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Plastics — Determination of dynamic mechanical properties —

Part 11: Glass transition temperature

Plastiques — Détermination des propriétés mécaniques dynamiques —

Partie 11: Température de transition vitreuse

Reference number
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Foreword

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International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 2.

The main task of technical committees is to prepare International Standards. Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

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.

ISO 6721-11 was prepared by Technical Committee ISO/TC 61, *Plastics*, Subcommittee SC 2, *Mechanical properties*.

ISO 6721 consists of the following parts, under the general title *Plastics — Determination of dynamic mechanical properties*:

— *Part 1: General principles*

— *Part 2: Torsion-pendulum method*

— *Part 3: Flexural vibration — Resonance-curve method*

— *Part 4: Tensile vibration — Non-resonance method*

— *Part 5: Flexural vibration — Non-resonance method*

— *Part 6: Shear vibration — Non-resonance method*

— *Part 7: Torsional vibration — Non-resonance method*

— *Part 8: Longitudinal and shear vibration — Wave-propagation method*

— *Part 9: Tensile vibration — Sonic-pulse propagation method*

— *Part 10: Complex shear viscosity using a parallel-plate oscillatory rheometer*

— *Part 11: Glass transition temperature*

— *Part 12: Compressive vibration — Non-resonance method*

Introduction

This part of ISO 6721 covers the use of dynamic mechanical analysis (DMA) procedures, in the temperature scanning mode, to determine a value for the glass transition temperature of plastics. It provides an alternative procedure to the use of differential scanning calorimetry (DSC) (see ISO 11357-2) for this measurement.

DMA is used to determine the variation of the storage modulus, loss modulus and tan delta as a function of temperature and frequency. From these data, a value for the glass transition is determined. Many types of commercial equipment are available that use this technique and, in principle, it applies to all the loading modes described in ISO 6721-1.

The procedures minimize errors due to thermal lag of the specimen, which varies with the heating rate used, through assuming the specimen temperature is given by the measured oven temperature[1)]. This eliminates the need for the temperature of the specimen to be measured directly by, for example, a thermocouple embedded in the specimen.

1) See SIMS G.D., GNANIAH S.J.P., *Calibration Procedures for Increased Confidence in DMA Measurements*, ICCM 11, Edinburgh, July 2009.

Plastics — Determination of dynamic mechanical properties —

Part 11: Glass transition temperature

WARNING — The use of this part of ISO 6721 may involve hazardous materials, operations and equipment. The document does not purport to address all of the safety problems associated with its use. It is the responsibility of the user to establish appropriate health and safety practices and to determine the applicability of regulatory limitations prior to its use.

1 Scope

This part of ISO 6721 specifies methods for determining a value of the glass transition temperature (T_g) from the dynamic mechanical properties measured during a linear temperature scan under heating conditions. The glass transition temperature is an indicator of the transition from a glassy state to a rubbery state.

Usually referred to as dynamic mechanical analysis (DMA), the methods and their associated procedures can be applied to unreinforced and filled polymers, foams, rubbers, adhesives and fibre-reinforced plastics/composites. Different modes (e.g. flexure, compression, tension) of dynamic mechanical analysis can be applied, as appropriate, to the form of the source material.

NOTE For tests undertaken in the flexure or torsion mode, an additional procedure is included to identify the severity of the influences of thermal lag on the measured data (see Annex B).

2 Normative 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 6721-1:2011, *Plastics — Determination of dynamic mechanical properties — Part 1: General principles*

3 Terms and definitions

For the purposes of this document, the terms and definitions given in ISO 6721-1 and the following apply.

3.1
glass transition temperature
T_g
temperature of the point of inflection of the decrease in the storage modulus curve corresponding to the transition

NOTE 1 This temperature often agrees with the temperature at the peak of the loss modulus data.

NOTE 2 It is expressed in degrees Celsius (°C).

NOTE 3 See Figure 1, data point 1.

3.2
temperature at onset
T_{onset}
temperature corresponding to the onset of the transition from glassy state, as defined by the intercept of two tangents in the storage modulus curve

NOTE 1 The first tangent is extrapolated from a linear portion of the curve prior to the transition, and the second tangent is extrapolated from the point of inflection of the decrease in the curve corresponding to the glass-rubber transition .

NOTE 2 It is expressed in degrees Celsius (°C).

NOTE 3 See Figure 1, data point 5.

3.3
temperature at peak of loss modulus data
T_{loss}
temperature of the peak of the loss modulus curve

NOTE 1 It is expressed in degrees Celsius (°C).

NOTE 2 See Figure 1, data point 2.

3.4
temperature at peak of tan delta data
$T_{tan\ delta}$
temperature of the peak in the tan delta curve

NOTE 1 It is expressed in degrees Celsius (°C).

NOTE 2 See Figure 1, data point 3.

3.5
reference glass transition temperature
$T_{g(0)}$
value of the extrapolated temperature at 0 °C/min heating rate that is used for specification and contract requirements

NOTE 1 It is expressed in degrees Celsius (°C).

NOTE 2 See Figure 2.

3.6
QA glass transition temperature
$T_{g(n)}$
value taken from the calibration curve at n °C/min heating rate that is used for quality assurance purposes, by agreement, with heating rate dependent equipment (i.e. not the extrapolated $T_{g(0)}$ value]

NOTE 1 It is expressed in degrees Celsius (°C).

NOTE 2 See 9.3.2.

4 Principle

A specimen of known geometry is placed or held in a suitable mechanical loading system in an enclosed temperature chamber, or oven, that can be heated at a controlled rate. The specimen is mechanically oscillated at a fixed frequency, and changes in the viscoelastic response of the material are monitored and recorded as a function of the test temperature. The dynamic properties (storage modulus, loss modulus and tan delta) are determined from the load and displacement data recorded throughout the test (see ISO 6721-1). The glass transition temperature (T_g) is determined as the point of inflection in the storage modulus vs. the temperature plot. The test procedure described minimizes errors due to the thermal lag, which varies with the heating rate used, of the specimen temperature through assuming the specimen temperature is given by the measured oven temperature.

5 Equipment

5.1 Dynamic mechanical analyser

The test equipment shall be capable of heating at rates from 1 °C/min to 10 °C/min over the required temperature range and mechanically oscillating the specimen at the reference frequency of 1 Hz. The equipment should be capable of applying the temperature ramp profile to within ±5 % of the required heating rate.

The instrument shall continuously monitor and record the load applied to the specimen, and the corresponding displacement as a function of the measured temperature, in order to determine the storage modulus, loss modulus and tan delta. The load and displacement capabilities of the equipment shall be sufficient for the specimens tested.

The equipment shall be calibrated, as required by the equipment user manual — see Annex A.

5.2 Devices for measuring test specimen dimensions

These shall be in accordance with ISO 6721-1:2011, 5.6.

6 Test specimen

6.1 General

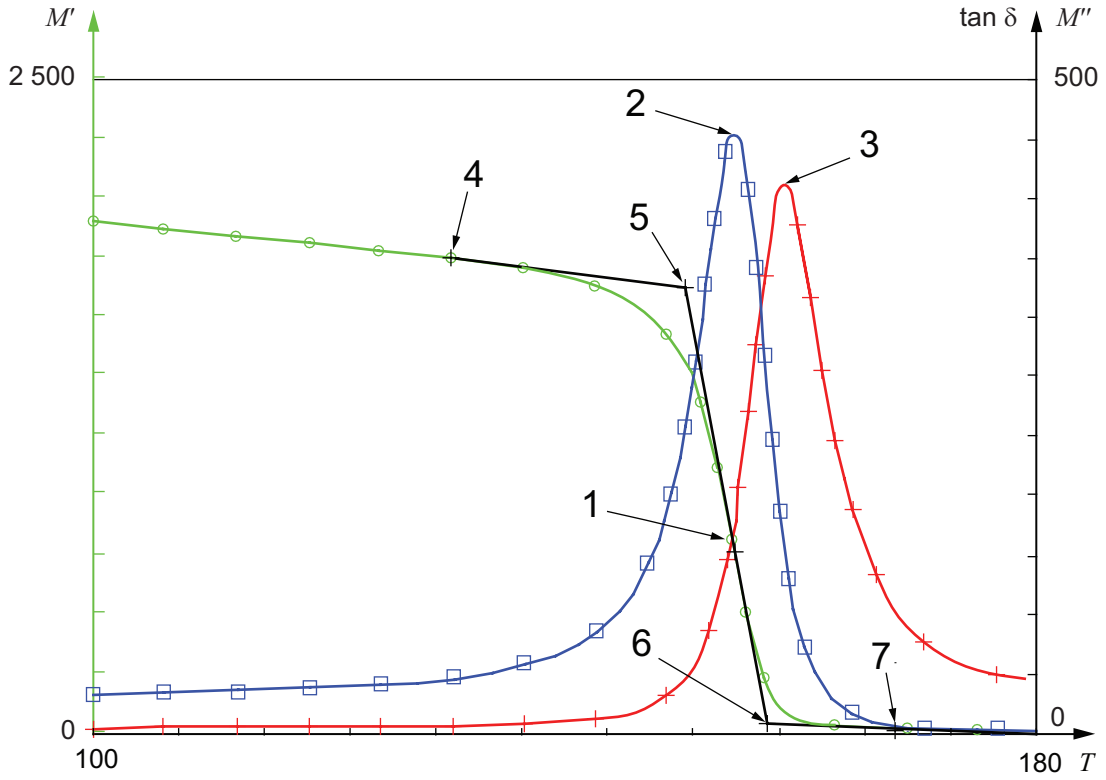
The test specimen shall be in accordance with ISO 6721-1:2011, 6.1.

6.2 Shape and dimensions

The dimensions of the specimen shall be as required by the equipment for the selected test mode.

6.3 Preparation

The preparation of the test specimen shall be in accordance with ISO 6721-1:2011, 6.3.



Key

1	inflection point (storage modulus) (= T_g)	T	temperature, °C
2	peak (loss modulus) (= T_{loss})	M'	storage modulus, MPa
3	peak (tan delta) (= $T_{tan\ delta}$)	M''	loss modulus, MPa
4	start point (storage modulus)	tan δ	tan delta
5	onset (storage modulus)(= T_{onset})		
6	endset (storage modulus)		
7	end point (storage modulus)		

Figure 1 — Plot of dynamic mechanical data against temperature

7 Number of specimens

This shall be in accordance with ISO 6721-1:2011, Clause 7.

Prepare additional specimens (at least three) to assess the heating rate dependency of the method according to Clause 9.2

8 Conditioning

This shall be in accordance with ISO 6721-1:2011, Clause 8.

9 Test procedure

9.1 Test atmosphere

This shall be in accordance with ISO 6721:2011, 9.1

NOTE Measurements can be undertaken under static air conditions or an inert atmosphere. However, it is important that the calibration and the specimen tests be performed under identical conditions.

9.2 Assessment of heating rate dependence

9.2.1 Heating rate dependence — Procedure

Calibrate the instrument in accordance with Annex A. Position the temperature sensor in the instrument as closely as possible to the sample under test, but ensuring it is not touching it. The position of the sensor shall remain undisturbed for subsequent specimen tests. If moved, recalibration may be necessary (see Annex A).

Undertake tests according to Method A (see 9.3.1) to assess the heating rate dependence of the material/equipment.

9.2.2 Heating rate dependence — Results

If the temperature at the inflection points is shown to vary by more than ±2 °C between the different heating rates, use Method A (see 9.3.1).

NOTE For this case, a quality assurance procedure to reduce the testing time is also available (see 9.3.2).

If the results are shown to vary by less than ±2 °C between the different heating rates, use Method B (see 9.3.3).

9.3 Operation

9.3.1 Method A — Rate-dependent results

Mount the specimen into the instrument.

Apply a constant rate temperature scan from at least 50 °C below to 50 °C above the transition region(s) of interest at heating rates of 3 °C/min, 5 °C/min and 10 °C/min**.** Use a new specimen for each heating rate.

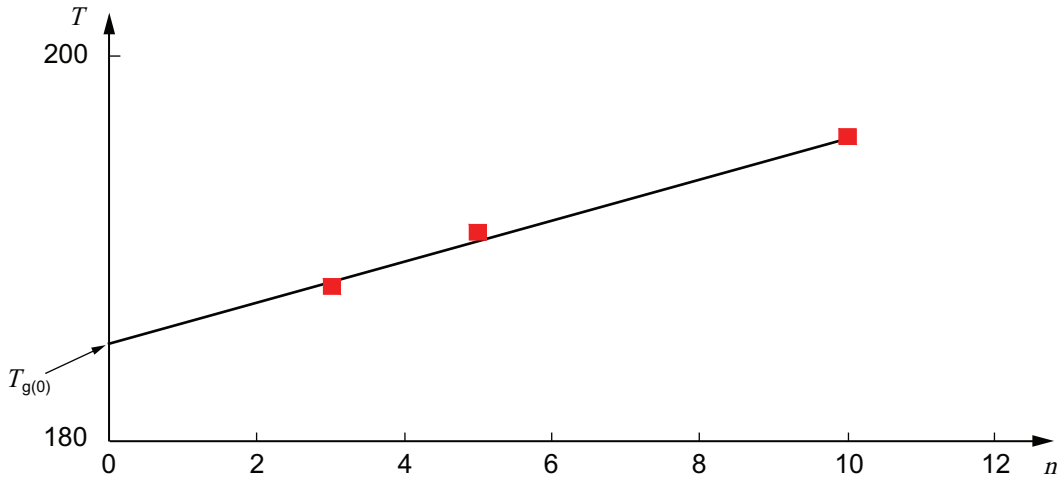
The reference test frequency of 1 Hz shall be used.

The load/displacement on the specimen shall be selected so that the specimen deformation is within the elastic range of the material being tested. The applied level shall remain constant to within ±10 % of the initial value applied.

Record the load and displacement data as a function of temperature, so that the storage modulus, loss modulus and tan delta can be calculated and plotted against temperature (see Figure 1). Determine the temperature at the inflection point for the storage modulus curve (see Figure 1, data point 1) at each heating rate.

Plot the temperature of the inflection points as a function of heating rate, as shown in Figure 2. Extrapolate the data to meet the y-axis at 0 °C/min using a linear fit. Report the extrapolated value to 0 °C/min as $T_{g(0)}$. These data form the “calibration curve” shown in Figure 2.

NOTE The determination of the extrapolation value can be aided by an additional scan at 1 °C/min, but care is needed if the material state (e.g. degree of cure) changes during the scan.



Key

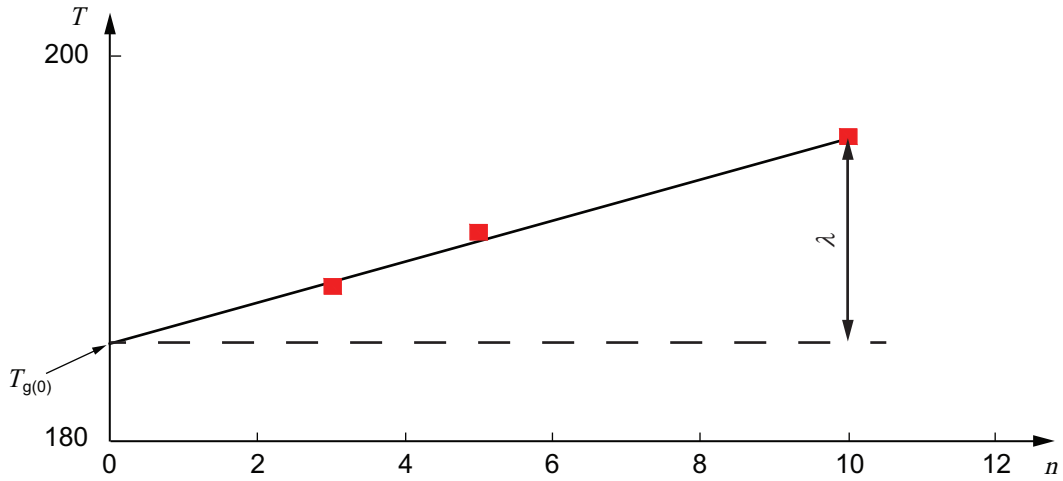
n	heating rate, °C/min
T	temperature, °C
$T_{g(0)}$	extrapolation to value at 0 °C/min heating rate
■	measured data at stated heating rate

Figure 2 — Determination of $T_{g(0)}$ at 0 °C/min from calibration curve

9.3.2 Method QA — Quality control testing — Rate dependent results

Determine the offset λ °C at the required heating rate from the "calibration curve" to be applied to $T_{g(0)}$. The value $T_{g(n)} = [T_{g(0)} + \lambda]$ shall be used for subsequent testing (e.g. $T_{g(10)}$ in this case) (see Figure 3).

Measured QA values, such as $T_{g(10)}$, should not be used for comparison with other results at this rate, but undertaken on different equipment, or at a different site or by a different operator. These comparisons should only be undertaken using $T_{g(0)}$.



Key

λ	offset temperature at specified heating rate, °C
n	heating rate, °C/min
T	temperature, °C
$T_{g(0)}$	extrapolation to value at 0 °C/min heating rate
■	measured data at stated heating rate

Figure 3 — Determination of $T_{g(n)}$ at required heating rate from calibration curve

9.3.3 Method B — Rate-independent results

Undertake the procedure in Method A at a single temperature ramp rate selected within the range used previously (see 9.3.1). Plot the storage modulus vs. temperature curve from the recorded data and determine T_g from the inflection point of the storage modulus data.

10 Expression of results

Report the value of $T_{g(0)}$, $T_{g(n)}$ or T_g determined from Method A (9.3.1), QA (9.3.2) or B (9.3.3), as appropriate.

If required, also report T_{onset}, T_{loss} and $T_{tan\ delta}$.

11 Precision

It is intended that precision data be added in this part of ISO 6721 when an existing interlaboratory comparison is completed[1)].

12 Test report

The test report shall include the information required in ISO 6721-1, Clause 12, plus the following:

a) the method used (A, QA or B);

b) a plot of the storage modulus, loss modulus and tan delta against temperature, with the analysis points indicated;

1) VAMAS TWA5 organization (http://www.vamas.org)

c) values of $T_{g(0)}$, $T_{g(n)}$ or T_g (as appropriate to the test method used), together with, if required, T_{onset}, T_{loss} and $T_{tan\ delta}$, i.e.

Method A — $T_{g(0)}$,

Method QA — $T_{g(n)}$, or

Method B — T_g;

d) the calibration curve (see Figure 2), if used.

Annex A
(normative)

Calibration procedures

A.1 Equipment calibration

The instrument shall be mechanically calibrated for the type of clamps to be used in subsequent tests in accordance with the manufacturer's recommendations. The procedures may vary, depending upon the type of instrumentation or clamps used.

The mechanical calibration will generally involve measurement of the compliance of the instrument using a stiff, usually steel, bar.

It is recommended that the instrument be calibrated regularly, or when the testing mode is changed.

A.2 Temperature calibration

a) Check the ambient temperature reading of the instrument against a calibrated temperature sensor.

b) The temperature reading of the instrument is acceptable if the temperature difference between the instrument and the calibrated temperature sensor at ambient is within ±1 °C.

c) If the difference is not within ±1 °C, check for any offset to the temperature that may have been applied as a result of instrument calibrations. If so, disable the temperature offset and repeat step a).

d) If the difference is not within ±1 °C, further investigation of the temperature sensor in the equipment may be necessary.

It is recommended that the instrument be calibrated regularly, when the test atmosphere is changed or the temperature sensor is moved or changed.

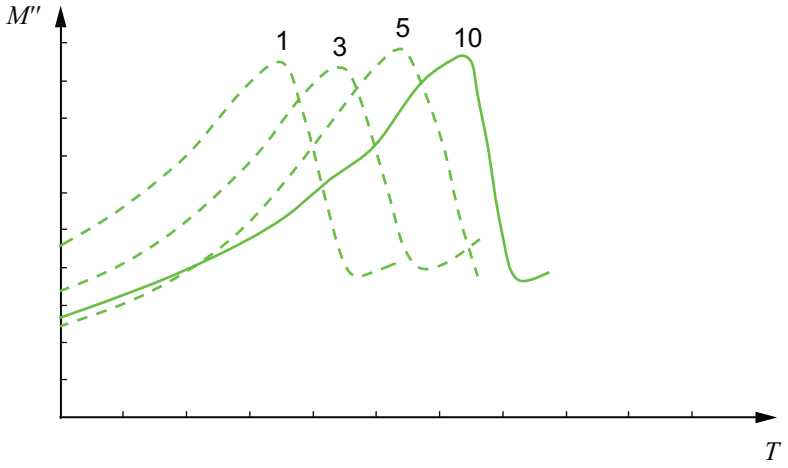
Annex B
(informative)

Assessment of heating rate sensitivity using reference sample

B.1 Assessment procedure — Flexure or torsion only

This evaluation uses a temperature reference specimen of bar geometry consisting of a carbon fibre/epoxy laminate with an indium film centrally encapsulated[2)].

Using the relevant loading mode, test the indium temperature reference specimen at each of the four different heating rates, n (1, 3, 5 and 10) °C/min and plot loss modulus against temperature for each rate. From the sharp drop in the loss modulus curve (see Figure B.1), the melting point of the embedded indium within the specimen can be determined.



Key

T temperature, °C

M'' loss modulus, MPa

Figure B.1 — Abrupt decrease in loss modulus curve indicates melting of indium within reference specimen

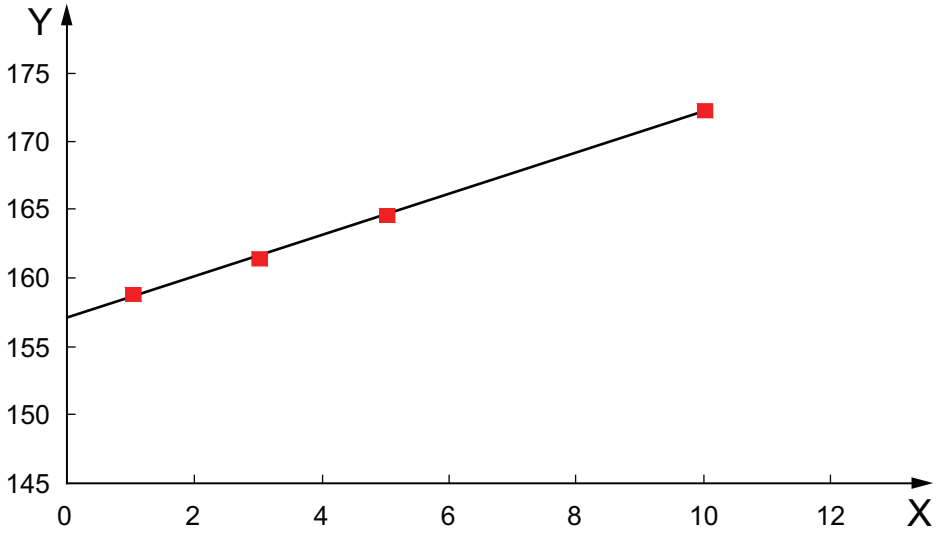
B.2 Data analysis

Analyse the data as follows:

a) record the temperature just prior to the drop in loss modulus associated with the melting of the embedded indium;

b) plot the temperatures determined against heating rate and note the sensitivity of the data to the heating rate (see Figure B.2.)

2) *Equipment temperature reference specimens* available from the National Physical Laboratory, Materials Division, Hampton Road, Teddington, Middlesex, TW11 0LW (www.npl.co.uk) Tel: 020 8977 3222. The specimen can be used several times.



Key

X (*n*) heating rate, °C

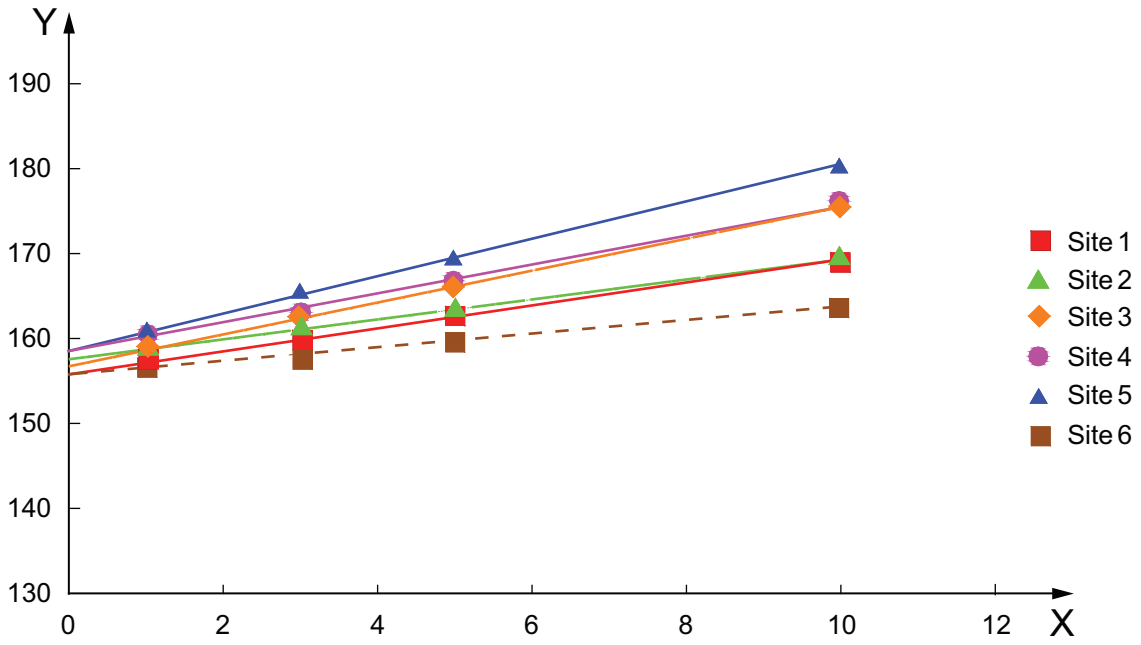
Y apparent indium melting point, °C

Figure B.2 — Plot of apparent indium melting temperature (from loss-modulus curve) vs. heating rate

B.3 Interlaboratory trial

The results of an interlaboratory trial on the use of the temperature reference specimen are given in Figure B.3.

Results were received from six participating sites using instrumentation from three different manufacturers and two test modes. The average difference for the “zero degree extrapolation” for the melting point of indium was 0,6 °C (from 0,2 °C to 1,2 °C). This is based on the six sets of results received.



Key

X heating rate, °C

Y apparent indium melting point, °C

Figure B.3 — Plot of apparent indium melting temperature vs. heating rate for six sites

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