Melting point	**GM 1.2.1.0011.15** **Instead of SpH X** **Instead of SpH XI, ed. 1** **Instead of SpH XII, p. 1, GM 42-0034-07**

Melting point is the temperature at which a substance changes its state from solid into liquid.

Methods used for determination of melting point depending on physical properties of a substance include capillary method (method 1), open capillary method (method 2), instantaneous melting method (method 3) and dropping point method (method 4). For solids that can be easily ground use methods 1 and 3, for atmospheric substances that cannot be ground and that melt at a temperature below the melting point of water (such as lipids, wax, paraffin, vaselines, resins) – methods 2 and 4.

Decomposition temperature is determined for substances that decompose when heated. Decomposition temperature is the temperature that leads to rapid change of physical state or colour of a substance (foaming, brown discolouration).

Apparatus and techniques described below can be used for determination of melting point. Suitable reference substances with a melting point close to the melting point of the test substance are used for callibration of apparatus.

1. Capillary method

Melting point determined using capillary method is the temperature at which the last solid particle of the packed column in a capillary changes its state to liquid.

Apparatus 1. The main apparatus components are:

- Glass vial containing liquid (for example, water, liquid paraffin or silicone oil) used as a bath and equipped with a heating device. The bath liquid should be selected depending on the required temperature;
- Mixing device that ensures uniformity of temperature within the bath;
- Suitable thermometer with a scale division of no more than 0.5 °C. Difference between upper and lower limits in the range of measured temperature is not more than 100 °C.
- Capillaries closed at one end made out of neutral strong glass with diameter between 0.9 and 1.1 mm, wall thickness of 0.10-0.15 mm and length of 10 cm.

Apparatus 2. The main apparatus components are:

- A 100-150 mL round-bottom vial; neck length – 20 cm; neck diameter – 3-4 cm;
- Heat-resistant tube inserted into the vial with 1.0 cm above the bottom of the vial; tube diameter – 2.0-2.5 cm;
- Shortened mercury-in-glass thermometer with a scale division of no more than 0.5 °C inserted into the tube in such manner that the space between its bottom and the bottom of the vial is 1.0 cm;
- Heat source (gas burner, electrical heating);

– Capillaries closed at one end made out of neutral strong glass with diameter between 0.9 and 1.1 mm, wall thickness of 0.10-0.15 mm and length of 6-8 cm.

¾ of the vial is filled with appropriate liquid:

– Liquid paraffin or liquid silicones; concentrated sulphuric acid – for substances with melting point between 80 and 260 °C;
– Potassium sulphate solution in concentrated sulphuric acid (3:7 by weight) - for substances with melting point over 260 °C;
– Purified water - for substances with melting point below 80 °C.

Notes.

1. Glass tubes out of which capillaries are drawn up must be washed and dried.
2. When preparing potassium sulphate solution in concentrated sulphuric acid the solution is boiled for 5 minutes while vigorously stirring. If not stirred, 2 layers may form, which can lead to explosion.

Apparatus 3. Apparatus that determines melting point with range of 20-360 °C equipped with electrical heating PTP type or PTP-M type (fig. 1) with range of 20-340 °C.

The main apparatus components are:

– Base with control panel and nomographic chart;
– Glass heating block, which is heated through a constantan double-wound wire;
– Optical device;
– Device for thermometer installation;
– Device for capillary installation;
– Shortened thermometer with a 0.5 °C scale division;
– Heating element (electrical heating);
– 20 cm capillaries for PTP-type apparatus; 8 cm capillaries for PTP-M-type apparatus.

Functioning principal of the apparatus is based on temperature exposure of test substances in vertically placed capillaries closed at one end.

Other devices based on capillary method may also be used if the accuracy and precision of measurements are not worse than with the devices described above.

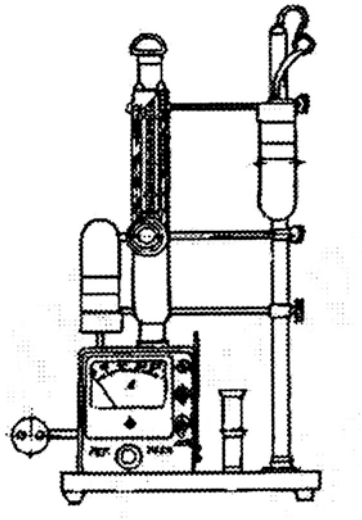

Figure 1 – PTP-M apparatus for determination of melting point

Method. Unless otherwise specified in the general monograph, finely ground substance is dried at a temperature of 100-105 °C for 2 hours or in a desiccator with sulphuric acid for 24 hours or in a vacuum with anhydrous silica gel for 24 hours.

Sufficient amount of the test substance is placed into a capillary to obtain a 5 mm packed column. The necessary packing density can be achieved if the capillary is dropped closed end down onto a 0.5-1.0 glass tube placed vertically onto a glass. Preserve the capillary with test substance until the beginning of determination in a desiccator.

Increase the bath (apparatus) temperature. At a temperature that is approximately 10 °C below the suspected melting point the heating of the apparatus is adjusted in such manner that the rate of temperature increase for the remainder of the test is approximately 1 °C per minute. When the temperature reaches the point of approximately 5-10 °C below the melting point, the capillary is affixed to a thermometer in such manner that the closed end remains in the middle of thermometer bulb; then the capillary is placed into the apparatus.

Continue heating at the following rates:

- for substances that are stable when heated when determining melting point below 100 °C – with a rate of 0.5-1.0 °C per minute;
- when determining melting point of 100 - 150 °C – with a rate of 1.0-1.5 °C per minute;
- when determining melting point over 150 °C – with a rate of 1.5-2.0 °C per minute;
- for substances that are unstable when heated – 2.5-3.5 °C per minute.

Record the temperature at which the last solid particle of the packed column in a capillary changes its state to liquid.

Perform at least 2 analyses. Melting point is the arithmetic mean of several measurements conducted under same conditions with variance of no more than 1 °C.

Note. Vial and tube must remain open during melting point test.

2. Open capillary method

Use a glass capillary open at both ends with an approximate length of 80 mm, outer diameter of 1.4-1.5 mm and inner diameter of 1.0-1.2 mm.

Prepare the substance as indicated in the general monograph and place in each of the 5 capillaries in an amount that forms a 10 mm column. Leave the capillaries at a temperature indicated in the general monograph for a certain amount of time.

Affix one of the capillaries to a thermometer with a 0.2 °C scale division in such manner that the substance is close to thermometer bulb.

Place the thermometer with an affixed capillary into a glass in such manner that the space between the bottom of the glass and the end of thermometer bulb is 1 cm. Fill the glass with water to reach 5 cm of the column.

Increase the temperature at a rate of 1 °C per minute.

Melting point is the temperature, at which the substance in the capillary begins to rise. In those cases when the substance does not rise, the melting point is the temperature at which the substance becomes clear.

Repeat the procedure 4 times with other capillaries and calculate the arithmetic mean of 5 measurements. Variance should be no more than 1 °C.

3. Instantaneous melting method

Apparatus. The apparatus is comprised of a metal block manufactured out of a material with high thermal conductivity that will not interact with the test substance, for example, out of brass. Top surface should be flat and carefully polished. Heat up the block evenly using a microadjustable gas burner or a fine adjustment electrical heating system. The block has a sufficiently wide cylindrical cavity for insertion of a thermometer, with that the mercury column must remain in the same position both during callibarton and during determination of melting point. Cylindrical cavity is parallel to the polished top surface with a 3 mm distance in-between.

Method. Heat up the block quickly to a temperature that is approximately 10 °C below the suspected melting point and adjust the heating rate to approximately 1 °C per minute. At fixed intervals, drop several particles of finely ground substance that has been dried out in a vacuum with anhydrous silica gel for 24 hours onto the surface of the block in a close proximity to the thermometer bulb; clean the surface after each test. Record the temperature t_1, at which the substance melts instantaneously after making contact with metal. Stop heating the block. As the block cools down, drop several particles of the test substance at regular intervals onto the surface; clean the surface after each test. Record the temperature t_2, at which the substance stops to melt instantaneously after making contact with metal.

Calculate the melting point (T_{mlt}) using the following equation:

$$T_{mlt} = \frac{t_1 + t_2}{2}$$

where t_1 is the first temperature value;

t_2 is the second temperature value.

4. Dropping point method

This method is used to determine temperature at which the first drop of melted test substance falls out of the test cup.

Apparatus. Apparatus consists of two metal cells (A and B) connected by thread. Cell (A) is affixed to a mercury thermometer. A metal cap (D) is freely affixed to the bottom of cell (B) via two compactors (E). The exact position of the cup is determined by 2 mm clamps (E) that can also be used to centre the thermometer. Hole (C) in the wall of cell (B) is used for pressure adjustment. Diverting surface of the cup should be flat and the edges of the exit hole should be positioned at a straight angle to the surface. The shape and size of the bottom part of the thermometer is illustrated on Figure 2. The thermometer is calibrated from 0 to 110 °C, and the distance of 1 mm on the scale signifies 1 °C difference in temperatures. Mercury ball has a diameter of (3.5 ± 0.2) mm and height of (6.0 ± 0.3) mm.

The device is installed along the axis of test tubes with an approximate length of 200 mm and outer diameter of approximately 40 mm.

The device is affixed to a test tube with help of a test tube into which a thermometer is inserted and which has a side slot. The hole in the cup should be placed at approximately 15 mm from the bottom of the tube. The entire device is submerged into a 1 L glass filled with water. The distance between the bottom of the glass and the bottom of the test tube should be approximately 25 mm. The water level should reach the top part of the cell (A). Stirring device should be used in order to ensure uniformity of temperature within the bath.

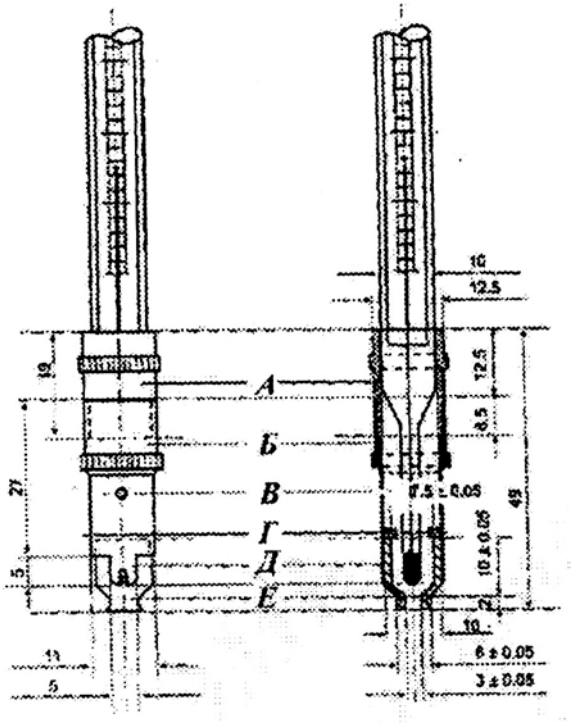

Figure 2 – Dropping point apparatus.
Sizes are provided in mm

Method. Fill the cup to the edges with unmelted test substance, unless otherwise specified in the general monograph. Remove excess substance from both sides using a spatula. After connecting cells (A) and (B) push the cup through in its spot within the cell (B) as far as it can go. Using a spatula remove the excess substance that was pushed out. Place the apparatus in a water bath as described above. Heat the water bath to a temperature that is approximately 10 °C below the suspected melting point and adjust the heating rate to approximately 1 °C per minute. Record the temperature at which the first drops falls. Perform at least 3 measurements using new sample of substance each time. The variance in obtained results must not exceed 3 °C. Calculate arithmetic mean of the obtained results.