Designation: E324 – 16

Standard Test Method for Relative Initial and Final Melting Points and the Melting Range of Organic Chemicals[1]

This standard is issued under the fixed designation E324; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

This standard has been approved for use by agencies of the U.S. Department of Defense.

1. Scope

1.1 This test method covers the determination, by a capillary tube method, of the initial melting point and the final melting point, which define the melting range, of samples of organic chemicals whose melting points without decomposition fall between 30 and 250°C.

1.2 This test method is applicable only to crystalline materials that are sufficiently stable in storage to met the requirements of a satisfactory standard sample as defined in Section 7.

1.3 This test method is not directly applicable to opaque materials or to noncrystalline materials such as waxes, fats, and fatty acids.

1.4 Review the current Safety Data Sheets (SDS) for detailed information concerning toxicity, first aid procedures, handling, and safety precautions.

1.5 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.6 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D852 Test Method for Solidification Point of Benzene
D1015 Test Method for Freezing Points of High-Purity Hydrocarbons
D1016 Test Method for Purity of Hydrocarbons from Freezing Points
D1493 Test Method for Solidification Point of Industrial Organic Chemicals (Withdrawn 2004)[3]
D1982 Test Method for Titer of Fatty Acids
D6809 Guide for Quality Control and Quality Assurance Procedures for Aromatic Hydrocarbons and Related Materials
D6875 Test Method for Solidification Point of Industrial Organic Chemicals by Thermistor
E1 Specification for ASTM Liquid-in-Glass Thermometers
E11 Specification for Woven Wire Test Sieve Cloth and Test Sieves
E180 Practice for Determining the Precision of ASTM Methods for Analysis and Testing of Industrial and Specialty Chemicals (Withdrawn 2009)[3]
E1547 Terminology Relating to Industrial and Specialty Chemicals

3. Terminology

3.1 *Definitions:*

3.1.1 See Terminology E1547 for definition of terms used in this test method.

3.1.2 *initial melting point, n*—the temperature at which positive evidence of liquefaction is observed (see 9.4.1).

3.1.3 *final melting point, n*—the temperature at which the last crystal disappears into the melt.

4. Summary of Test Method

4.1 1 This test method determines initial and final melting points by a relative procedure, utilizing a standard sample that has been assigned jointly accepted melting point values by the concerned parties (such as a supplier and a consumer, or NIST and a manufacturer). The absolute values of the initial and final melting points are not critical factors, as long as the producer and consumer agree to use the standard sample and its empirically assigned values as the basis for testing and specifications agreements. Simultaneous readings are taken of

---

[1] This practice is under the jurisdiction of ASTM Committee D16 on Aromatic Hydrocarbons and Related Chemicals and is the direct responsibility of Subcommittee D16.15 on Industrial and Specialty General Standards.

Current edition approved Nov. 1, 2016. Published November 2016. Originally approved in 1967. Last previous edition approved in 1999 as E324 – 99 which was withdrawn April 2001 and reinstated in November 2016. DOI: 10.1520/E0324-16.

[2] For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

[3] The last approved version of this historical standard is referenced on www.astm.org.

these temperatures for an unknown and the agreed standard sample of the same chemical; the respective initial melting points and the respective final melting points are recorded. The differences in melting point values between the assigned and the observed melting points for the standard are added algebraically to the corresponding figures for the unknown, thereby giving the corrected values reported.

5. Significance and Use

5.1 It has long been recognized that narrow melting range and high final melting point are good indications of high purity in crystalline organic compounds. Several ASTM test methods use these criteria to assay the purity of organic compounds (Note 1). Test Method D1016 uses the cryoscopic constants plus the melting point of 100 % pure material to calculate the mol percent purity of the sample under test.

NOTE 1—Other ASTM test methods using melting (or freezing point) data to indicate sample purity are Test Methods D852, D1015, D1016, D1493, D1982, and D6875.

5.2 The relatively simple and rapid test prescribed in this test method shows the sample under test to be either more or less pure than the standard sample. For specification purposes, a minimum allowable purity can be assured by setting limits on the differences in final melting points and the melting ranges between the standard sample and the sample under test.

6. Apparatus

6.1 *Capillary Melting Point Apparatus*[4] consisting of a silicone fluid bath (Note 2), stirrer, immersion heater coil, transformer control, and adjustable magnifier constructed and operated in such a way that the temperature around the samples and thermometer is uniform, and can be easily controlled within the limits required by this test method. A means shall be provided so that the capillary tubes can be introduced into the bath and properly positioned without removing the thermometer from the heating bath.

NOTE 2—The silicone fluid used in this study had a viscosity of about 50 cSt (mm2/s) at 25°C and a flash point over 300°C.

6.2 *Melting Point Capillary Tubes*—The capillary tube to contain the sample shall be a glass tube approximately 90 to 120 mm long and 0.9 to 1.1 mm in internal diameter with walls 0.2 to 0.3 mm thick and closed at one end.

6.3 *Thermometer,* of the partial immersion type and of suitable range selected from Specification E1. It shall be divided into subdivisions of 0.5°C and capable of being read to 0.1°C.

6.4 *Sieve*—The 125-µm sieve used in preparation of the standard sample and of samples of material to be tested shall meet the requirements of Specification E11.

7. Standard Sample

7.1 The standard sample shall be homogeneous and of the same basic chemical composition as the unknown to be analyzed. This condition is satisfied when both materials are quite pure, or when both the standard and unknown have been made by the same industrial process. Significant deviations from identity in chemical composition lead to some loss of precision.

7.2 The standard sample must be uniformly blended, and the particle size must be fine enough so that a test specimen of approximately 0.1 g will yield reproducible melting point data. In preparing a standard sample from coarse crystalline material the sample should be ground fine, passed through a 125-µm sieve, and blended thoroughly before subdividing and storing for use in this test.

7.3 The standard sample shall be stored under such conditions that its quality will not deteriorate. This is vital to the success of the method, since deterioration of the standard sample, causing lowered initial and final melting temperatures, will result in falsely high indications of the purity of the materials under test. Many chemicals are somewhat hygroscopic, and it may be agreed that the standard or both the standard and the sample are to be conditioned by appropriate means before the melting range is determined.

7.4 In the case of two laboratories determining the melting point or melting range of a material (as in the case of the laboratories of a supplier and of a consumer), it is necessary that the standard used by each be a portion of the same standard sample with preassigned values of the initial and final melting points.

8. Sampling

8.1 A bulk sample shall be withdrawn by means appropriate to the processing, shipment, or storage conditions. This bulk sample shall be blended and subdivided, with grinding steps where appropriate, until a blended sample of 1 to 10 g with a particle size passing 125-µm sieve is obtained.

9. Procedure

9.1 Grind approximately 0.1-g test specimens of the standard sample and of the unknown sample as finely as possible in mortars or on pieces of flat glass with spatulas. Charge the melting point capillary tubes with the finely ground test specimens to form packed columns in the bottom of the tubes from 3 to 4 mm in height. The capillary tubes are packed tightly by adding the powdered test specimen in three or four increments, and being sure that each increment is well packed.[5]

9.2 Preheat the oil bath to approximately 15°C below the expected melting range. Then adjust the temperature rise rate to 1 ± 0.2°C/min during the actual melting of the sample.

9.3 Without removing the thermometer from the heating bath, place the packed capillary tubes containing the standard and unknown sample in the heating bath when the temperature is about 5°C below the expected initial melting point. Hold the packed capillary tubes adjacent to the thermometer bulb in such a way that they and the thermometer bulb are at a uniform temperature.

---

[4] The interlaboratory study was made and the precision data obtained using a Thomas-Hoover "Uni-Melt" apparatus. Similar data may be obtained on other capillary melting point apparatus suitably designed for this procedure and available from other suppliers.

[5] In the "Uni-Melt" apparatus, a vibrator suitable for packaging the tubes is part of the equipment; alternative ways of packing the tube firmly are permissible.

9.4 Observe the samples closely through the magnifier and record the initial melting point and the final melting point to obtain the melting range.

9.4.1 The initial melting point is defined as the temperature at which positive evidence of liquefaction is observed. Just before this temperature is reached, samples show varying degrees of shrinkage away from the walls of the capillary tube. Then, the main column of sample collapses against the side or the bottom of the capillary, or both. After a further rise in temperature, which may vary from 0.2°C to more than 1°C, the portion of the sample in contact with the tube is observed to form a distinct liquid film which wets the surface. The liquefaction or wetting may occur at the bottom, sides, front, or rear of the capillary tube. When wetting occurs at the back, the point may be missed unless care is taken to watch the rear of the tube. The capillary tube may be rotated to view the rear side. The area of the wetted surface should represent 25 to 50 % of the area of the tube in contact with the sample and visible to the operator. The temperature at this point is taken as the initial melting point. The minute droplets resulting from the small particles which adhere to the wall of the capillary tube after the shrinkage of the sample should not be considered in arriving at the initial melting point. Neither should a darkening or change of color of the sample be considered, but such changes should be noted along with any additional evidence of decomposition.

9.4.2 The final melting point is the temperature at which the last sample cryStal disappears into the melt.

10. Calibration

10.1 Calculate the corrected initial and final melting points in degrees Celsius as follows:

$$A_i = B_i + D_i - C_i \quad (1)$$

$$A_f = B_f + D_f - C_f \quad (2)$$

where:

A_i = corrected initial melting point of unknown sample,
A_f = corrected final melting point of unknown sample,
B_i = observed initial melting point of unknown sample,
B_f = observed final melting point of unknown sample,
D_i = assigned initial melting point of standard sample,
D_f = assigned final melting point of standard sample,
C_i = observed initial melting point of standard sample, and
C_f = observed final melting point of standard sample.

11. Report

11.1 Report as the melting range the initial melting point and the final melting point to the nearest 0.1°C.

12. Precision and Bias

12.1 *Precision:*

12.1.1 The following criteria should be used for judging the acceptability of results (see Note 3).

12.1.2 *Repeatability (Single Analyst)*—The standard deviation for a single melting point value has been estimated to be 0.18°C at 228 DF. The 95 % limit for the differences between two such values is 0.5°C.

NOTE 3—The above precision estimates are based on an interlaboratory study in 1973 on five samples melting at approximately 75, 105, 150, 200, and 235°C. One analyst in each of 13 laboratories performed duplicate determinations and repeated one day later, for a total of 260 determinations.[6] Practice E180 was used in developing these precision estimates.

12.2 The use of a thermometric correction automatically compensates for variations in equipment and heating techniques, and very importantly, the variation between different analysts in the selection of melting stages as characteristic of the recorded initial and final temperatures.

12.3 *Bias*—Since there is no accepted reference material suitable for determining the bias in this test method for measuring melting point, bias has not been determined.

13. Quality Guidelines

13.1 Laboratories shall have a quality control system in place.

13.1.1 Confirm the performance of the test instrument or test method by analyzing a quality control sample following the guidelines of standard statistical quality control practices.

13.1.2 A quality control sample is a stable material isolated from the production process and representative of the sample being analyzed.

13.1.3 When QA/QC protocols are already established in the testing facility, these protocols are acceptable when they confirm the validity of test results.

13.1.4 When there are no QA/QC protocols established in the testing facility, use the guidelines described in Guide D6809 or similar statistical quality control practices.

14. Keywords

14.1 analysis; capillary tube; melting point; melting range

---

[6] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:E15-1020. Contact ASTM Customer Service at service@astm.org.

ASTM International takes no position respecting the validity of any patent rights asserted in connection with any item mentioned in this standard. Users of this standard are expressly advised that determination of the validity of any such patent rights, and the risk of infringement of such rights, are entirely their own responsibility.

This standard is subject to revision at any time by the responsible technical committee and must be reviewed every five years and if not revised, either reapproved or withdrawn. Your comments are invited either for revision of this standard or for additional standards and should be addressed to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee, which you may attend. If you feel that your comments have not received a fair hearing you should make your views known to the ASTM Committee on Standards, at the address shown below.

This standard is copyrighted by ASTM International, 100 Barr Harbor Drive, PO Box C700, West Conshohocken, PA 19428-2959, United States. Individual reprints (single or multiple copies) of this standard may be obtained by contacting ASTM at the above address or at 610-832-9585 (phone), 610-832-9555 (fax), or service@astm.org (e-mail); or through the ASTM website (www.astm.org). Permission rights to photocopy the standard may also be secured from the Copyright Clearance Center, 222 Rosewood Drive, Danvers, MA 01923, Tel: (978) 646-2600; http://www.copyright.com/