Standard Test Method for
Temperature Calibration on Cooling of Differential Scanning Calorimeters[1]

1. Scope

1.1 This test method covers the temperature calibration of differential scanning calorimeters on cooling using the difference between transition temperatures upon heating and cooling in the temperature range of 50 to 185°C. An offset in the indicated temperature between heating and cooling experiments, within this temperature range, may be used to provide temperature calibration on cooling at other temperature ranges.

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 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~~ *safety, health, and* ~~health~~*environmental practices and determine the applicability of regulatory limitations prior to use.* Specific precautionary statements are given in Section 6.

1.4 *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]

D3418 Test Method for Transition Temperatures and Enthalpies of Fusion and Crystallization of Polymers by Differential Scanning Calorimetry

E473 Terminology Relating to Thermal Analysis and Rheology

E794 Test Method for Melting And Crystallization Temperatures By Thermal Analysis

E928 Test Method for Purity by Differential Scanning Calorimetry

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

E1970 Practice for Statistical Treatment of Thermoanalytical Data

3. Terminology

3.1 Specific technical terms used in this test method are defined in Terminology E473.

4. Summary of Test Method

4.1 The temperature sensor of the DSC, used to determine the temperature of a transition, is located close to but external to the test specimen. This arrangement causes the indicated temperature to lead or lag the actual specimen temperature on heating/cooling causing the reported temperature to be higher on heating and lower on cooling than the actual specimen transition temperature. A DSC apparatus temperature, that has been calibrated for heating experiments, needs to be re-calibrated for cooling experiments. Such a calibration on cooling is performed using a liquid crystal material, the transition(s) for which are not subject to super-heating or super-cooling.

4.2 The transition temperature of a rapid, non-superheating and non-supercooling transition is determined upon heating and upon cooling. The difference between these two indicated temperatures provides an offset temperature value between heating and

cooling experiments at the indicated rate. This offset temperature value, when used with a precise temperature calibration upon heating, may serve as an instrument calibration function upon cooling.

5. Significance and Use

5.1 This test method is useful in calibrating the temperature signal of a differential scanning calorimeter for cooling experiments such as the determination of crystallization temperatures in Test Method D3418 and Test Method E794.

5.2 This test method may be used for research, development, analytical, specification acceptance, quality assurance, and control purposes.

6. Precautions

6.1 Toxic or corrosive effluents, or both, may be released when heating the material of this test method and may be harmful to personnel and to the apparatus.

7. Apparatus

7.1 *Differential Scanning Calorimeter (DSC)*—The essential instrumentation required providing the minimum differential scanning calorimeter capability for this test method includes:

7.1.1 *A DSC Test Chamber,* composed of:

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

7.1.1.2 *A Temperature Sensor,* that indicates specimen or furnace temperature to ±0.01 °C. ±0.01°C.

7.1.1.3 *A Differential Sensor,* to detect a heat flow difference (DSC) between the specimen and reference with a range of at least 100 mW readable to ±1 µW (DSC).

7.1.1.4 A means of sustaining a purge gas rate of 10 to 100 ± 5 mL/min in the test chamber.

NOTE 1—Typically inert purge gases that inhibit specimen oxidation are 99+ % pure nitrogen, argon or helium. Subambient operation requires dry purge gases. Dry gases are recommended for all experiments unless the effect of moisture is part of the study.

7.1.2 *A Temperature Controller,* capable of executing a specific temperature program by operating the furnace or furnaces between selected temperature limits at a rate of temperature change of 10 °C/min 10°C/min constant to within ±0.1°C/min or at an isothermal temperature constant to ±0.1°C.

7.1.3 *A Recording Device,* capable of recording and displaying fractions of the heat flow signal (DSC curve), including the signal noise, on the Y-axis versus fractions of temperature signal, including the signal noise, on the X-axis.

7.1.4 *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 requirements of this test method.

NOTE 2—DSC containers are commonly composed of aluminum or other inert material of high thermal conductivity. Aluminum has been tested and found compatible with the materials used in this standard. test method.

7.1.5 *Cooling Capability,* at constant cooling rates of up to 10°C/min in the temperature range of 185 to 50°C, to hasten cool down from elevated temperatures, or to sustain an isothermal subambient temperature, or both.

7.2 *A Balance,* to weigh specimen and/or containers to ±10 µg with a capacity of 100 mg or greater.

8. Calibration Materials

8.1 For the temperature range covered by many applications, the liquid crystal transitions of 99.8 to 99.9 % pure materials in Table 1 may be used for calibration. The calibrating liquid crystal materials[3] are known as M-24, BP-53 and BCH-52.

NOTE 3—The purity of these liquid crystal materials may be determined by Test Method E928 using the first liquid crystal transition prior to use (see Table 2).

8.2 The approximate heat of transitions for these samples is shown in Table 2. The enthalpy of transition for M-24 is so small that it is detectable only on the most sensitive DSC instrument.

8.3 The actual specimen used for this test should be premelted in the crucible for the lowest variance.

9. Calibration

9.1 Perform any temperature calibration procedures recommended by the manufacturer of the differential scanning calorimeter as described in the operations manual.

---

[3] The sole source of supply of these materials known to the committee at this time is EMD Chemicals Inc., 480 S. Democrat Road, Gibbstown, NJ 08027–1296. The part numbers for these chemicals are as follows: M-24 is pn 1.00008.9005, BP-53 is pn 1.00007.9005 and BCH-52 is pn 1.00006.9005. If you are aware of alternative suppliers, please provide this information to ASTM headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee, which you may attend.

TABLE 1 Transition Temperatures for Selected Liquid Crystal Calibration Materials

Liquid Crystal Material[A]	Transition Type[B]	Transition Temperature,[C]	
		K	°C
M-24	Cr → S_A	327.5	54.5
	S_A → N	340.2	67.1
BP-53	S_A → N	393.6	120.5
BCH-52	N → I	437.9	164.8

[A] M-24 = 4-Cyano-4'-octyloxybiphenyl
  BP-53 = 4-(4-Pentyl-cyclohexyl)-benzoic acid-4-propyl-phenyl ester
  BCH-52 = 4'-Ethyl-4-(4-propyl-cyclohexyl)-biphenyl
[B] Ch = Cholesteric
  Cr = Crystalline
  I = Isotropic liquid
  N = Nematic
  S_A = Smectic A
  S_C = Smectic C
  S_{C*} = Chiral smectic C
  S_{I*} = Smectic I*
  S_{J*} = Smectic J*
[C] The transition temperatures are dependent upon the purity of the liquid crystal material. These transition temperatures are those for 99.9+ mol % pure materials. ~~See Footnotes 5.~~

9.2 Perform the temperature calibration of the differential scanning calorimeter using ~~Practice~~ Test Method E967 and the heating rate of 10°C/min. Indium is recommended as at least one of the calibration materials.

Note 4—For the purposes of this ~~standard,~~ test method, temperature calibration on heating is performed at 10°C/min and on cooling at 10°C/min. Other rates for either heating or cooling may be used but shall be reported.

10. Procedure

10.1 Select a suitable calibrating liquid crystal material from Table 1.

10.2 Into a clean, tared specimen container weigh 3.0 to 5.0 mg of the liquid crystal calibration material.

Note 5—Larger specimen masses should not be used, as they will result in increased thermal lag effects.

10.3 Load the specimen into the test chamber, purge with dry nitrogen (or other inert purge gas) at the flow rate to be used for the subsequent application.

10.4 Heat the specimen rapidly to the maximum temperature for the material shown in Table 2 and hold isothermally for 1 min.

Note 6—The transition temperature to the isotropic phase depends upon the calibration material selected and its purity.
Note 7—The samples are not stable above the maximum temperature listed in Table 2. Discard the specimen and make a new one if it has been exposed to a temperature above the maximum temperature.

10.5 Cool the specimen at 10°C/min to 30°C and hold isothermally for 1 min. Record the resultant thermal curve upon cooling (see Note 4).

Note 8—Liquid crystalline transitions are very narrow. Data collection rates of one data point every 0.05°C (preferably every 0.01°C) shall be used to achieve the precision required.

10.6 Heat the specimen at ~~10 °C/min to 30 °C~~ 10°C/min to 30°C above the temperature of the transition to the isotropic phase as indicated in Table 1. Record the resulting thermal curve upon heating (see Note 4).

10.7 From the resultant thermal curve upon cooling from 10.5, determine the extrapolated onset temperature (T_c) to ±0.01°C for each transition in Table 2 observed as illustrated in Fig. 1.

Note 9—Use only a transition where the signal returns to baseline before the transition onset.
Note 10—Retain all available significant figures for these calculations and round to the final result to the number of significant figures described in section 13

10.8 From the resultant thermal curve upon heating from 10.6, determine the extrapolated onset temperature (T_h) to ± 0.01°C for each transition in Table 2 observed as illustrated in Fig. 2 (see Note 9).~~Fig. 3Fig. 4Fig. 5Fig. 6~~

10.9 Calculate the offset temperature (ΔT) for each liquid crystal transition to ±0.01°C according to 11.1.

11. Calculation

11.1 Calculate the offset temperature (ΔT) to ±0.01°C for each transition according to Eq 1:

$$\Delta T = T_h - T_c \tag{1}$$

TABLE 2 Temperatures of the Crystal to First Liquid Crystal Transition of the Calibrating Materials

| Liquid Crystal Material[A] | Transition Type[B] | Temperature,[C] | | Enthalpy | Maximum Temperature |
		K	°C	J/g	°C
M-24	$S_A \rightarrow N$	340.2	67.1	0.08	97
BP-53	$S_A \rightarrow N$	393.6	120.5	0.6	130
BCH-52	$N \rightarrow I$	437.9	164.8	1.3	184

[A] M-24 = 4-Cyano-4'-octyloxybiphenyl

BP-53 = 4-(4-Pentyl-cyclohexyl)-benzoic acid-4-propyl-phenyl ester BCH-52 = 4'-Ethyl-4-(4-propyl-cyclohexyl)-biphenyl

[B] Ch = Cholesteric

Cr = Crystalline

I = Isotropic liquid

N = Nematic

S_A = Smectic A

S_C = Smectic C

S_{C^*} = Chiral smectic C

S_{I^*} = Smectic I*

S_{J^*} = Smectic J*

[C] The transition temperatures are dependent upon the purity of the liquid crystal material. These transition temperatures are those for 99.9+ mol % pure materials. See Footnotes 5, 6, and 7.
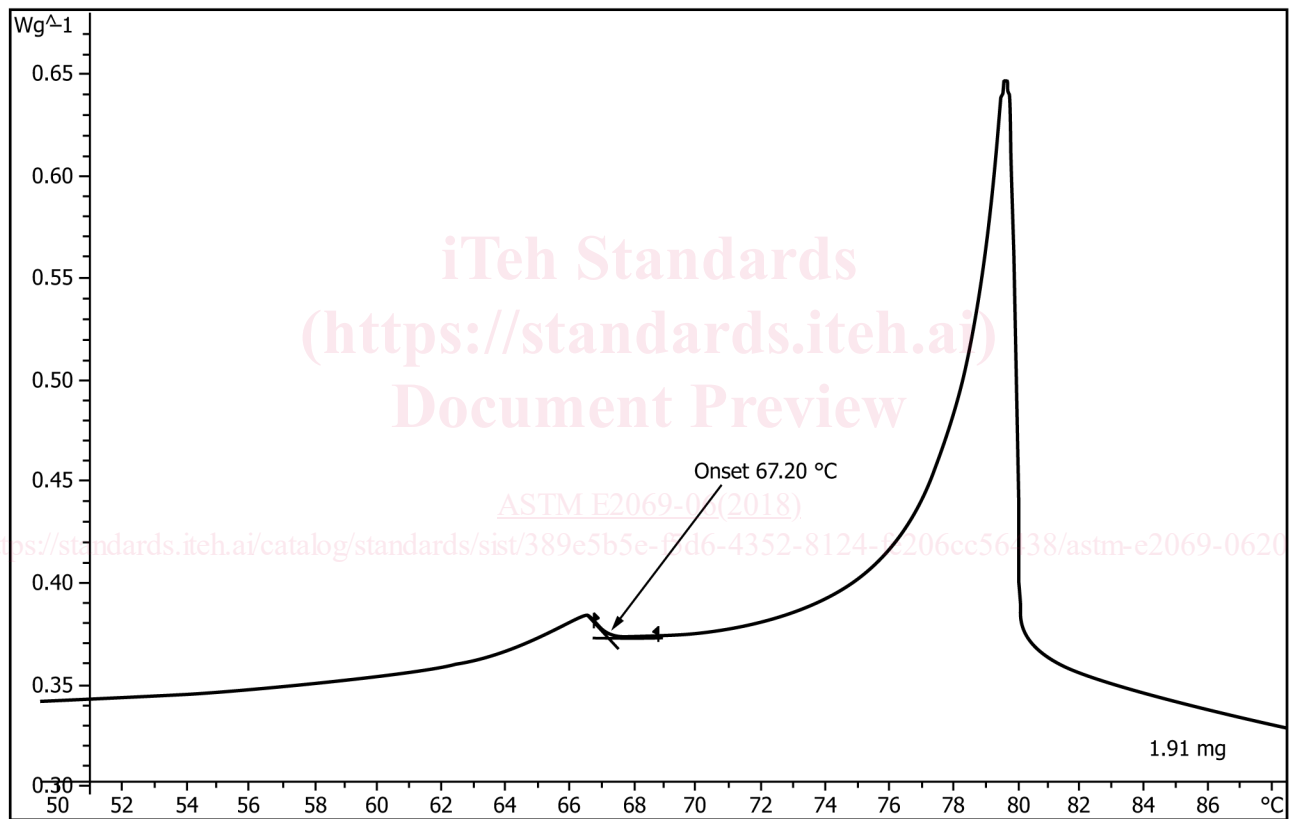

FIG. 1 Cooling Curve for M-24

where:

T_h = the transition temperature of a specific liquid crystal transition observed on heating,

T_c = the temperature of the same transition measured on cooling, and

ΔT = the offset temperature for the specific liquid crystal transition.

11.2 In an application cooling experiment, where the differential scanning calorimeter has been calibrated upon heating, the temperature of a cooling transition within or without the 50 to ~~185 °C~~ 185°C temperature range may be determined using Eq 2:

$$T_x = T_o + \Delta T \tag{2}$$

where:

T_x = the temperature of the unknown transition upon cooling,

T_o = the observed temperature upon cooling, and

ΔT = the offset temperature determined for the specific heating rate-cooling rate combination determined in this test method.