Standard Test Method for
Determining Specific Heat Capacity by Differential Scanning Calorimetry[1]

This standard is issued under the fixed designation E1269; 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 determination of specific heat capacity by differential scanning calorimetry.

1.2 This test method is generally applicable to thermally stable solids and liquids.

1.3 The normal operating range of the test is from − 100 to 600 °C. The temperature range can be extended, depending upon the instrumentation and specimen holders used.

1.4 The values stated in SI units are to be regarded as the standard.

1.5 Computer or electronic-based instrumentation, techniques, or data treatment equivalent to this test method may be used.

NOTE 1—Users of this test method are expressly advised that all such instruments or techniques may not be equivalent. It is the responsibility of the user of this test method to determine equivalency prior to use.

1.6 This method is similar to ISO 11357–4, but contains additional methodology not found in that method. Additionally, ISO 11357–4 contains practices not found in this standard. This method is similar to Japanese Industrial Standard K 7123, but contains additional methodology not found in that method.

1.7 *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 9.

2. Referenced Documents

2.1 *ASTM Standards:*[2]

E473 Terminology Relating to Thermal Analysis and Rheology

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

E968 Practice for Heat Flow Calibration of Differential Scanning Calorimeters

E1142 Terminology Relating to Thermophysical Properties

2.2 *ISO Standard:*

ISO 11357–4 Plastics: Differential Scanning Calorimetry (DSC)- Determination of Specific Heat Capacity[3]

2.3 *Japanese Industrial Standard:*

K 7123 Testing Methods for Specific Heat Capacity of Plastics[3]

3. Terminology

3.1 *Definitions*—Technical terms used in this test method are described in Terminologies E473 and E1142.

4. Summary of Test Method

4.1 This test method consists of heating the test material at a controlled rate in a controlled atmosphere through the region of interest. The difference in heat flow into the test material and a reference material or blank due to energy changes in the material is continually monitored and recorded.

5. Significance and Use

5.1 Differential scanning calorimetric measurements provide a rapid, simple method for determining specific heat capacities of materials.

5.2 Specific heat capacities are important for reactor and cooling system design purposes, quality control, and research and development.

6. Interferences

6.1 Since milligram quantities of specimen are used, it is essential that specimens are homogeneous and representative.

6.2 The occurrence of chemical changes or mass loss on heating during the measurement may invalidate the test. Therefore, the temperature range and specimen holders should be chosen so as to avoid these processes.

6.3 Water samples have a special interference. The large heat of evaporation causes the specific heat capacity to be too large if there is too much head space in the sealed crucible. Completely fill the crucible for most accurate results.

7. Apparatus

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

7.1.1 *DSC Test Chamber,* composed of the following:

7.1.1.1 *Furnace(s),* to provide uniform controlled heating (cooling) of a specimen and reference to a constant temperature or at a constant rate within the applicable –100 to 600 °C temperature range of this test method.

7.1.1.2 *Temperature Sensor,* to provide an indication of the specimen temperature to ± 10 mK (0.01 °C).

7.1.1.3 *Differential Sensor,* to detect heat flow difference between the specimen and reference equivalent to 1 µW.

7.1.1.4 A means of sustaining a test chamber environment of inert purge gas at a purge flow rate of 10 to 50 mL/min ± 5 mL/min.

Note 2—Typically, 99+ % pure nitrogen, argon, or helium are employed when oxidation in air is a concern. Use of dry purge gas is recommended and is essential for operation at subambient temperatures.

7.1.2 *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 to 20 °C/min constant to ± 0.1 °C/min or at an isothermal temperature constant to ± 0.1 °C.

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

7.1.4 While not required, the user may find useful software to perform the mathematical treatments described in this test method.

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

7.1.6 Cooling capability to hasten cool down from elevated temperatures, to provide constant cooling rates of up to 10 °C/min, to achieve subambient operation, or to sustain an isothermal subambient temperature, or a combination thereof.

7.2 *Balance,* with a capacity of 100 mg or greater to weigh specimens or containers, or both, to ± 10 µg.

8. Reagents and Materials

8.1 Specific heat capacity standard: synthetic sapphire disk, 10 to 100 mg.

Note 3—Interlaboratory studies indicate that physical forms of the synthetic sapphire other than disks give lower precision and greater bias in the results.

9. Hazards

9.1 *Safety Precautions*—If a specimen is heated to decomposition, toxic or corrosive products may be released.

9.2 *Technical Precautions:*

9.2.1 The same heating rate should be used for both the calibration and specimen runs.

9.2.2 Precision of heating rate, placement of the specimen holder, use of flat specimen holders, and the establishment of equilibrium are essential. Instrument settings should not be adjusted once a specific heat capacity calibration has been performed.

10. Sampling

10.1 Powdered or granular specimens should be mixed prior to sampling and should be sampled by removing portions from various parts of the container. These portions, in turn, should be combined and mixed to ensure a representative specimen for the determinations.

10.2 Liquid specimens may be sampled directly after stirring. Make sure the crucible is as full as possible if the sample is water or aqueous. Do not exceed the pressure limit for the crucible.

10.3 Solid specimens may be sampled by cutting or slicing with a clean knife or razor blade. Sample uniformity should be ascertained, since segregation within the solid is possible.

Note 4—Solid specimens should be so sampled as to maximize contact with the surface of the specimen holder.

10.4 Samples are usually analyzed as received. If some heat or mechanical treatment is applied to the specimen prior to analysis, this treatment should be noted in the report.

11. Calibration

11.1 Specific heat capacity is a quantitative measurement of energy made as a function of temperature. Thus, the instrument used in its measurement must be calibrated in both the temperature and heat flow modes. Since specific heat capacity is not a rapidly changing function of temperature, the instrument's temperature mode is ordinarily calibrated and checked only occasionally. The heat flow information, however, is much more critical and becomes an integral part of the specific heat capacity measurement through the use of a reference material.

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

11.3 Perform a temperature calibration for the apparatus using Practice E967.

11.4 Perform a heat flow calibration for the apparatus using Practice E968.

11.5 *Heat Flow Calibration:*

11.5.1 Synthetic sapphire disk (α-aluminum oxide; alumina) is recommended as a heat flow calibration standard for specific heat capacity measurements for both heating and cooling

experiments. Specific heat capacity values for synthetic sapphire are given in Table 1.

NOTE 5—It is possible to use other standard materials or other physical forms of synthetic sapphire, but their use should be noted in the report. The potential adverse impact of increased interfacial resistance encountered with granular/textured samples may be minimized with the use of a powdered synthetic sapphire standard. It is preferred that the physical form of the sample be similar to that of the standard. Synthetic sapphire is usually available from your DSC supplier.

11.5.2 The heat flow calibration may be performed at some regular interval or prior to every specific heat capacity determination or test specimens.

NOTE 6—A frequency of calibration of at least once a day is recommended. Other time intervals may be selected for heat flow calibration but should be noted in the report.

11.5.3 If the heat flow calibration is performed at a regular interval, the calorimetric sensitivity, E, may be calculated using the specific heat capacity values for synthetic sapphire given in Table 1 and the following equation:

$$E = [b/(60 \cdot Dst)] [Wst \cdot Cp(st) + \Delta W \cdot Cp(c)] \qquad (1)$$

Refer to Section 13 for the procedure and Section 14 for the list of symbols.

11.5.4 If the heat flow calibration is performed prior to every specific heat capacity determination, it is unnecessary to calculate the calorimetric sensitivity, E. Refer to Section 13 for the procedure.[4]

12. Conditioning

12.1 Specimens and specimen holders for specific heat capacity determinations may be handled in ordinary laboratory environments for screening or qualitative measurements. However, if quantitative data are needed over a wide temperature range, specimen conditioning may be required. Specimens which will be exposed to low temperatures should be protected from moisture. Specimens that will be exposed to very high temperatures should be protected from the effects of oxidation.

12.2 Any volatile specimens suspected of being sensitive to moisture or oxidation should be hermetically sealed in a dry, inert environment. All materials which will come in contact with the specimen should also be purged in a dry, inert environment. Vacuum degassing of specimens to be heated to a very high temperature is recommended.

12.3 Conditioning of nonvolatile specimens run in crimped lid or open pans may be accomplished in the DSC apparatus, using the inert purge stream of the instrument. This conditioning procedure will not protect specimens that are hermetically sealed under normal laboratory atmospheric conditions.

12.4 The specimen should be held at the starting temperature for several minutes before initiation of the temperature program. An equilibrium time of four minutes is suggested. However, other equilibrium times may be used but shall be reported.

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[4] The boldface numbers in parentheses refer to the list of references at the end of this standard.

13. Procedure

13.1 *Reference Material*—Synthetic sapphire.

13.1.1 Purge the DSC apparatus with dry nitrogen (or other inert gas) at a flow rate of 10 to 50 ± 5 mL per min throughout the experiment.

13.1.2 Weigh a clean, empty specimen holder plus lid to a precision of ±0.01 mg. Record as the tare weight.

13.1.3 Position the empty specimen holder plus lid and a reference specimen holder plus lid (weight-matched, if possible) in the DSC apparatus.

NOTE 7—The same reference specimen holder + lid should be used for the sapphire standard run and for the test specimen run.

13.1.4 Heat or cool the DSC test chamber to the initial temperature for the experiment at 20 °C/min.

13.1.5 Hold the DSC test chamber isothermally at the initial temperature for at least 4 min to establish equilibrium. Record this thermal curve (refer to 12.4).

13.1.6 Heat the test specimen from the initial to final temperature at a rate of 20 °C/min. Continue to record the thermal curve.

NOTE 8—The precision of this test method is enhanced by this high heating rate. Other heating rates may be used but shall be reported.

13.1.7 Record a steady-state isothermal baseline at the upper temperature limit. Refer to 12.4.

13.1.7.1 Terminate the thermal curve after this period.

13.1.7.2 Cool the DSC test chamber to ambient temperature.

13.1.8 Place the sapphire standard into the same specimen holder plus lid used in 13.1.2.

13.1.9 Weigh sapphire standard and specimen holder plus lid to a precision of ±0.01 mg and record the weight.

13.1.10 Follow 13.1.4 – 13.1.7.

NOTE 9—The procedure (13.1.1 – 13.1.9) may be performed at some regular interval, or prior to every specific heat capacity determination of test specimens. Refer to 11.5.

13.2 Unknown Specimens—13.1.1 – 13.1.7.

NOTE 10—Calculations are simplified if the same specimen holder is used for the empty specimen holder and the specimen plus specimen holder scans. In cases where two different specimen holders have to be used, a correction for the difference in weights of the two specimen holders can be made. Refer to 14.1.

13.2.1 Place the test specimen (after conditioning, if necessary) into the empty specimen holder plus lid.

NOTE 11—The specimen size and the instrument sensitivity should be adjusted to give optimum displacement to improve the precision of the measurement. Masses of about 5 to 15 mg for organic liquids and solids and 20 to 50 mg for inorganic specimens are recommended. Low bulk density specimens may be compressed into pellets or melted (if stable) and charged as liquids.

13.2.2 Weigh the specimen plus specimen holder plus lid to a precision of ±0.01 mg and record the weight.

NOTE 12—Volatile specimens should be charged, hermetically sealed, and the gross weight recorded. Nonvolatile specimens should be weighed after crimping.

13.2.3 Repeat 13.1.3 – 13.1.7.

TABLE 1 Sapphire (α – Al₂O₃) Specific Heat Capacity[A]

Temperature		Specific Heat Capacity
(°C)	(K)	J/(g*K)
−123.15	150	0.3133
−113.15	160	0.3525
−103.15	170	0.3912
−93.15	180	0.4290
−83.15	190	0.4659
−73.15	200	0.5014
−63.15	210	0.5356
−53.15	220	0.5684
−43.15	230	0.5996
−33.15	240	0.6294
−23.15	250	0.6577
−13.15	260	0.6846
−3.15	270	0.7102
6.85	280	0.7344
16.85	290	0.7574
26.85	300	0.7792
36.85	310	0.7999
46.85	320	0.8194
56.85	330	0.8380
66.85	340	0.8556
76.85	350	0.8721
86.85	360	0.8878
96.85	370	0.9027
106.85	380	0.9168
116.85	390	0.9302
126.85	400	0.9429
136.85	410	0.9550
146.85	420	0.9666
156.85	430	0.9775
166.85	440	0.9879
176.85	450	0.9975
186.85	460	1.0074
196.85	470	1.0164
206.85	480	1.0250
216.85	490	1.0332
226.85	500	1.0411
236.85	510	1.0486
246.85	520	1.0559
256.85	530	1.0628
266.85	540	1.0694
276.85	550	1.0758
286.85	560	1.0819
296.85	570	1.0877
306.85	580	1.0934
316.85	590	1.0988
326.85	600	1.1040
336.85	610	1.1090
346.85	620	1.1138
356.85	630	1.1184
366.85	640	1.1228
376.85	650	1.1272
386.85	660	1.1313
396.85	670	1.1353
406.85	680	1.1393
416.85	690	1.1431
426.85	700	1.1467
446.85	720	1.1538
466.85	740	1.1605
486.85	760	1.1667
506.85	780	1.1727
526.85	800	1.1784
546.85	820	1.1839
566.85	840	1.1890
586.85	860	1.1939
606.85	880	1.1986
626.85	900	1.2031
636.85	910	1.2053
646.85	920	1.2074
666.85	940	1.2116
686.85	960	1.2155
706.85	980	1.2194
726.85	1000	1.2230

[A] See Ref (1).[4]

TABLE 2 Aluminum Specific Heat Capacity[A]

Temperature		Specific Heat Capacity
(°C)	(K)	J/(g*K)
-123.15	150	0.684
-113.15	160	0.710
-103.15	170	0.734
-93.15	180	0.754
-83.15	190	0.773
-73.15	200	0.789
-63.15	210	0.804
-53.15	220	0.818
-43.15	230	0.831
-33.15	240	0.843
-23.15	250	0.853
-13.15	260	0.863
-3.15	270	0.873
6.85	280	0.882
16.85	290	0.890
26.85	300	0.897
76.85	350	0.930
126.85	400	0.956
176.85	450	0.978
226.85	500	0.997
276.85	550	1.016
326.85	600	1.034
376.85	650	1.052
426.85	700	1.073
476.85	750	1.098
526.85	800	1.128

[A] Calculated from a least-square representation of the measured heat capacity and enthalpy increment values from: Downie, D.B.; Martin, J.F., Giauque, W.F.; Meads, P.F.; *J Chem. Thermodynam,*12, 779–786 (1980) and Ditmars, D.A.; Plint, C.A.; Shukla, R.C. *Int. J. Thermophys*, 6, 499–515 (1985). These results are to be used for crucibles made of pure aluminum. Crucibles made from an alloy of aluminum may be different.

13.2.4 Reweigh the specimen holder plus specimen. If a mass loss ≥0.3 % of the initial mass occurred, the measurement is invalid. Any change in mass should be noted in the report.

14. Calculation

14.1 Measure the distance, *Dst*, between the empty specimen holder and sapphire standard at temperature, *T*. Refer to Fig. 1.

14.2 Measure the distance, *Ds*, between the empty specimen holder and test specimen also at temperature, *T*. Refer to Fig. 1.

14.3 If the heat flow calibration is performed at a regular interval (Refer to 11.5.3), the calorimetric sensitivity, *E*, may be calculated using the specific heat capacity values for the synthetic sapphire given in Table 1 and the following equation:

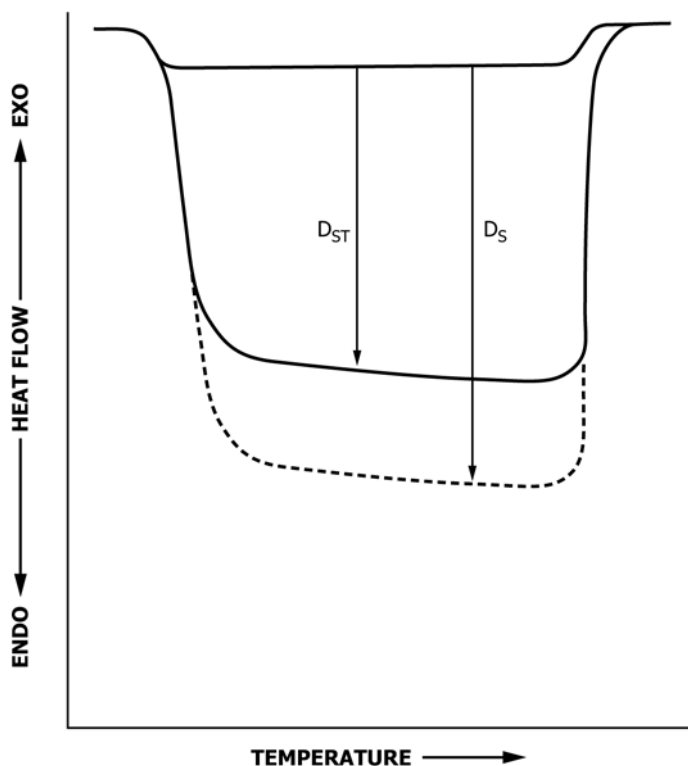$$E = [b/(60 \cdot Dst)][Wst \cdot Cp(st) + \Delta W \cdot Cp(c)] \qquad (2)$$

FIG. 1 Specific Heat Capacity Thermal Curves of Standard Sapphire, and Unknown Specimens

where:

b = heating rate, °C/min,
$Cp(st)$ = specific heat capacity of the sapphire standard, $J/(g*K)$,
$Cp(c)$ = specific heat capacity of the specimen holder, $J/(g*K)$,
E = calorimetric sensitivity of the DSC apparatus,
Dst = vertical displacement between the specimen holder and the sapphire DSC thermal curves at a given temperature, mW,
Wst = mass of sapphire, mg, and
ΔW = difference in mass between the empty specimen holder and the standard specimen holder, mg, in cases where two sealed specimen holders have to be used or in cases where the empty specimen holder is not also used as the standard specimen holder.

NOTE 13—If W is ≤0.1 % of the specimen weight, the second correction term on the right hand side of Eq 1 may be neglected.

14.3.1 Using calorimetric sensitivity, E, calculated in 14.3, calculate the specific heat capacity of the test specimen as follows:

$$Cp(s) = \frac{60 \cdot E \cdot Ds}{Ws \cdot b} - \frac{\Delta W \cdot Cp(c)}{Ws} \qquad (3)$$

where:

$Cp(s)$ = specific heat capacity of the specimen, $J/(g*K)$,
Ds = vertical displacement between the specimen holder and the specimen DSC thermal curves at a given temperature, mW,

ΔW = difference in mass between the empty specimen holder and the test specimen holder if the same holder is not used for both runs.

Other symbols are defined in 14.3.

14.4 If the heat flow calibration is performed prior to every specific heat capacity determination (Refer to 11.5.4), calculate the specific heat capacity as follows, assuming the specimen, sapphire standard, and empty specimen holders are weight-matched to within 0.1 % of the sample weight:

$$Cp(s) = Cp(st) \cdot \frac{Ds \cdot Wst}{Dst \cdot Ws} \qquad (4)$$

where:

$Cp(s)$ = specific heat capacity of the specimen, $J/(g*K)$,
$Cp(st)$ = specific heat capacity of the sapphire standard, $J/(g*K)$,
Ds = vertical displacement between the specimen holder and the specimen DSC thermal curves at a given temperature, mW,
Dst = vertical displacement between the specimen holder and the sapphire DSC thermal curves at a given temperature, mW, and
Ws = mass of specimen, mg Wst = mass of sapphire standard, mg.

15. Report

15.1 Report the following information:

15.1.1 Complete identification and description of the test specimen, including the source and manufacturer's code,

15.1.2 Description of the apparatus used for the test method, including the manufacturer's name and model number,

15.1.3 Description of the data analysis program or software, if used for data acquisition and calculation,

15.1.4 Statement of the material, dimensions, and geometry of the specimen holders,

15.1.5 Statement of the specimen thermal history, conditioning (if any), and atmosphere under which the specimen was sealed,

15.1.6 Statement of the standard used for heat flow calibration, if other than synthetic sapphire,

15.1.7 Statement of the frequency of heat flow calibration,

15.1.8 Statement of the equilibrium times, if other than four minutes. Refer to 12.4,

15.1.9 Statement of the change in mass, if any, as a result of the specific heat capacity measurement. Refer to 13.2.4,

15.1.10 Statement of the mass of all specimen holders, if not weight-matched,

15.1.11 Statement of the scan rate used,

15.1.12 Statement identifying the purge gas atmosphere by flow rate, purity, and composition,

15.1.13 Specific heat capacity in $J/(g*K)$. Indicate whether the value is a single measurement at a series of temperatures or the mean value for replicates determined on separate specimens, and

15.1.14 Statement of the temperature(s) at which the specific heat capacity determination was performed.

15.1.15 The specific dated version of this method used.

16. Precision and Bias

16.1 An interlaboratory study was conducted in 1990 in which seven laboratories test three materials (diphenyl ether, NIST 1475 linear polyethylene and indium metal) over the temperature range from 40 to 80 °C and determined the specific heat capacity at 67 °C.

16.2 *Precision:*

16.2.1 Within laboratory variability may be described using the repeatability value (*r*) obtained by multiplying the relative standard deviation by 2.8. A mean repeatability value of *r* = 6.2 % was obtained. The repeatability value estimates the 95 % confidence limit.

16.2.2 Between laboratory variability may be described using the reproducibility value (*R*) obtained by multiplying the relative standard deviation by 2.8. A mean reproducibility value of *R* = 8.4 % was obtained. The reproducibility value estimates the 95 % confidence limit.

16.3 *Bias:*

16.3.1 An estimation of bias is obtained by comparing the mean specific heat capacity values obtained for each material to their values reported in the literature. That is, bias = (mean specific heat capacity) - (literature value).

16.3.1.1 The mean specific heat capacity value for diphenyl ether was 1.70 *J/(g*K)* compared with a literature value of 1.683 *J/(g*K)* (**2,3**). This is a bias of +0.95 %.

16.3.1.2 The mean specific heat capacity value for the NIST linear polyethylene was 2.18 *J/(g*K)* compared with a certified value of 2.200 *J/(g*K)* (**4**). This is a bias of –1.1 %.

16.3.1.3 The mean specific heat capacity value for indium metal was 0.243 *J/(g*K)* versus literature values of 0.241 *J/(g*K)* and 0.239 *J/(g*K)* (**5,6**). This is a bias of either +0.8 or +1.8 depending on which reference is used (**7,8**).

NOTE 14—The precision and bias developed from the results of the interlaboratory test of this test method are applicable only for the temperature range studied. Some differences may be encountered when applying this test method at other temperature intervals included within the scope of this test method.

REFERENCES

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