A.1. MELTING/FREEZING TEMPERATURE

1. METHOD

The majority of the methods described are based on the OECD Test Guideline (1). The fundamental principles are given in references (2) and (3).

1.1. INTRODUCTION

The methods and devices described are to be applied for the determination of the melting temperature of substances, without any restriction in respect to their degree of purity .

The selection of the method is dependent on the nature of the substance to be tested. In consequence the limiting factor will be according to, whether or not the substance can be pulverized easily, with difficulty, or not at all.

For some substances, the determination of the freezing or solidification temperature is more appropriate and the standards for these determinations have also been included in this method.

Where, due to the particular properties of the substance, none of the above parameters can be conveniently measured, a pour point may be appropriate.

1.2. DEFINITIONS AND UNITS

The melting temperature is defined as the temperature at which the phase transition from solid to liquid state occurs at atmospheric pressure and this temperature ideally corresponds to the freezing temperature.

As the phase transition of many substances takes place over a temperature range, it is often described as the melting range.

Conversion of units (K to °C)

$t = T - 273{,}15$

t: Celsius temperature, degree Celsius (°C)

T: thermodynamic temperature, kelvin (K)

1.3. REFERENCE SUBSTANCES

Reference substances do not need to be employed in all cases when investigating a new substance. They should primarily serve to check the performance of the method from time to time and to allow comparison with results from other methods.

Some calibration substances are listed in the references (4).

1.4. PRINCIPLE OF THE TEST METHOD

The temperature (temperature range) of the phase transition from the solid to the liquid state or from the liquid to the solid state is determined. In practice while heating/cooling a sample of the test substance at atmospheric pressure the temperatures of the initial melting/freezing and the final stage of melting/freezing are determined. Five types of methods are described, namely capillary method, hot stage methods, freezing temperature determinations, methods of thermal analysis, and determination of the pour point (as developed for petroleum oils).

In certain cases, it may be convenient to measure the freezing temperature in place of the melting temperature.

1.4.1. Capillary method

1.4.1.1. Melting temperature devices with liquid bath

A small amount of the finely ground substance is placed in a capillary tube and packed tightly. The tube is heated, together with a thermometer, and the temperature rise is adjusted to less than about 1 K/min during the actual melting. The initial and final melting temperatures are determined.

1.4.1.2. Melting temperature devices with metal block

As described under 1.4.1.1., except that the capillary tube and the thermometer are situated in a heated metal block, and can be observed through holes in the block.

1.4.1.3. Photocell detection

The sample in the capillary tube is heated automatically in a metal cylinder. A beam of light is directed through the substance, by way of a hole in the cylinder, to a precisely calibrated photocell. The optical properties of most substances change from opaque to transparent when they are melting. The intensity of light reaching the photocell increases and sends a stop signal to the digital indicator reading out the temperature of a platinum resistance thermometer located in the heating chamber. This method is not suitable for some highly coloured substances.

1.4.2. Hot Stages

1.4.2.1. Kofler hot bar

The Kofler hot bar uses two pieces of metal of different thermal conductivity, heated electrically, with the bar designed so that the temperature gradient is almost linear along its length. The temperature of the hot bar can range from 283 to 573 K with a special temperature-reading device including a runner with a pointer and tab designed for the specific bar. In order to determine a melting temperature, the substance is laid, in a thin layer, directly on the surface of the hot bar. In a few seconds a sharp dividing line between the fluid and solid phase develops. The temperature at the dividing line is read by adjusting the pointer to rest at the line.

1.4.2.2. Melt microscope

Several microscope hot stages are in use for the determination of melting temperatures with very small quantities of material. In most of the hot stages the temperature is measured with a sensitive thermocouple but sometimes mercury thermometers are used. A typical microscope hot stage melting temperature apparatus has a heating chamber which contains a metal plate upon which the sample is placed on a slide. The centre of the metal plate contains a hole permitting the entrance of light from the illuminating mirror of the microscope. When in use, the chamber is closed by a glass plate to exclude air from the sample area.

The heating of the sample is regulated by a rheostat. For very precise measurements on optically anisotropic substances, polarized light may be used.

1.4.2.3. Meniscus method

This method is specifically used for polyamides.

The temperature at which the displacement of a meniscus of silicone oil, enclosed between a hot stage and a cover-glass supported by the polyamide test specimen, is determined visually.

1.4.3. Method to determine the freezing temperature

The sample is placed in a special test tube and placed in an apparatus for the determination of the freezing temperature. The sample is stirred gently and continuously during cooling and the temperature is measured at suitable intervals. As soon as the temperature remains constant for a few readings this

temperature (corrected for thermometer error) is recorded as the freezing temperature.

Supercooling must be avoide d by maintaining equilibrium between the solid and the liquid phases.

1.4.4. Thermal analysis

1.4.4.1 Differential thermal analysis (DTA)

This technique records the difference in temperatures between the substance and a reference material as a function of temperature, while the substance and reference material are subjected to the same controlled temperature programme. When the sample undergoes a transition involving a change of enthalpy, that change is indicated by an endothermic (melting) or exothermic (freezing) departure from the base line of the temperature record.

1.4.4.2 Differential scanning calorimetry (DSC)

This technique records the difference in energy inputs into a substance and a reference material, as a function of temperature, while the substance and reference material are subjected to the same controlled temperature programme. This energy is the energy necessary to establish zero temperature difference between the substance and the reference material. When the sample undergoes a transition involving a change of enthalpy, that change is indicated by an endothermic (melting) or exothermic (freezing) departure from the base line of the heat flow record.

1.4.5. Pour point

This method was developed for use with petroleum oils and is suitable for use with oily substances with low melting temperatures.

After preliminary heating, the sample is cooled at a specific rate and examined at intervals of 3 K for flow characteristics. The lowest temperature at which movement of the substance is observed is recorded as the pour point.

1.5. QUALITY CRITERIA

The applicability and accuracy of the different methods used for the determination of the melting temperature/melting range are listed in the following table:

TABLE: APPLICABILITY OF THE METHODS

A. Capillary methods

Method of measurement	Substances which can be pulverized	Substances which are not readily pulverized	Temperature range	Estimated accuracy ([1])	Existing standards
Melting temperature devices with liquid bath	yes	only to a few	273 to 573 K	± 0,3 K	JIS K 0064
Melting temperature with metal block	yes	only to a few	293 to >573 K	± 0,5 K	ISO 1218 (E)
Photocell detection	yes	Several with appliance devices	253 to 573 K	± 0,5 K	

([1]) Dependent on type of instrument and on degree of purity of the substance

B. Hot stages and freezing methods

Method of measurement	Substances which can be pulverized	Substances which are not readily pulverized	Temperature range	Estimated accuracy ([1])	Existing standards
Kofler hot bar	yes	no	283 to >573 K	± 1K	ANSI/ASTM D 3451-76
Melt microscope	yes	only to a few	273 to >573 K	± 0,5 K	DIN 53736
Meniscus method	no	Specifically for polyamides	293 to >573 K	± 0,5 K	ISO 1218 (E)
Freezing temperature	yes	yes	223 to 573 K	± 0,5 K	e.g. BS 4695

([1]) Dependent on type of instrument and on degree of purity of the substance

C. Thermal analysis

Method of measurement	Substances which can be pulverized	Substances which are not readily pulverized	Temperature range	Estimated accuracy ([1])	Existing standards
Differential Thermal Analysis	yes	yes	173 to 1273 K	up to 600K ± 0,5K up to 1273K ± 2,0K	ASTM E 537-76
Differential Scanning Calorimetry	yes	yes	173 to 1273 K	up to 600K ± 0,5K up to 1273K ± 2,0K	ASTM E 537-76

([1]) Dependent on type of instrument and on degree of purity of the substance

D. Pour point

Method of measurement	Substances which can be pulverized	Substances which are not readily pulverized	Temperature range	Estimated accuracy ([1])	Existing standards
Pour Point	for petroleum oils and oily substances	for petroleum oils and oily substances	223 to 323 K	± 0,3 K	ASTM D 97-66

([1]) Dependent on type of instrument and on degree of purity of the substance

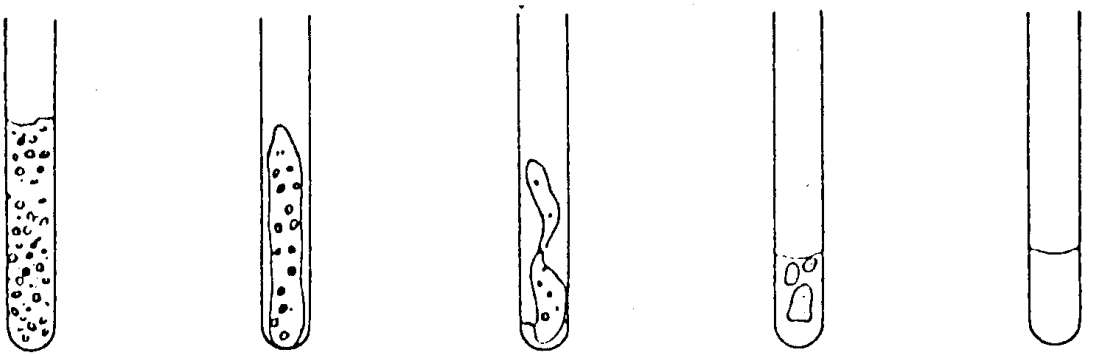
1.6. DESCRIPTION OF THE METHODS

The procedures of nearly all the test methods have been described in international and national standards (see Appendix 1).

1.6.1. Methods with capillary tube

When subjected to a slow temperature rise, finely pulverised substances usually show the stages of melting shown in figure 1.

Figure 1



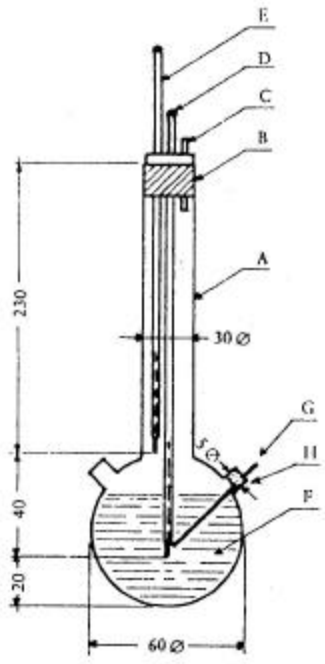
Stage A (Beginning of melting): fine droplets adhere uniformly to the inside wall of the capillary tube.
Stage B a clearance appears between the sample and the inside wall due to shrinkage of the melt.
Stage C the shrunken sample begins to collapse downwards and liquefies.
Stage D a complete meniscus is formed at the surface but an appreciate amount of the sample remains solid.
Stage E (Final stage melting): there are no solid particles.

During the determination of the melting temperature, the temperatures are recorded at the beginning of the melting and at the final stage.

1.6.1.1. Melting temperature devices with liquid bath apparatus

Figure 2 shows a type of standardized melting temperature apparatus made of glass (JIS K 0064); allspecifications are in millimeters.

Figure 2



A: Measurement vessel
B: Stopper
C: Vent
D: Thermometer
E: Auxiliary thermometer
F: Bath liquid
G: Capillary tube made of glass, 80 to 100 mm in length, 1,0 ± 0,2 mm inner diameter, 0,2 to 0,3 mm wall thickness
H: Side tube

Bath liquid:

A suitable liquid should be chosen. The choice of the liquid depends upon the melting temperatute to be detetmined, e.g. liquid paraffin for melting temperatures no higher than 473 K, silicone oil for melting temperatures no higher than 573 K.

For melting temperatures above 523 K, a mixture consisting of three parts sulphuric acid and two parts potassium sulphate (in mass ratio) can be used. Suitable precautions should be taken if a mixture such as this is used.

Thermometer:

Only those thermometers should be used which fulfill the requirements of the following or equivalent standards:

ASTM E 1-71, DIN 12770, JIS K 8001.

Procedure:

The dry substance is finely pulverized in a mortar and is put into the capillary tube, fused at one end, so that the filling level is approximately 3 mm after being tightly packed. To obtain a uniform packed sample, the capillary tube should be dropped from a height of approximately 700 mm through a glass tube vertically onto a watch glass.

The filled capillary tube is placed in the bath so that the middle part of the mercury bulb of the thermometer touches the capillary tube at the part where the sample is located. Usually the capillary tube is introduced into the apparatus about 10 K below the melting temperature.

The bath liquid is heated so that the temperature rise is approximately 3 K/min. The liquid should be stirred. At about 10 K below the expected melting temperature the rate of temperature rise is adjusted to a maximum of 1 K/min.

Calculation:

The calculation of the melting temperature is as follows:

$$T = T_D + 0{,}00016\ (T_D - T_E)\ n$$

where:

T = corrected melting temperature in K
T_D = temperature reading of thermometer D in K
T_E = temperature reading of thermometer E in K
n = number of graduations of mercury thread on thermometer D at emergent stem.

1.6.1.2 Melting temperature devices with metal block

Apparatus:

This consists of:

-a cylindrical metal block, the upper part of which is hollow and forms a chamber (see figure 3),

-a metal plug, with two or more holes, allowing tubes to be mounted into the metal block,

-a heating system, for the metal block, provided for example by an electrical resistance enclosed in the block,

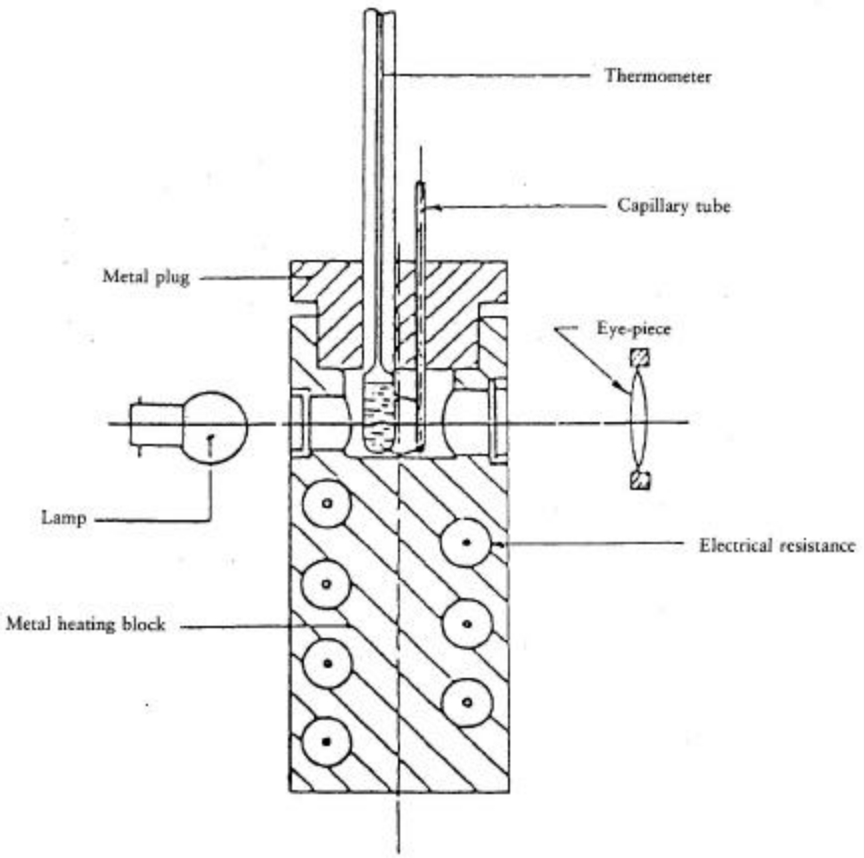
-a rheostat for regulation of power input, if electric heating is used,

-four windows of heat-resistant glass on the lateral walls of the chamber, diametrically disposed at right-angles to each other. In front of one of these windows is mounted an eye-piece for observing the capillary tube. The other three windows are used for illuminating the inside of the enclosure by means of lamps,

-a capillary tube of heat-resistant glass closed at one end (see 1.6.1.1).

See standards mentioned in 1.6.1.1. Thermoelectrical measuring devices with comparable accuracy are also applicable.

Figure 3



1.6.1.3. Photocell detection

Apparatus and procedure:

The apparatus consists of a metal chamber with automated heating system. Three capillary are filled accordingly to 1.6.1.1 and placed in the oven.

Several linear increases of temperature are available for calibrating the apparatus and the suitable temperature rise is electrically adjusted at a pre-selected constant and linear rate. recorders show the actual oven temperature and the temperature of the substance in the capillary tubes.

1.6.2. Hot stages

1.6.2.1. Kofler hot bar

See Appendix.

1.6.2.2. Melt microscope

See Appendix.

1.6.2.3. Meniscus method (polyamides)

See Appendix.

The heating rate through the melting temperature should be less than 1 K/min.

1.6.3. Methods for the determination of the freezing temperature

See Appendix.

1.6.4. Thermal analysis

1.6.4.1. Differential thermal analysis

See Appendix.

1.6.4.2. Differential scanning calorimetry

See Appendix.

1.6.5. Determination of the pour point

See Appendix.

2. **DATA**

A thermometer correction is necessary in some cases.

3. **REPORTING**

The test report shall, if possible, include the following information:

-method used,

-precise specification of the substance (identity and impurities) and preliminary purification step, if any,

-an estimate of the accuracy.

The mean of at least two measurements which are in the range of the estimated accuracy (see tables) is reported as the melting temperature.

If the difference between the temperature at the beginning and at the final stage of melting is within the limits of the accuracy of the method, the temperature at the final stage of melting is taken as the melting temperature; otherwise the two temperatures are reported.

If the substance decomposes or sublimes before the melting temperature is reached, the temperature at which the effect is observed shall be reported.

All information and remarks relevant for the interpretation of results have to be reported, especially with regard to impurities and physical state of the substance.

4. **REFERENCES**

(1) OECD, Paris, 1981, Test Guideline 102, Decision of the Council C(81) 30 final.

(2) IUPAC, B. Le Neindre, B. Vodar, eds. Experimental thermodynamics, Butterworths, London 1975, vol. II, 803-834.

(2) R. Weissberger ed.: Technique of organic Chemistry, Physical Methods of Organic Chemistry, 3rd ed., Interscience Publ., New York, 1959, vol. I, Part I, Chapter VII.

(3) IUPAC, Physicochemical measurements: Catalogue of reference materials from national laboratories, Pure and applied chemistry, 1976, vol. 48, 505-515.

Appendix

For additional technical details, the following standards may be consulted for example.

1. Capillary methods

1.1. Melting temperature devices with liquid bath

ASTM E 324-69	Standard test method for relative initial and final melting points and the melting range of organic chemicals
BS 4634	Method for the determination of melting point and/or melting range
DIN 53181	Bestimmung des Schmelzintervalles von Harzen nach Kapilarverfarehn
JIS K 00-64	Testing methods for melting point of chemical products.

1.2. Melting temperature devices with metal block

DIN 53736	Visuelle Bestimmung der Schmelztemperatur von teilkristallinen Kunststoffen
ISO 1218 (E)	Plastics- polyamides -determination of 'melting point'

2. Hot stages

2.1. Kofler hot bar

ANSI/ ASTM D 3451-76	Standard recommended practices for testing polymeric powder coatings

2.2. Melt microscope

DIN 53736	Visuelle Bestimmung der Schmelztemperatur von teilkristallinen Kunststoffen.

2.3. Meniscus method (polyamides)

ISO 1218 (E)	Plastics -poly ami des -determination of 'melting point'
ANSI/ ASTM D 2133-66	Standard specification for acetal resin injection moulding and extrusion materials
NF T 51-050	Resines de polyamides. Determination du 'point de fusion' Methode du menisque

3. Methods for the determination of the freezing temperature

BS 4633	Method for the determination of crystallizing point
BS 4695	Method for Determination of Melting Point of petroleum wax (Cooling Curve)
DIN 51421	Bestimmung des Gefrierpunktes von Flugkraftstoffen, Ottokraftstoffen und Motorenbenzolen
ISO 2207	Cires de petrole: determination de la temperature de figeage
DIN 53175	Bestimmung des Erstarrungspunktes von Fettsiiuren
NF T 60-114	Point de fusion des paraffines
NF T 20-051	Methode de determination du point de cristallisation (point de congelation)
ISO 1392	Method for the determination of the freezing point

4. Thermal analysis

4.1. Differential thermal analysis

ASTM E 537-76	Standard method for assessing the thermal stability of chemicals by methods of differential thermal analysis
ASTM E 473-85	Standard definitions of terms relating to thermal analysis
ASTM E 472-86	Standard practice for reporting thermoanalytical data
DIN 51005	Thermische Ana!yse, Begriffe

4.2. Differential scanning calorimetry

ASTM E 537-76	Standard method for assessing the thermal stability of chemicals by methods of differential thermal analysis
ASTM E 473-85	Standard definitions of terms relating to thermal analysis
ASTM E 472-86	Standard practice for reporting thermoanalytical data
DIN 51005	Thermische Analyse, Begriffe

5. Determination of the pour point

NBN 52014	Echantillonnage et analyse des produits du petrole: Point de trouble et point d'ecoulement limite -Monsterneming en ontleding van aardolieproducten: Troebelingspunt en vloeipunt
ASTM D 97-66	Standard test method for pour point of petroleum oils
ISO 3016	Petroleum oils -Determination of pour point.