OECD GUIDELINE FOR THE TESTING OF CHEMICALS

Adopted by the Council on 27th July 1995

Melting Point / Melting Range

INTRODUCTION

1. This guideline is a revised version of the original Guideline 102 which was adopted in 1981. Mainly the format has been changed. The differences of substance between this version and that from 1981 are few. The meniscus method, which is applicable to polyamides, has not been retained and the pour point is included. The revision was based on the EC method "Melting/Freezing Temperature" published in 1992 (1).

INITIAL CONSIDERATIONS

2. Frequently the transition from solid to liquid phase takes place over a temperature range. Therefore, the term "melting range" is often used and, in practice, the temperatures of the initial and final stages of melting are determined. The melting point ideally is identical with the solidification or freezing point. For some substances (rather products and mixtures) however, the determination of the freezing or solidification temperature is easier. Where, due to the particular properties of the substance (or product), none of the above parameters can be conveniently measured, a pour point may be appropriate.

3. The fundamental principles are given in references 2 and 3. Several methods and devices are described in this guideline. They can be applied irrespective of the degree of purity of the substance. The melting point of a substance is considerably affected by impurities. For this reason it serves as a measure of a substance's purity. The selection of a particular method depends mainly on the state of physical aggregation of the sample and on whether or not the substance can be pulverized easily, with difficulty, or not at all. Standards describing the various devices and procedures are listed in the Appendix.

DEFINITIONS AND UNITS

4. The melting point is defined as the temperature at which the phase transition from the solid to the liquid state at atmospheric pressure takes place.

5. The conversion of kelvins to degrees Celsius is according to the formula

$$T = t + 273.15$$, where

T is the Kelvin or thermodynamic temperature and t the Celsius temperature.

REFERENCE SUBSTANCES

6. Reference substances do not need to be employed when investigating a substance. Some calibration substances are listed in reference 4.

PRINCIPLE OF THE TEST

7. The temperature or temperature range of the phase transition from the solid to the liquid state or from the liquid to the solid state is determined.

COMPARISON OF THE METHODS

8. The temperature range and accuracy of the different methods are listed in Table 1.

Table 1

Method	Temperature range (in K)	Estimated accuracy (in K)
Capillary/liquid bath	273 to 573	± 0.3
Capillary/metal block	293 to >573	± 0.5
Kofler hot bar	293 to >573	± 1.0
Melt microscope	293 to >573	± 0.5
Differential thermal analysis and differential scanning calorimetry	173 to 1273	± 0.5 up to 600 K ± 2.0 up to 1273 K
Freezing temperature	223 to 573	± 0.5
Pour point	223 to 323	± 3.0

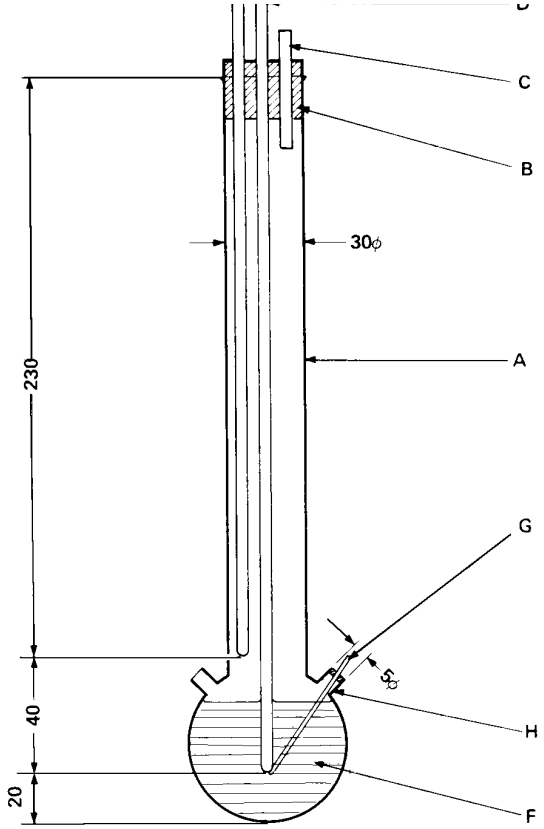
DESCRIPTION OF THE METHODS

Capillary tube in a liquid bath

Apparatus

9. The apparatus made of glass is shown in Figure 1. The choice of the bath liquid depends upon the melting temperature to be determined, e.g. liquid paraffin for temperatures not higher than 473 K and silicone oil for temperatures not higher than 573 K. For temperatures above 523 K, a mixture of three parts sulfuric acid and two parts of potassium sulphate (weight ratio) can be used. Precautions should be taken if a mixture such as this is used. Only thermometers, fulfilling the requirements of the standards ASTM E 1-71, DIN 12770, and JIS K 8001, or equivalent, should be used. The middle part of the mercury bulb of the thermometer should touch the capillary at the position where the sample is located.

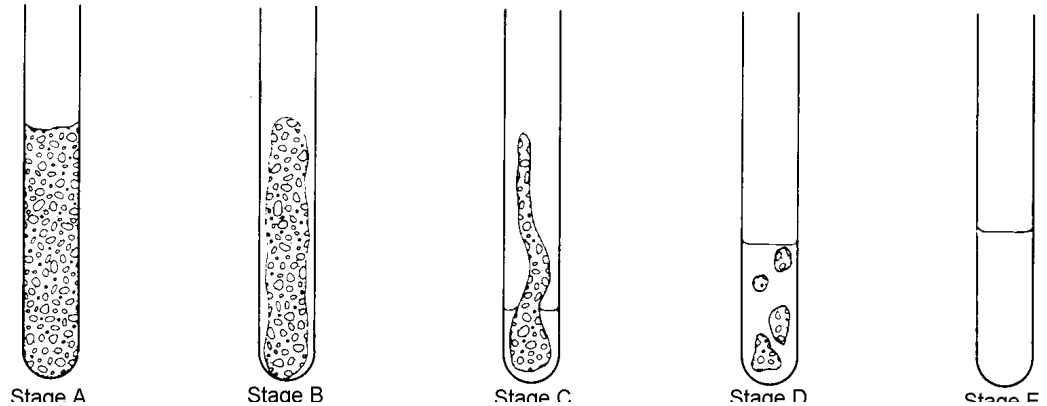
Figure 1



Dimensions in mm

A. Vessel
B. Stopper
C. Vent
D. Thermometer
E. Auxiliary thermometer
F. Bath liquid
G. Sample tube; max 5 mm outer diameter; capillary tube, approx 100 mm long and approx 1 mm inner diameter, and approx 0.2 to 0.3 mm wall-thickness
H. Side tube

Figure 2



Stage A, beginning of melting, fine droplets adhere uniformly to the wall of the tube
Stage B, a clearance between the sample and the wall due to shrinkage of the melt
Stage C, the shrunken sample collapses and liquefies
Stage D, a complete meniscus is formed but part of the sample remains solid
Stage E, final stage of melting, no solid particles are left

Procedure

10. The dry substance is finely pulverized and put into a capillary tube, fused at one end, so that the filling level is approximately 3 mm after the sample has been tightly packed. To obtain a uniformly packed sample, the capillary tube should be dropped from a height of approximately 700 mm through a glass tube onto a watch glass. The bath is heated so that the temperature rise is approximately 3 K/min. The bath should be stirred. Usually the capillary tube is put into the

apparatus when the temperature has risen to about 10 K below the melting temperature. From then on, and throughout the actual melting, the temperature rise is adjusted to maximum 1K/min. When subjected to a slow temperature rise, finely pulverized substances usually show the stages of melting shown in Figure 2. During the determination of the melting temperature, the temperatures are recorded at the beginning of the melting (stage A in the figure) and at the final stage (stage E in the figure).

Calculations

11. A corrected melting temperature is calculated using the formula

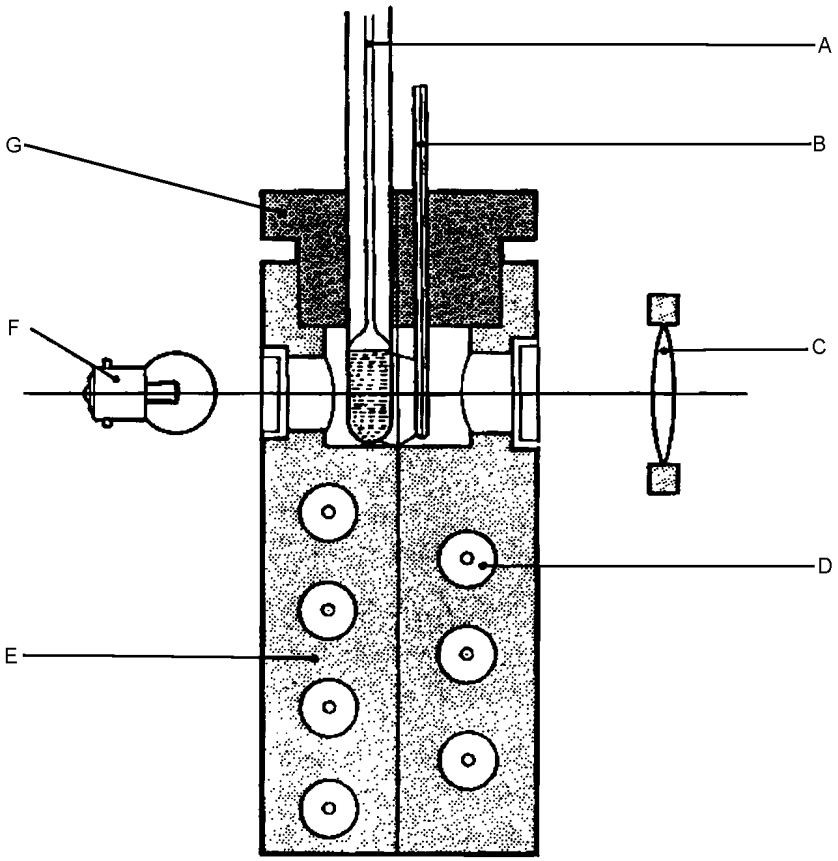
$$T = T_D + 0.00016 (T_D - T_E) n \text{ , where}$$

T = corrected melting temperature,
T_D = reading of thermometer D,
T_E = reading of thermometer E,
n = number of graduations of the mercury column on the emergent stem of thermometer D.

Capillary tube in a metal block

Apparatus for visual observation

Figure 3



A. Thermometer
B. Capillary tube
C. Eye-piece
D. Electrical resistance
E. Metal heating block
F. Lamp
G. Metal plug

12. The apparatus shown in Figure 3 consists of:

- a cylindrical metal block, the upper part of which is hollow and forms a chamber;
- a metal plug, with two or more holes, allowing capillary tubes to be mounted in the block;
- an electrical heating system with regulated power input;
- four windows of heat-resistant glass on the lateral walls of the chamber, diametrically disposed at right angles;
- an eyepiece for observing the capillary tube, mounted in front of one of these windows (the other three windows are used for illuminating the inside of the enclosure);
- a thermometer according to standards mentioned in paragraph 9 or thermoelectrical measuring devices of comparable accuracy.

Apparatus with photocell detection

13. A capillary tube, filled as described in paragraph 10, is placed in a heated metal block. The temperature rise is adjusted at a suitable pre-selected linear rate. A beam of light is directed through the sample to a photocell. On melting of the sample, the intensity of the light reaching the photocell increases and a stop signal is sent to the digital indicator reading out the temperature of the heating chamber.

Kofler hot bar

Apparatus

14. The Kofler hot bar uses two pieces of metal of different thermal conductivity. The bar is heated electrically and is designed so that the temperature gradient is almost linear along its length. The temperature of the hot bar can range approximately from room temperature to 573 K. The bar is fitted with a graduated temperature scala and a movable pointer.

Procedure

15. The substance is laid in a thin layer on the hot bar. A sharp dividing line develops between the solid and fluid phase within a few seconds. The temperature at the dividing line is read by adjusting the pointer to the dividing line.

Melt microscope

16. The specimen holder of a melt microscope is a metal plate which is part of a heating chamber. A hole in the metal plate permits the entrance of light from an illuminating device. The sample is placed on a slide over the hole and may be covered by another slide to minimise exposure to air. The plate is heated gradually until melting is observed and the temperature is recorded. The accuracy of the measurement can be increased for crystalline substances through the use of polarised light.

Differential thermal analysis (DTA)

17. Samples of the test substance and of a reference material are subjected to the same controlled temperature programme. When the test substance undergoes a phase transition, the corresponding change of enthalpy gives an endothermic (melting) or exothermic (freezing) departure from the base line of the temperature record.

Differential scanning calorimetry (DSC)

18. Samples of the test substance and of a reference material are subjected to the same controlled temperature programme. The difference in energy input necessary to maintain identical temperatures between the substance and the reference material is recorded. When the sample undergoes a phase

transition, the corresponding change of enthalpy gives a departure form the base line of the heat flow record.

Freezing temperature

19. A sample of the substance is placed in a test tube and stirred continuously. As the sample is cooled, its temperature is measured at regular intervals. As soon as the temperature remains constant for a few readings (corrected for thermometer error), this temperature is recorded as the freezing temperature. Supercooling must be avoided by maintaining equilibrium between the solid and the liquid phases.

Pour point

20. This method was developed for petroleum oils and is suitable for oily substances with low melting temperatures. After preliminary heating, the sample is cooled and its flow characteristics are examined at intervals of 3 K. The lowest temperature at which movement of the substance is observed is recorded as the pour point.

TEST REPORT

21. The test report shall include the following information:

- method used;
- chemical identity and impurities (preliminary purification step, if any);
- estimated accuracy;
- melting temperature (the mean of at least two measurements which are in the range of the estimated accuracy; if the difference between the temperature at the beginning and at the final stage of melting is within the limits of the accuracy, 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 melting occurs, the temperature at which the effect is observed is reported);
- all information and remarks relevant for the interpretation of the results, especially with regards to impurities and physical state of the substance.

LITERATURE

(1) Official Journal of the European Communities L 383 A, 5-14 (1992)

(2) Le Neindre, B. and Vodar B., eds. (1975). IUPAC, Experimental Thermodynamics, Vol.II, Butterworths, London, pp. 803 to 834

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

(4) IUPAC (1976). Physicochemical measurements: Catalogue of reference materials from national laboratories, Pure and Applied Chemistry, 48, 505 to 515

APPENDIX

LIST OF STANDARDS

Capillary tube in a 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	Bindemittel für Lacke und ähnliche Beschichtungsstoffe; Bestimmung des Schmelzbereiches von Harzen nach Kapillar-Verfahren
JIS K 00-64	Testing methods for melting point of chemical products

Capillary tube in a metal block

DIN 53736	Visuelle Bestimmung der Schmelztemperatur von teilkristallinen Kunststoffen

Kofler hot bar

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

Melt microscope

DIN 53736	Visuelle Bestimmung der Schmelztemperatur von teilkristallinen Kunststoffen

Differential thermal analysis and differential scanning calorimetry

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

Freezing temperature

BS 4633	Method for the determination of crystallizing point
BS 4695	Method for the determination of melting point of petroleum wax (cooling curve)

DIN 51421	Bestimmung des Gefrierpunktes von Flugkraftstoffen, Ottokraftstoffen und Motorenbenzolen
DIN 53175	Bestimmung des Erstarrungspunktes von Fettsäuren
ISO 1392	Method for the determination of the crystallizing point
ISO 2207	Petroleum waxes - Determination of congealing point
JIS K 00 - 65	Test methods for freezing point of chemical products
NF T 60-114	Point de fusion des paraffines
NF T 20-051	Méthode de détermination du point de cristallisation

Pour point

ASTM D 97-66	Standard test method for pour point of petroleum oils
ISO 3016	Petroleum oils - Determination of pour point
NBN 52014	Echantillonnage et analyse des produits de pétrole: Point de trouble et point d'écoulement limite