Designation: E 2069 – 00

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

This standard is issued under the fixed designation E 2069; 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 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 60 to 140 °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 SI units are the 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 and health practices and determine the applicability of regulatory limitations prior to use.* Specific precautionary statements are given in Section 6.

2. Referenced Documents

2.1 *ASTM Standards:*

D 3418 Test Method for Transition Temperatures of Polymers by Thermal Analysis[2]

E 473 Terminology Relating to Thermal Analysis[3]

E 794 Test Method for Melting and Crystallization Temperatures by Thermal Analysis[3]

E 928 Test Method for Determination of Purity by Differential Scanning Calorimetry[3]

E 967 Practice for Temperature Calibration of Differential Scanning Calorimeters and Differential Thermal Analyzers[3]

E 1970 Practice for Statistical Treatment of Thermoanalytical Data[3]

3. Terminology

3.1 Specific technical terms used in this test method are defined in Terminology E 473.

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 recalibrated 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 D 3418 and Test Method E 794.

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:

[1] This test method is under the jurisdiction of ASTM Committee E-37 on Thermal Measurements and is the direct responsibility of Subcommittee E37.01 on Test Methods and Recommended Practices.

Current edition approved March 10, 2000. Published June 2000.

[2] *Annual Book of ASTM Standards*, Vol 08.02.

[3] *Annual Book of ASTM Standards*, Vol 14.02.

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/furnace temperature to ±0.01 °C.

7.1.1.3 *A Differential Sensor*, to detect heat flow (power) difference between the specimen and reference equivalent to 10 µW.

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*, operating the furnace(s) between selected temperature limits, capable of controlling the rate of temperature change of 10 °C/min constant to ± 0.1 °C/min or at an isothermal temperature constant to ± 0.2 °C.

7.1.3 *A Recording Device*, digital or analog, 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, etc. and lids) that are inert to the specimen and reference materials of suitable structural shape and integrity to contain the specimen and reference material.

7.1.5 *Cooling Capability*, at constant cooling rates of up to 10 °C/min in the temperature range of 140 to 60 °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[4] are known as CE-3 {(+)-4-n-hexyloxyphenyl 4'-(2"-methylbutyl)-biphenyl-4-carboxylate}(CAS no. 62614-61-3), CE-8 {(+)-4(2'-methylbutyl)phenyl 4'-n-octylbiphenyl-4-carboxylate} and LC-1 {N-(4-n-octyloxy-2-hydroxybenzal)4'-n-butylaniline}.

NOTE 2—The purity of these liquid crystal materials may be determined by Test Method E 928 using the first liquid crystal transition prior to use (see Table 2).

[4] The sole source of supply of these materials known to the committee at this time is Chromophore, Inc., 2307 Spring Branch Road, Huntsville AL 35801. 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
CE-3	$S_{C^*} \rightarrow$ Ch	352.0	78.8
	Ch → I	436.7	163.5
CE-8	$S_{J^*} \rightarrow S_{I^*}$	337.1	63.9
	$S_{I^*} \rightarrow S_{C^*}$	342.4	69.2
	$S_A \rightarrow$ Ch	408.0	134.8
	Ch → I	413.9	140.7
LC-1	$S_C \rightarrow$ N	342.6	69.4
	N → I	362.4	89.4

[A] CE-3 = {(+)-4-n-hexyloxyphenyl 4′-(2″-methylbutyl)-biphenyl-4-carboxylate}
CE-8 = {(+)-4(2′-methylbutyl)phenyl 4′-n-octylbiphenyl-4-carboxylate}
LC-1 = {N-(4-n-octyloxy-2-hydroxybenzal)4′-n-butylaniline}
[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.

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

Liquid Crystal Material[A]	Transition Type[B]	Temperature,[C] K	°C
CE-3	Cr → S_{C^*}	339.2	66.0
CE-8	Cr → S_{J^*}	329.0	55.8
LC-1	Cr → S_C	312.4	39.2

[A] CE-3 = {(+)-4-n-hexyloxyphenyl 4′-(2″-methylbutyl)-biphenyl-4-carboxylate}
CE-8 = {(+)-4(2′-methylbutyl)phenyl 4′-n-octylbiphenyl-4-carboxylate}
LC-1 = {N-(4-n-octyloxy-2-hydroxybenzal)4′-n-butylaniline}
[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.

9. Calibration

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

9.2 Perform the temperature calibration of the differential scanning calorimeter using Practice E 967 and the heating rate of 10 °C/min. Indium is recommended as at least one of the calibration materials.

NOTE 3—For the purposes of this standard, 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.

NOTE 4—CE-3 and LC-1 may be used at all heating/cooling rates