This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.

Designation: E967 – 18

Standard Test Method for Temperature Calibration of Differential Scanning Calorimeters and Differential Thermal Analyzers[1]

This standard is issued under the fixed designation E967; 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.

1. Scope

1.1 This test method describes the temperature calibration of differential thermal analyzers and differential scanning calorimeters over the temperature range from −40°C to +2000°C.

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

1.3 This test method is similar to ISO standard 11357–1.

1.4 *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, health, and environmental practices and determine the applicability of regulatory limitations prior to use.* Specific precautionary statements are given in Section 7.

1.5 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]

E473 Terminology Relating to Thermal Analysis and Rheology

E1142 Terminology Relating to Thermophysical Properties

2.2 *ISO Standards:*[3]

11357–1 Plastics-Differential Scanning Calorimetry (DSC)-Part 1: General Principles

3. Terminology

3.1 *Definitions*—Specific technical terms used in this test method are defined in Terminologies E473 and E1142.

4. Summary of Test Method

4.1 This test method consists of heating the calibration materials at a controlled rate in a controlled atmosphere through a region of known thermal transition. The heat flow into the calibration material or the difference of temperature between the calibration material and a reference sample is monitored and continuously recorded. A transition is marked by the absorption of energy by the specimen resulting in a corresponding endothermic peak in the heating curve.

NOTE 1—Heat flow calibrations are sometimes determined in conjunction with temperature calibration. Some differential scanning calorimeters permit both heat flow and temperature calibrations to be obtained from the same experimental procedure.

5. Significance and Use

5.1 Differential scanning calorimeters and differential thermal analyzers are used to determine the transition temperatures of materials. For this information to be meaningful in an absolute sense, temperature calibration of the apparatus and comparison of the resulting data to that of known standard materials is required.

5.2 This test method is useful in calibrating the temperature axis of differential scanning calorimeters and differential thermal analyzers.

6. Apparatus

6.1 Apparatus shall be of either type listed below:

6.1.1 *Differential Scanning Calorimeter (DSC),* capable of heating a test specimen and a reference material at a controlled rate and of automatically recording the differential heat flow between the sample and the reference material to the required sensitivity and precision.

6.1.1.1 *A Furnace(s),* to provide uniform controlled heating or cooling of a specimen and reference to a constant temperature or at a constant rate within the applicable temperature range of this test method.

6.1.1.2 *A Temperature Sensor,* to provide an indication of the specimen temperature.

[1] This test method is under the jurisdiction of ASTM Committee E37 on Thermal Measurements and is the direct responsibility of Subcommittee E37.01 on Calorimetry and Mass Loss.

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[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] Available from International Organization for Standardization (ISO), 1, ch. de la Voie-Creuse, CP 56, CH-1211 Geneva 20, Switzerland, http://www.iso.org.

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6.1.1.3 *Differential Sensors,* to detect a heat flow (power) difference between the specimen and reference.

6.1.1.4 *Test Chamber Environment,* a means of sustaining a test chamber environment of nitrogen or other inert purge gas at a purge rate of 10 to 50 mL/min.

6.1.1.5 *A Temperature Controller,* capable of executing a specific temperature program by operating the furnace(s) between selected temperature limits at a rate of temperature change of 10°C/min.

6.1.1.6 *Data Collection Device,* to provide a means of acquiring, storing, and displaying measured or calculated signals, or both. The minimum output signals required for DSC are heat flow, temperature, and time.

6.1.2 *Differential Thermal Analyzer (DTA),* capable of heating a test specimen and reference material at a controlled rate and of automatically recording the differential temperature between sample and reference material both to the required sensitivity and precision.

6.2 *Containers (pans, crucibles, vials, lids, closures, seals, etc.),* that are inert to the specimen and reference materials and that are of suitable structural shape and integrity to contain the specimen and reference in accordance with the specific requirements of this test method.

6.3 *Nitrogen,* or other inert purge gas supply.

6.4 *A Balance,* to weigh specimens or containers (pans, crucibles, vials, etc.), or both to ±0.1 mg. The balance should have a capacity greater than 20 mg.

7. Precautions

7.1 Toxic or corrosive effluents, or both, may be released when heating some material and could be harmful to personnel and to apparatus.

7.2 This test method assumes linear temperature indication. Care must be taken in the application of this test method to ensure that calibration points are taken sufficiently close together so that linear temperature indication may be approximated. Linear temperature indications means that there exists a linear, or first order, dependence on the temperature determined by the instrument's temperature sensor on the true temperature of the sample material in its container and that this relation is adequately expressed by Eq 1.

8. Calibration Materials

8.1 For the temperature range covered by many applications, the melting transition of >99.99 % pure materials in Table 1 may be used for calibration.

9. Procedure

9.1 *Two Point Calibration:*

9.1.1 Select two calibration materials from Table 1, with melting temperatures one above and one below the temperature range of interest. The calibration materials should be as close to the temperature range of interest as practical.

9.1.2 Determine the apparent transition temperature for each calibration material.

TABLE 1 Melting Temperature of Calibration Material

NOTE 1—The values in Table 1 were determined under special, highly accurate steady state conditions that are not attainable or applicable to thermal analysis techniques. The actual precision of this test method is given in Section 12 of this test method.

Calibration Material	Melting Temperature[A]	
	(°C)	(K)
Mercury	–38.834	234.316
Water	0.01[B]	273.16
Cyclohexane	6.71[C]	279.86
Phenoxybenzene	26.87	300.02
Gallium	29.765[B]	302.915
Benzoic Acid	122.37	395.52
Indium	156.5985[D]	429.7485
Tin[E]	231.928[B,D]	505.078
Bismuth	271.402[D]	544.552
Cadmium	321.069[D]	594.219
Lead	327.462[D]	600.612
Zinc	419.527[B,D]	692.677
Antimony	630.628[D]	903.778
Aluminum	660.323[D]	933.473
Silver	961.78[B,D]	1234.93
Gold	1064.18[B,D]	1337.33
Copper	1084.62[B]	1357.77
Nickel	1455[D]	1728
Cobalt	1494[D]	1767
Palladium	1554[D]	1827
Platinum	1772	2045
Rhodium	1963	2236

[A] Rossini, F. D., *Pure Applied Chemistry*, Vol 22, 1970, p. 557.
[B] The melting temperatures of these materials have been selected as primary fixed points for the International Practical Temperature Scale of 1990. See Mangum, B. W., and Furukawa, G. T., *Guidelines for Realizing the International Practical Temperature Scale of 1990 (ITS-90)*, NIST Technical Note 1265.
[C] Shimizu, Y., Ohte, Y., and Kato, K., "Certified Reference Material NMIJ CRM 5401-a," *Thermochimica Acta*, Vol 568, 2013, pp. 61–66.
[D] Updated melting temperatures were taken from Boettinger, W. J., Kattner, U. R., Moon, K.-W., and Perepezko, J.H., *DTA and Heat-flux DSC Measurements of Alloy Melting and Freezing*, NIST Special Publication 960-15, November 2006.
[E] Some materials have different crystalline forms (for example, tin) or may react with the container. These calibration materials should be discarded after their initial melt.

9.1.2.1 Into a clean specimen holder, place a 5 mg to 15 mg weighed amount of calibration material. Other specimen masses may be used but must be indicated in the report.

9.1.2.2 Load the specimen into the instrument chamber, purge the chamber with dry nitrogen (or other inert gas) at a flow rate of 10 to 50 mL/min throughout the experiment.

9.1.2.3 Heat (or cool) the calibration material rapidly to 30°C below the calibration temperature and allow to stabilize.

9.1.2.4 Heat the calibration material at 10°C/min through the transition until baseline is reestablished above the transition. Other heating rates may be used but must be noted in the report. Record the resulting thermal curve.

NOTE 2—Temperature scale calibration may be affected by temperature scan rate, specimen holder, purge gas and purge gas flow rate. The temperature calibration shall be made under the same conditions used for test specimens.

9.1.2.5 From the resultant curve, measure the temperatures for the desired points on the curve, T_e, T_p (see Fig. 1) retaining all available decimal places.

where:

T_e = extrapolated onset temperature for fusion, °C, and
T_p = melting peak temperature, °C.

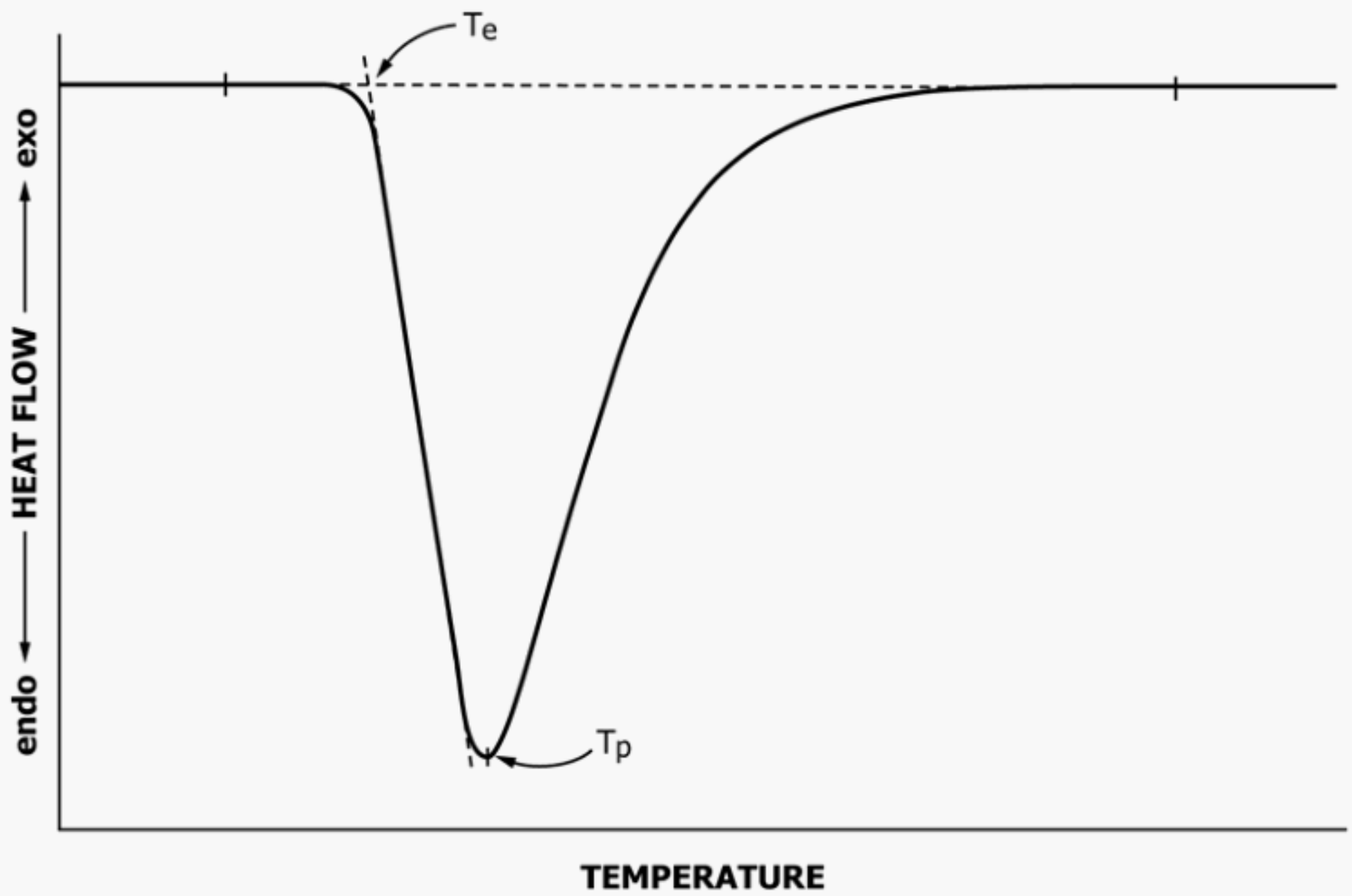

FIG. 1 Reference Material Melting Endotherm

NOTE 3—The actual temperature displayed on the temperature axis differs depending upon the instrument type; for example, sample temperature, program temperature, sample program temperature average. Follow the instructions of the particular instrument manufacturer to obtain sample temperature at the point of interest.

NOTE 4—The available precision of the temperature measurements depends upon instrument capabilities and the temperature range of the test. Below 300°C, measurements to ±0.5°C are common while at greater than 700°C ± 2°C is reasonable.

NOTE 5—For high-purity crystalline materials (not polymers), T_e is taken as the transition temperature when measured by differential scanning calorimeters and other instruments where the test specimen is not in intimate contact with the temperature sensor. For instruments in which the temperature sensor is in intimate contact with the sample, (such as some differential thermal analyzers), T_p is taken as the transition temperature.

9.1.3 Using the apparent transition temperatures thus obtained, calculate the slope (*S*) and intercept (*I*) of the calibration Eq 1 (see Section 10). The slope and intercept values reported should be mean values from duplicate determinations based on separate specimens.

9.2 *One-Point Calibration:*

9.2.1 If the slope value (*S*) previously has been determined in 9.1 (using the two-point calibration calculation in 10.2) to be sufficiently close to 1.0000, a one-point calibration procedure may be used.

NOTE 6—If the slope value differs by only 1 % from unity (that is, $S < 0.9900$ or $S > 1.0100$), a 1°C error will be produced if the test temperature differs by 100°C from the calibration temperature.

9.2.2 Select a calibration material from Table 1. The calibration temperature should be centered as close as practical within the temperature range of interest.

9.2.3 Determine the apparent transition temperatures of the calibration material using steps 9.1.2.1 – 9.1.2.5.

9.2.4 Using the apparent transition temperature thus obtained, calculate the intercept (*I*) of the calibration equation using all available decimal places. The value reported should be a mean value based upon duplicate determinations on separate specimens.

9.3 If practical, adjustment to the temperature scale of the instrument should be made so that temperatures are accurately indicated directly.

10. Calculations

10.1 For the purposes of this procedure, it is assumed that the relationship between observed temperature (*TO*) and actual specimen temperature (*T*) is a linear one governed by the following equation:

$$T = (TO \times S) + I \tag{1}$$

where:

S and *I* = the slope and intercept, respectively. (See 10.2 for the values for S and I, used in Eq 1.)

NOTE 7—For some instruments, the assumption of a linear relation between observed and actual specimen temperature may not hold. Under such conditions, calibration temperatures sufficiently close together shall be used so that the instrument calibration is achieved with a series of linear relations.

10.2 *Two-Point Calibration:*

10.2.1 Using the standard temperature values taken from Table 1 and the corresponding observed temperatures taken from experimental 9.1.2.5, calculate the slope and intercept using the following equations:

$$S = (TS_1 - TS_2)/(TO_1 - TO_2) \tag{2}$$

$$I = [(TO_1 \times TS_2) - (TS_1 \times TO_2)]/(TO_1 - TO_2) \tag{3}$$

where:

S = slope (nominal value = 1.00),
I = intercept,

TS_1 = reference transition temperature for standard 1 taken from Table 1,
TS_2 = reference transition temperature for standard 2 taken from Table 1,
TO_1 = observed transition temperature for standard 1 determined in Section 9, and
TO_2 = observed transition temperature for standard 2 observed in Section 9.

NOTE 8—*I* has the same units (that is, °C or K) as TS_1, TS_2, TO_1 and TO_2 which are consistent with each other. The value for *I* will be different depending upon the units used. *S* is a dimensionless number whose value is independent of the units of *I* and *T*.

10.2.2 *S* should be calculated to four significant figures and *I* should be calculated retaining all available decimal places.

10.3 *One-Point Calibration*—If the slope value determined above is sufficiently close to 1.000, only the intercept need be determined through a one-point calibration procedure.

$$I = TS_1 - TO_1 \tag{4}$$

10.4 Using the determined values for *S* and *I*, Eq 1 may be used to calculate the actual specimen transition temperature (*T*) from an observed transition temperature (*TO*). Values of T may be rounded to the nearest 0.1°C.

11. Report

11.1 The report shall include the following:

11.1.1 Complete identification and description of the reference materials used including source and purity,

11.1.2 Description of the instrument used for tests,

11.1.3 Statement of the mass, dimensions, geometry, and material of the specimen, material of the specimen holder and temperature program,

11.1.4 Identification of the sample atmosphere by gas flow rate, purity, and composition, and

11.1.5 Results of the calibration procedure including values for slope and intercept. Values of *S* and *I* shall be reported to the nearest 0.0001.

11.1.6 The specific dated version of this test method.

12. Precision and Bias

12.1 The precision of this test method was determined in an interlaboratory test in which 14 laboratories participated using four instrument models.[4] In this test, two highly pure metallic melting point calibration materials (indium and zinc) were used to obtain values for the calibration constants *S* and *I*. Using these constants, the melting point of a third highly pure material (lead), intermediate to these two calibration materials, was determined.

12.2 The following criteria may be used to judge the acceptability of actual sample temperature information determined using the two-point calibration procedure of this test method.

12.2.1 *Repeatability (Single Analyst)*—The standard deviation of results (each the average of duplicates), obtained by the same analyst on different days, has been estimated to be 0.41°C, with 11 degrees of freedom. Two such averages should be considered suspect (95 % confidence level) if they differ by more than 1.3°C.

12.2.2 *Reproducibility (Multilaboratory)*—The standard deviation of results (each the average of duplicates), obtained by the analysts in different laboratories, has been estimated to be 0.48°C, with 10 degrees of freedom. Two such averages should be considered suspect (95 % confidence limit) if they differ by more than 1.5°C.

12.3 The bias of actual sample temperature information determined by using the two-point calibration procedure of this test method was determined by comparing the results obtained for the intermediate temperature material with that judged to be the true value.[5]

12.3.1 The average deviation of results (each the average of four determinations) from the true value was 0.52°C, with 11 degrees of freedom. This represents better than a three-fold improvement over the case where a one-point calibration procedure was used (employing only indium as the calibration material and assuming the value of $S = 1.000$), a commonly used calibration procedure.

12.4 As a guide to the users of this test method, the following information, gleaned from the interlaboratory test, is offered.

12.4.1 Values for *S* averaged 1.1 % from unity for the 14 laboratories participating in this study. Instruments supplied by the Perkin Elmer Corporation[6] tended to offer values of *S* less than unity while those supplied by TA Instruments, Inc.,[7] tended to provide values of *S* greater than unity. Insufficient information was available from instruments offered by other suppliers to draw similar conclusions.

13. Keywords

13.1 calibration; differential scanning calorimetry; differential thermal analysis; melting temperature

[4] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:E37-1005. Contact ASTM Customer Service at service@astm.org.

[5] Rossini, F. D. *Pure Applied Chemistry*, Vol 22, 1970, p. 557

[6] Available from Perkin Elmer Corporation, 940 Winter Street, Waltham, MA 02451, http://www.perkinelmer.com.

[7] Available from TA Instruments, Inc., Corporate Headquarters, 159 Lukens Drive, New Castle, DE 19720, http://www.tainstruments.com.

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