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

This standard is issued under the fixed designation E 968; 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 Values given in SI units are to be regarded as the 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:*~~
~~E473Terminology Relating to Thermal Analysis~~ ASTM Standards: [2]
E 473 Terminology Relating to Thermal Analysis and Rheology
E 793 Test Method for ~~Heats~~Enthalpies of Fusion and Crystallization by Differential Scanning Calorimetry
E 967~~Practice for Temperature Calibration of Differential Scanning Calorimeters and Differential Thermal Analyzers~~[2] Test Method for Temperature Calibration of Differential Scanning Calorimeters and Differential Thermal Analyzers
E 1142 Terminology Relating to Thermophysical Properties

3. Terminology

3.1 *Definitions*— Specific technical terms used in this practice are in accordance with Terminologies ~~E474~~E 473 and E 1142.

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, ~~measuring~~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.

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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 E 793).

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[3]	Heat of Fusion, J/g[4]
~~Indium~~	~~429.8~~	~~28.42 ± 0.36~~
Indium	429.75	28.58 ± 0.07

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

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[3] Rossini, F. D., *Pure Applied Chemistry,* Vol 22, 1970, p. 557.
[3] Preston–Thomas, H., *Metrologia,*, Vol 27, 1990, p. 3.
[4] Hultgren, R. et al, *Selected Values of Thermodynamic Properties of the Elements,* American Society of Metals, Metals Park, OH, 1973.
[4] Stolen, S., Gronvold, F., Thermochimica Acta, Vol 327, 1999, p.1. E37

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 E 967.

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:

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