °C
Y1	modulated heat flow rate/mW, and c_p/Jg^{-1} K^{-1}
Y2	derivated modulated temperature/K min^{-1}
	c_p
	derivated modulated temperature
	modulated heat flow rate

NOTE 1 The specific heat capacity c_p of polystyrene has been calculated using the results in Figures 1 and 2 according to Formula (2).

NOTE 2 Measured conditions are: underlying scanning rate of 1,0 K/min, a modulation frequency of 10 mHz, a modulation amplitude of ± 0,5 K of an input of sinusoidal waveform.

Figure 2 — Specific heat capacity c_p of polystyrene

9 Precision and bias

The precision and bias of the method described are not known because interlaboratory data are not available at the time of publication.

10 Test report

The test report shall include the following information:

a) a reference to this document, i.e. ISO 19935-2:2020;

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 heat 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 and the specific heat capacity;

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.

Annex A
(informative)

Example of the c_p values of polystyrene (PS)

The example of the c_p values of polystyrene (PS) as a function of temperature is shown in Tables A.1 to A.2, measured with the sinusoidal wave at 10 mHz and a scanning rate of 3 K/min on cooling and heating[1][2].

Table A.1 — Specific heat capacity of polystyrene measured with 3 K/min, an amplitude of 0,5 K and a frequency of 10 mHz on cooling (σ is a coefficient of variation)

Sample No.	Id.1	Id.2	Id.3	Id.4	Id.5	Average	σ
Sample mass	7,53 mg	7,30 mg	7,35 mg	7,27 mg	7,06 mg		
T/°C	c_p/Jg^{-1}K^{-1}	c_p/Jg^{-1}K^{-1}	c_p/Jg^{-1}K^{-1}	c_p/Jg^{-1}K^{-1}	c_p/Jg^{-1}K^{-1}	c_p/Jg^{-1}K^{-1}	%
50	1,34	1,35	1,35	1,35	1,32	1,34	0,87
60	1,36	1,39	1,39	1,40	1,38	1,38	1,14
70	1,41	1,43	1,43	1,43	1,41	1,42	0,72
80	1,46	1,47	1,46	1,47	1,45	1,46	0,57
90	1,53	1,54	1,53	1,54	1,52	1,53	0,62
100	1,72	1,73	1,73	1,74	1,72	1,73	0,51
110	1,88	1,89	1,89	1,90	1,88	1,89	0,53
120	1,92	1,93	1,93	1,94	1,91	1,93	0,47
130	1,95	1,96	1,96	1,97	1,95	1,96	0,43
140	1,98	1,99	1,99	2,00	1,98	1,99	0,41
150	2,01	2,02	2,02	2,03	2,01	2,02	0,47

Table A.2 — Specific heat capacity of polystyrene measured with 3 K/min, an amplitude of 0,5 K and a frequency 10 mHz on heating (σ is a coefficient of variation)

Sample No.	Id.1	Id.2	Id.3	Id.4	Id.5	Average	σ
Sample mass	7,53 mg	7,30 mg	7,35 mg	7,27 mg	7,06 mg		
T/°C	c_p/Jg^{-1}K^{-1}	c_p/Jg^{-1}K^{-1}	c_p/Jg^{-1}K^{-1}	c_p/Jg^{-1}K^{-1}	c_p/Jg^{-1}K^{-1}	c_p/Jg^{-1}K^{-1}	%
50	1,33	1,34	1,34	1,34	1,32	1,33	0,62
60	1,38	1,38	1,38	1,39	1,37	1,38	0,60
70	1,42	1,43	1,43	1,44	1,41	1,43	0,60
80	1,47	1,47	1,47	1,48	1,46	1,47	0,53
90	1,52	1,53	1,53	1,53	1,51	1,53	0,52
100	1,70	1,70	1,70	1,73	1,69	1,70	0,84
110	1,89	1,90	1,91	1,91	1,89	1,90	0,46
120	1,92	1,93	1,93	1,93	1,91	1,92	0,43
130	1,95	1,96	1,96	1,96	1,94	1,95	0,38
140	1,98	1,99	1,99	1,99	1,97	1,99	0,38
150	2,01	2,02	2,02	2,02	2,01	2,02	0,35

Annex B
(informative)

Example of the calibration constant K(ω) determined with the literature values of α-Al_2O_3[3]

Compared with the literature values of α-Al_2O_3, the calibration constant K(ω) is determined at 10 mHz, with an amplitude of 0,5 K, on heating at 1 K/min (condition 1), and 3 K/min (condition 2). See Table B.1.

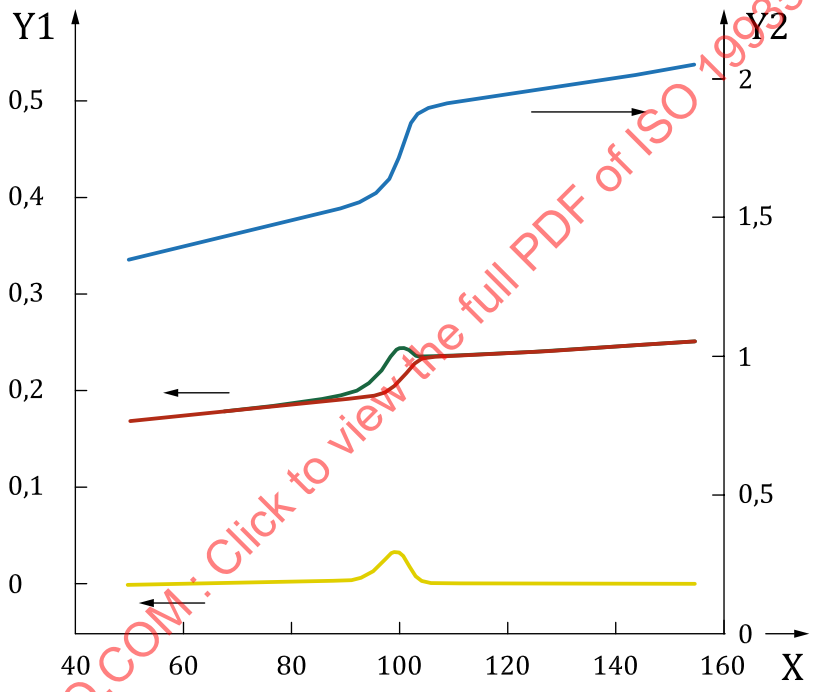
Table B.1 — Specific heat capacity of sapphire measured with heating rates of 10 mHz with 1 K/min and 3 K/min and an amplitude of 0,5 K

Sample No.		**SRM720 (α-Al_2O_3)**	**SRM720 (α-Al_2O_3)**	**Sapphire cond. 1**	K(ω)	**Sapphire cond. 2**	K(ω)
T/°C	T/K	C_p/Jmol^{-1}K^{-1}	c_p/Jg^{-1}K^{-1}	c_p/Jg^{-1}K^{-1}		c_p/Jg^{-1}K^{-1}	
36,85	310	81,5	0,799	0,801	0,998	0,801	0,998
46,85	320	83,4	0,818	0,820	0,998	0,821	0,998
56,85	330	85,3	0,837	0,839	0,998	0,839	0,998
66,85	340	87,1	0,854	0,857	0,998	0,857	0,998
76,85	350	88,8	0,871	0,873	0,998	0,874	0,997
86,85	360	90,4	0,887	0,889	0,998	0,890	0,997
96,85	370	91,9	0,901	0,904	0,998	0,904	0,997
106,85	380	93,4	0,916	0,918	0,998	0,918	0,998
116,85	390	94,7	0,929	0,931	0,998	0,932	0,998
126,85	400	96,0	0,942	0,944	0,998	0,944	0,998
136,85	410	97,3	0,954	0,956	0,999	0,956	0,999
146,85	420	98,5	0,966	0,967	0,999	0,967	0,999

Annex C
(informative)

Example of a reversing heat flow rate curve based on a modulated heat flow rate curve and a comparison with the specific heat capacity

Figure C.1 shows a reversing heat flow rate curve based on a modulated heat flow rate curve and a comparison of this reversing curve with the specific heat capacity curve. The elimination of an enthalpy relaxation is presented.



Key

X	T / °C
Y1	heat flow rate (Endo. up)/mW
Y2	reversing c_p/Jg^{-1} K^{-1}
	total heat flow rate
	reversing heat flow rate
	non-reversing heat flow rate
	reversing specific heat capacity

Figure C.1 — Specific heat capacity curve of polystyrene determined from the reversing heat flow rate curve