1.2.1 Melting temperature and melting range

A. Determination of melting temperature and melting range of pulverizable substances

The melting range of a solid substance is the range between the corrected temperature at which the substance begins to collapse or form droplets on the wall of a transparent glass capillary tube and the corrected temperature at which it is completely melted as shown by the disappearance of the solid phase.

The statement in a monograph "melting range a-b °C" means that the melting range determined by the method below must fall within these limits.

The melting temperature of a substance is the corrected temperature at which the solid substance is completely melted to a liquid or a decomposed state.

Apparatus

A suitable apparatus for the determination consists of a glass vessel with appropriate liquid, a controlled source of heat, a thermometer, a capillary tube and a magnifying glass.

The glass vessel should have a suitable construction, contain an appropriate liquid and be fitted with a stirring device capable of rapid mixing of the liquid (certain liquid silicones are suitable). The controlled source of heat should be capable of raising the temperature of the liquid heating medium at the required rate.

Standardized thermometers should cover the range -10 to +360 °C, the length of one degree on the scale being not less than 0.8 mm. These thermometers should preferably be of the mercury-in-glass, solid-stem type with a cylindrical bulb and made of approved thermometric glass suitable for the range covered; each thermometer should have a safety chamber.

Thermometers used for determination of melting temperatures may be calibrated for total or partial immersion. A total-immersion thermometer should read correctly when it is immersed at least to the end of the liquid column in the medium, the temperature of which is to be measured. A partial-immersion thermometer should read correctly when it is immersed to a prescribed depth and when the emergent liquid column is under prescribed conditions. When total-immersion thermometers are used partially immersed, an auxiliary thermometer is required for the determination of the emergent-stem correction. These two thermometers should be surrounded with a glass tube above the surface of the heating material.

The capillary tube should be made of borosilicate glass, closed at one end, and have the following dimensions: thickness of the wall, about 0.10–0.15 mm; length, suitable for the apparatus used; internal diameter, 0.9–1.1 mm.

A suitable magnifying glass should be used for observation of the capillary tube.

Other apparatus or methods may be used provided they are capable of equal accuracy and have been calibrated against the method of The International Pharmacopoeia by means of the WHO Melting Point Reference Substances.

<table>
<thead>
<tr>
<th>Substance</th>
<th>Assigned melting point</th>
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<tbody>
<tr>
<td>Azobenzene M.P.</td>
<td>68.9 °C</td>
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<tr>
<td>Vanillin M.P.</td>
<td>83.2 °C</td>
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<tr>
<td>Benzil M.P.</td>
<td>95.9 °C</td>
</tr>
<tr>
<td>Acetanilide M.P.</td>
<td>115.7 °C</td>
</tr>
<tr>
<td>Phenacetin M.P.</td>
<td>136.0 °C</td>
</tr>
<tr>
<td>Benzanilide M.P.</td>
<td>164.7 °C</td>
</tr>
<tr>
<td>Sulfanilamide M.P.</td>
<td>165.9 °C</td>
</tr>
<tr>
<td>Sulfapyridine M.P.</td>
<td>192.7 °C</td>
</tr>
<tr>
<td>Dicyandiamide M.P.</td>
<td>210.2 °C</td>
</tr>
<tr>
<td>Saccharin M.P.</td>
<td>230.0 °C</td>
</tr>
<tr>
<td>Caffeine M.P.</td>
<td>237.2 °C</td>
</tr>
<tr>
<td>Phenolphthalein M.P.</td>
<td>263.1 °C</td>
</tr>
</tbody>
</table>

1 The exact melting points assigned to the substances can be found in the leaflets accompanying the standards.

These substances are available from the WHO collaborating host organization for International Chemical Reference Substances.
Recommended procedure

Spread a small quantity of the finely powdered substance in a thin layer and dry it in a vacuum desiccator over silica gel, desiccant, R, phosphorus pentoxide R or other suitable desiccant for 24 hours, or at a temperature specified in the monograph.

Transfer a quantity of the dried powder to a dry capillary tube and pack the powder carefully by tapping the tube on a hard surface (ensure the capillary tube bottom is not damaged or cracked). Pack the sample column tightly to a height of about 3 mm.

Introduce the capillary tube into the heated bath at a temperature 5 °C below the expected lower limit of the melting range, the rise of temperature being regulated beforehand to 1 °C per minute, unless either the temperature of the introduction of the capillary tube into the bath or the rate of temperature rise are otherwise specified in the monograph. The capillary tube should be fitted in the bath in such a way that its closed end is at the level of the middle of the bulb of the standard thermometer.

When a thermometer calibrated for partial immersion is used, care must be taken that it is immersed exactly to its immersion mark when the readings are taken.

Unless otherwise specified in the monograph readings are taken of the temperature at which the substance is observed to collapse or form droplets on the wall of the tube and of the temperature at which it is completely melted as indicated by the disappearance of the solid phase.

To the temperature readings add the correction for deviation of the standard thermometer. When thermometers calibrated for total immersion are used partially immersed, add to the readings of the standard thermometer also the emergent-stem correction, which is obtained as follows:

\[
0.00015 \frac{N(T-t)}{t}
\]

where \(T\) is the temperature reading of the standard thermometer;
\(t\) is the temperature reading of the auxiliary thermometer;
\(N\) is the number of degrees of the scale of the standard thermometer between the surface of the heating material and the level of the mercury.

When needed the emergent-stem correction for thermometers calibrated for partial immersion may be calculated from the same formula as above, but replacing \(T\) by \(T_s\), which is the mean temperature of the emergent-stem of the thermometer at the time of calibration.

Both the above-mentioned corrections for emergent-stem and any deviation of the standard thermometer may conveniently be replaced by calibration of the apparatus by means of the WHO Melting Point Reference Substances.

B. Determination of melting point of low melting solids

The melting point of fats, waxes, etc., is the corrected temperature at which the column of substance in the capillary tube becomes transparent or moves upwards, when tested by the method described below.

Apparatus

A similar apparatus to that described under A for the determination of melting temperature and melting range of pulverizable substances should be used with the following modifications:

- water should be used in the heating vessel;
- an accurately standardized thermometer should cover the range -10 to +100 °C;
- a glass capillary tube should have the same dimensions as described under A but be open at both ends; soft glass capillary tubes may be used.

Recommended procedure

Unless otherwise specified in the monograph, melt the substance at as low a temperature as possible and then suck the liquid up to a height of about 10 mm in the capillary tube. Cool the charged tube at 10 °C or lower for 24 hours. If the monograph specifies that the melting temperature is to be determined without previous melting of the substance, charge the capillary tube by pushing it
into the unmelted substance so that a column about 10 mm long is forced in. The determination may then be carried out immediately.

Attach the tube to the thermometer in the water-bath by means of a rubber band or otherwise so that the lower end of the capillary tube is at the level of the middle of the bulb of the thermometer and the distance between the lower end of the capillary tube and the water level is about 20 mm. Heat the bath with constant stirring, the heating being regulated so that the temperature rise, at a temperature of 5 °C below the expected melting temperature, is about 1 °C per minute.