Designation: E968 – 02 (Reapproved 2014)

Standard Practice for
Heat Flow Calibration of Differential Scanning Calorimeters[1]

This standard is issued under the fixed designation E968; 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 practice covers the heat flow calibration of differential scanning calorimeters over the temperature range from − 130°C to +800°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 Computer or electronic based instruments, techniques or data manipulation equivalent to this practice may also be used.

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 whoever uses this standard to consult and establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.* See also Section 7.

2. Referenced Documents

2.1 *ASTM Standards:*[2]

E473 Terminology Relating to Thermal Analysis and Rheology

E793 Test Method for Enthalpies of Fusion and Crystallization by Differential Scanning Calorimetry

E967 Test Method for Temperature Calibration of Differential Scanning Calorimeters and Differential Thermal Analyzers

E1142 Terminology Relating to Thermophysical Properties

3. Terminology

3.1 *Definitions*—Specific technical terms used in this practice are in accordance with Terminologies E473 and E1142.

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *coefficient of variation, n*—a measure of relative precision calculated as the standard deviation of a series of values divided by their average. It is usually multiplied by 100 and expressed as a percentage.

NOTE 1—The term quantitative differential thermal analysis refers to differential thermal analyzers that are designed to obtain quantitative or semiquantitative heat flow results. This procedure may also be used to calibrate such apparatus.

4. Summary of Practice

4.1 Differential scanning calorimeters measure heat flow (power) into or out of a test specimen and provide a signal output proportional to this measurement. This signal often is recorded as a function of a second signal proportional to temperature or time. If this heat flow signal is integrated over time, the resultant value is proportional to energy (or enthalpy or heat). To obtain the desired energy information, the observed instrument response (such as the area under the curve scribed) must be multiplied by a proportionality constant that converts the units of instrument output into the desired energy units. This proportionality constant is called the instrument calibration coefficient (E). The value and dimensions (units) of E depend upon the particular differential scanning calorimeter and recording system being used and, moreover, may vary with temperature.

4.2 This practice consists of calibrating the heat flow response of a differential scanning calorimeter (that is, determining the calibration coefficient) by recording the melting endotherm of a high-purity standard material (where the heat of fusion is known to better than ±1.5 % (rel)) as a function of time. The peak is then integrated (over time) to yield an area measurement proportional to the enthalpy of melting of the standard material.

4.3 Calibration of the instrument is extended to temperatures other than that of the melting point of the standard material through the recording of the specific heat capacity of a (second) standard material over the temperature range of interest. The ratio of the measured specific heat capacity at the temperature of interest to that of the temperature of calibration provides an instrument calibration coefficient at the new temperature.

4.4 Once the calibration coefficient at a given temperature is determined, it may be used to determine the desired energy value associated with an enthalpic transition in an unknown specimen at that temperature (see Test Method E793).

---

[1] This practice 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.

Current edition approved March 15, 2014. Published April 2014. Originally approved in 1983. Last previous edition approved in 2008 as E968 – 02 (2008). DOI: 10.1520/E0968-02R14.

[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.

Copyright © ASTM International, 100 Barr Harbor Drive, PO Box C700, West Conshohocken, PA 19428-2959. United States

5. Significance and Use

5.1 Differential scanning calorimetry is used to determine the heat or enthalpy of transition. For this information to be meaningful in an absolute sense, heat flow calibration of the apparatus or comparison of the resulting data to that of a known standard is required.

5.2 This practice is useful in calibrating the heat flow axis of differential scanning calorimeters or quantitative differential thermal analyzers for subsequent use in the measurement of transition energies and specific heat capacities of unknowns.

6. Apparatus

6.1 *Differential Scanning Calorimeter (DSC)*—The essential instrumentation required to provide the minimum differential scanning calorimetric capability for this method includes:

6.1.1 A *DSC test chamber,* composed of the following:

6.1.1.1 A furnace(s) to provide uniform controlled heating (cooling) of a specimen and reference to a constant temperature or at a constant rate with the temperature range of –100 to 600°C.

NOTE 2—This temperature range may be extended to higher and lower temperatures depending upon the capabilities of the apparatus.

6.1.1.2 A *temperature sensor,* to provide an indication of the specimen/furnace temperature to ±0.01 K.

6.1.1.3 A *differential sensor,* to detect a heat flow (power) difference between the specimen and reference equivalent to 1 μW.

6.1.1.4 A means of sustaining a *test chamber environment,* of an inert purge gas at a purge gas rate of 10 to 100 mL/min ± 5 mL/min.

NOTE 3—Typically, 99.9+ % pure nitrogen, argon or helium are employed when oxidation in air is a concern. Unless effects of moisture are to be studied, use of dry purge gas is recommended and is essential for operation at subambient temperatures.

6.1.2 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 between 1 and 35 K/min constant to ±1 % and at an isothermal temperature constant to ±0.1 K.

6.1.3 A *recording device,* either digital or analog, capable of recording and displaying the heat flow (DSC curve) signal versus temperature, displaying any fraction including the signal noise.

6.1.4 *Containers,* (pans, crucibles, vials, etc. and associated lids), that are inert to the specimen and reference materials and that are of suitable structural shape and integrity to contain the specimen and reference.

NOTE 4—Most containers require special tool(s) for opening, closing or sealing. The specific tool(s) necessary to perform this action also are required.

6.1.5 *Cooling capability,* to achieve and sustain cryogenic temperatures, to hasten cool down from elevated temperatures, or to provide constant cooling rates, or a combination thereof.

6.1.6 Computer and software capability to perform the mathematical treatments of this method including peak integration.

6.2 A *balance,* with capacity of 100 mg to weight specimens, or containers, or both, to ±1 μg,

7. Precautions

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

8. Reagents and Materials

8.1 For the temperature range covered by many applications, the melting transitions of the following greater-than-99.9 % pure material may be used for calibration.

	Melting Temperature, K[A]	Heat of Fusion, J/g[B]
Indium	429.75	28.58 ± 0.07

[A] Preston–Thomas, H., *Metrologia*, Vol 27, 1990, p. 3.

[B] Stolen, S., Gronvold, F., *Thermochimica Acta*, Vol 327, 1999, p.1.

8.2 *Sapphire,* ($\alpha - Al_2O_3$), 20 to 80 mg, solid disk.

9. Calibration

9.1 Perform any calibration procedures described by the manufacturer in the operations manual.

9.2 Perform a temperature signal calibration according to Practice E967.

10. Procedure

10.1 *Calibration at a Specific Temperature*—The following procedure is used to calibrate the heat flow response of the instrument with the same type specimen holder, heating rate, purge gas, and purge gas flow rate as will be used for specimen measurement. A dry nitrogen purge gas with a flow rate of 10 to 50 ± 5 mL/min is recommended. Other purge gases and rates may be used but shall be reported.

10.1.1 Place a 5 to 10 ± 0.001-mg weighed amount of melt transition calibration material into a clean specimen holder.

10.1.2 Seal the specimen holder with a lid, minimizing the free space between the specimen and the lid. Load the specimen into the instrument.

10.1.3 Allow the specimen to equilibrate at a temperature 30°C below the melting temperature.

10.1.4 Heat the specimen at 10°C/min through the endotherm until the baseline is reestablished above the melting endotherm. Record the accompanying thermal curve of heat flow versus time.

NOTE 5—Other heating rates may be used but shall be reported.

10.1.5 Cool and reweigh the specimen. Reject the data if mass losses exceed 1 % of the original mass or if there is evidence of reaction with the specimen holder.

10.1.6 Calculate the calibration coefficient at the temperature of measurement using the procedure described in Section 11. Duplicate determinations shall be made on different specimens and the mean value determined and reported.

10.2 *Calibration at Other Temperatures*—Once a calibration coefficient at a specific temperature has been obtained by the procedure in 10.1, extension of the calibration coefficient to other temperatures may be accomplished using the interpolative technique described below.

10.2.1 Select a temperature range for calibration of the instrument. The range should be at least 30°C below the lowest temperature of interest (to permit attainment of dynamic equilibrium) to 10°C above the highest temperature of interest and include the temperature of calibration established in 10.1.

10.2.2 Condition the sapphire calibration material and specimen holder by heating to the maximum temperature determined in 10.2.1 and holding for 2 min. Cool to room temperature and store in a desiccator until needed.

NOTE 6—Any volatilization (such as from absorbed moisture) from the calibration material during the experiment will invalidate the test.

10.2.3 Establish a baseline as follows:

10.2.3.1 Load the instrument with the specimen pan and lid (from 10.2.2) to be used in 10.2.5.

10.2.3.2 Establish the initial temperature conditions of the experiment (determined in 10.2.1) and equilibrate for 5 min.

10.2.3.3 Heat the specimen holder and lid at 10°C/min throughout the temperature range established in 10.2.1. Record the accompanying thermogram of heat flow versus temperature.

NOTE 7—Other heating rates may be used but shall be reported.

10.2.4 After cooling the specimen holder and lid to room temperature, introduce and weigh 20 to 70 mg of the sapphire heat capacity reference material from 10.2.2 to an accuracy of 0.01 mg.

10.2.5 Cover the specimen holder with the same lid minimizing the free space between the specimen and the lid. Load the specimen into the instrument.

10.2.6 Take the specimen to the initial temperature determined in 10.2.1 and allow to equilibrate for 5 min.

10.2.7 Heat the specimen at 10°C/min through the temperature range of test recording the accompanying thermal curve.

10.2.8 Calculate the calibration coefficient at any temperature of interest within the temperature range described in Section 11. Duplicate determination shall be made on the same specimen and the mean value determined and reported.

11. Calculation

11.1 Calculate the calibration coefficient at a specific temperature as follows:

11.1.1 Using the thermal curve obtained in 10.1, construct a baseline on the differential heat flow curve by connecting the two points at which the melting endotherm deviates from the baseline before and after the melt (see Fig. 1). Integrate this area as a function of time to achieve the melting endothermic peak area in mJ.

11.1.2 Calculate the experimental calibration coefficient at the melting temperature of the standard reference material as follows:

$$E = (H\ m)/(A) \tag{1}$$

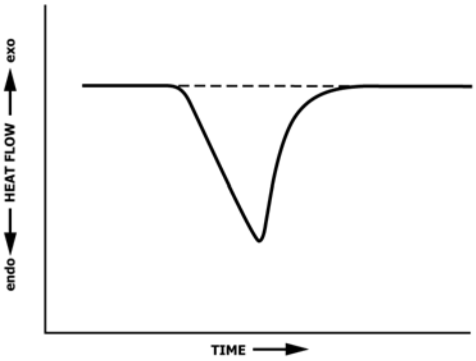

FIG. 1 Melting Endotherm

where:

E = calibration coefficient at the temperature of the melting endotherm,
H = enthalpy of fusion of the standard material, in J/g (mJ/g),
m = mass of the standard, in g, and
A = melting endotherm peak area, in mJ.

11.2 Calculate the calibration coefficient at other temperatures.

11.2.1 Measure the heat flow difference between the sapphire and baseline trace on the heat flow recorder axis in the thermal curve obtained in 10.2 at the temperature of interest T and the melting temperature T_s of the reference material. These values are $D\tau$ and D used in (Eq 2) (see Table 1 and Fig. 2).

11.2.2 Obtain specific heat capacity values of the sapphire at the temperature of interest (T) and at the melting temperature of the reference material (T_s) from Table 2. Interpolate between those values given in the table to obtain the specific heat capacity at the desired temperature. These values are $C\tau$ and C used in (Eq 2).

11.2.3 Calculate the calibration coefficient at temperature T as follows:

$$E\tau = E(C\tau\ D)/(C\ D\tau) \tag{2}$$

where:

$E\tau$ = calibration coefficient at temperature T,
E = calibration coefficient at the melting temperature of the standard reference material (T_s), as calculated in 11.1.2,
$C\tau$ = specific heat capacity of sapphire reference material at temperature of interest T, in J/(g · K),
C = specific heat capacity of the sapphire reference material at the melting temperature of the reference material (T_s), in J/(g · K),
D = difference in recorder heat flow deflection between blank and calibration runs at the melting temperature of the reference material (T_s), in mW, and
$D\tau$ = difference in recorder heat flow deflection between blank and calibration runs at the temperature of interest T, in mW.

NOTE 8—In cases where different specimen holders are used for the baseline and calibration runs, the difference in recorder heat flow deflections D and $D\tau$ may be corrected for small differences in specimen holder weight by adding the following value of ΔD to D and $D\tau$:

TABLE 1 Sapphire ($\alpha - Al_2O_3$) Specific Heat Capacity[A]

Temperature, K	Specific Heat Capacity, J/g·K	Temperature, K	Specific Heat Capacity, J/g·K
140	0.2739	630	1.1184
150	0.3133	640	1.1228
160	0.3525	650	1.1272
170	0.3912	660	1.1313
180	0.4290	670	1.1353
190	0.4659	680	1.1393
200	0.5014	690	1.1431
210	0.5356	700	1.1467
220	0.5684	710	1.1503
230	0.5996	720	1.1538
240	0.6294	730	1.1572
250	0.6577	740	1.1604
260	0.6846	750	1.1637
270	0.7102	760	1.1667
280	0.7344	770	1.1698
290	0.7574	780	1.1727
300	0.7792	790	1.1756
310	0.7999	800	1.1784
320	0.8194	810	1.1811
330	0.8380	820	1.1839
340	0.8555	830	1.1864
350	0.8721	840	1.1890
360	0.8878	850	1.1914
370	0.9027	860	1.1939
380	0.9168	870	1.1962
390	0.9302	880	1.1986
400	0.9429	890	1.2008
410	0.9550	900	1.2031
420	0.9665	910	1.2053
430	0.9775	920	1.2074
440	0.9879	930	1.2095
450	0.9978	940	1.2115
460	1.0073	950	1.2135
470	1.0164	960	1.2155
480	1.0250	970	1.2174
490	1.0332	980	1.2194
500	1.0411	990	1.2212
510	1.0486	1000	1.2230
520	1.0559	1010	1.2249
530	1.0628	1020	1.2266
540	1.0694	1030	1.2284
550	1.0758	1040	1.2301
560	1.0819	1050	1.2318
570	1.0877	1060	1.2335
580	1.0934	1070	1.2351
590	1.0988	1080	1.2367
600	1.1039	1090	1.2383
610	1.1090	1100	1.2400
620	1.1138		

[A] Archer, D. G., *Journal of Physical and Chemical Reference Data*, Vol 22, No. 8, 1993, pp. 1441–1453.

$$\Delta D = \frac{c_p \beta}{1000\, E} \left(W_c - W_b \right) \quad (3)$$

where:

c_p = specific heat of aluminum (or other specimen holder material of construction), in J/(g · K) for aluminum),

W_c = mass of the specimen holder for the calibration run, in g,

W_b = mass of the specimen holder for the blank run, in g, and

β = heating rate, in K/s (°C/s).

12. Report

12.1 The report shall contain the following:

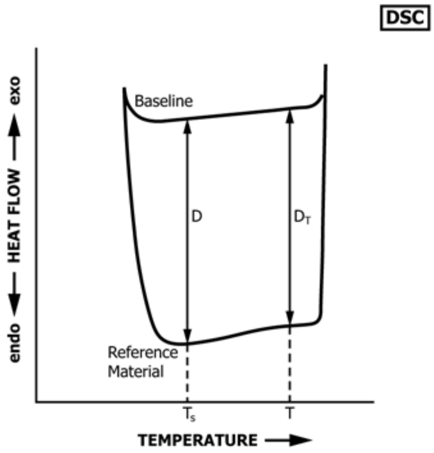

FIG. 2 Reference Material—Specific Heat Capacity

12.1.1 Complete identification and description of the reference materials used for the calibration, including source and manufacturer's code.

12.1.2 Description of the instrument used in the calibration.

12.1.3 Statement of the mass, dimensions, geometry, and material of the specimen holder, and the heating rate used.

12.1.4 Identification of the instrument purge by gas flow rate, purity and composition.

12.1.5 Calibration coefficient at the melting temperature of the standard and selected temperatures of interest.

12.1.6 The dated version of this standard used.

13. Precision and Bias

13.1 The precision of this practice was determined in an interlaboratory test in which thirteen laboratories participated using four instrument models. Based upon this test, the following conclusions are made:

13.1.1 *Repeatability (Single Analysis)*—The coefficient of variation of results (each the average of duplicate) for calibration coefficient derived from the melting endotherm of the indium, obtained by the same analyst on different days, has been estimated to be 0.94 % with 11 df.

13.2 The following criteria should be used for judging the acceptability of calibration coefficient values extended to temperatures other than that of the melting temperature of Indium (that is, 430 K):

13.2.1 *Repeatability (Single Analyst)*—The coefficient of variation of results (each the average of duplicates), obtained by the same analyst on different days, has been estimated to be 1.4 % with 18 df at temperatures within 265 K of the primary calibration temperature. Two such averages should be considered suspect (95 % confidence level) if they differ by more than 4.2 %.

13.2.2 *Reproducibility (Multilaboratory)*—The coefficient of variation of results (each the average of duplicates) obtained by analysts in different laboratories, has been estimated to be 2.7 % with 16 df at temperatures within 265 K of the primary calibration temperature. Two such averages should be considered suspect (95 % confidence level) if they differ by more than 8.2 %.

13.2.3 Repeatability and reproducibility appear to become poorer as the difference between the desired and primary calibration temperature increases. Beyond those limits stated previously, repeatability is anticipated to decrease by 0.7 % per each additional 100 K and reproducibility by 2.0 % per each additional 100 K.

13.3 An estimation of the accuracy of this procedure was obtained by comparing the heat of fusion values obtained for two high-purity metal samples using this calibration practice with values reported in the literature:

	Heat of Fusion (J/g)	
Material	Testing	Literature[4]
Lead	22.27 ± 0.68	23.08 ± 0.11
Zinc[5]	103.7 ± 2.9	108.09 ± 0.43

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/