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

This standard is issued under the fixed designation E2716; 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 describes the determination of specific heat capacity by sinusoidal modulated temperature differential scanning calorimetry. For the determination of specific heat capacity by a step-isothermal or multiple step-isothermal temperature program, the reader is referred to Test Method E1269.

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 may be extended depending upon the instrumentation and specimen holders used.

1.4 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.5 *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.*

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

E1269 Test Method for Determining Specific Heat Capacity by Differential Scanning Calorimetry

3. Terminology

3.1 *Definitions*—Specific technical terms found in this test method are defined in Terminologies E473 and E1142 including modulated temperature, isothermal, differential scanning calorimetry, frequency, heat capacity and specific heat capacity.

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *modulated temperature differential scanning calorimetry (MTDSC), n*—a version of differential scanning calorimetry that provides a sinusoidally varying temperature program to the test specimen in addition to the traditional temperature ramp program.

3.2.2 *quasi-isothermal modulated temperature differential scanning calorimetry, n*—a variation of modulated temperature differential scanning calorimetry in which a sinusoidally varying temperature program is applied to a test specimen around an underlying isothermal temperature

4. Summary of Test Method

4.1 The specific heat capacity of a test specimen may be determined using the modulated temperature approach in which an oscillatory or periodically repeating temperature program is imposed upon a test specimen producing an oscillatory (periodic) heat flow into or out of the specimen.

4.1.1 Test Method A consists of heating the test specimen in a controlled atmosphere through the temperature region of interest, using temperature modulation conditions that are appropriate for the measurement.

4.1.2 Test Method B consists of equilibrating and holding the test specimen at an isothermal temperature in a controlled atmosphere and then applying appropriate temperature modulation conditions for the measurement. This procedure can be repeated using as many isothermal temperature holds as are desired.

4.2 The accuracy of the heat capacity thus obtained depends upon the experimental conditions. For example, when a thin test specimen encapsulated in a specimen pan of high thermal conductivity is treated with temperature oscillations of long period (low frequency), the test specimen achieves a uniform

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[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.

temperature distribution and the resultant heat capacity information will be comparable with those of other non-oscillatory test methods.

5. Significance and Use

5.1 Modulated temperature differential scanning calorimetric measurements provide a rapid, simple method for determining specific heat capacities of materials, even under quasi-isothermal conditions.

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

5.3 The use of a stepped quasi-isothermal program may be used to follow structure changes in materials.

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 or gain, on heating during the measurement may invalidate the test. Therefore, the temperature range and specimen holder should be chosen so as to avoid these processes.

7. Apparatus

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

7.1.1 *A Modulated Temperature Differential Scanning Calorimeter (MTDSC) Test Chamber,* composed of (*1*) a furnace to provide uniform controlled heating/cooling of a specimen and reference to a constant temperature or at a constant rate within the applicable range –100 to 600°C (*2*) a temperature sensor (or other signal source) to provide an indication of the specimen temperature readable to 0.01°C; (*3*) a differential sensor to detect a heat flow difference between the specimen and reference equivalent to 1.0 W; and (*4*) a means of sustaining an environment of an inert purge gas at a rate of 50 ± 10 mL/min. (See 7.1.6 for more information on purge gases.)

7.1.2 A *Temperature Controller*, capable of executing a specific temperature program by (*1*) operating the furnace between selected temperature limits at a rate of temperature change of 1 to 10°C/min, (*2*) holding at an isothermal temperature to within ±0.1°C, and (*3*) sinusoidally varying the temperature with an amplitude of up to 1.5°C and a period of up to 100 s (frequency down to 10 mHz) superimposed upon the underlying rate.

7.1.3 A *Calculating Device*, capable of transforming the experimentally determined modulated temperature and modulated specimen heat flow signals into the required continuous output form of specific heat capacity (preferably in units of J/(g°C)) and average test temperature to the required accuracy and precision.

7.1.4 A *Data Collection Device*, to provide a means of acquiring, storing and displaying measured or calculated signals, or both. The minimum output signals required for MTDSC are amplitude of modulated heat flow, temperature, amplitude of modulated temperature and time.

7.1.5 A *Coolant System*, to provide oscillatory heating and cooling rates of at least 5°C/min.

7.1.6 *Inert Nitrogen*, or other low conductivity purge gas flowing at a rate of 50 mL/min.

NOTE 1—Helium, a commonly used purge gas, is unacceptable for this purpose, due to its very high thermal conductivity which results in reduced range, precision and accuracy.

7.2 A *Balance*, with a range of at least 200 mg and a resolution of ±0.001 mg to weigh specimens or containers, or both, (pans, crucibles, etc.) to an accuracy ±0.01 mg.

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

NOTE 2—The masses of the specimen holders should not differ by more than 0.05 mg, otherwise the mass difference in the containers must be considered in the calculation of Cp.

8. Reagents and Materials

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

NOTE 3—Interlaboratory studies have indicated that physical forms of 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 modulation conditions of amplitude and period should be used for both the heat capacity calibration and specimen runs.

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

10. Sampling, Test Specimens, and Test Units

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.

10.3 Solid specimens may be sampled by cutting or slicing with a clean knife or razor blade. Ascertain sample uniformity as segregation within the solid sample is possible.

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

11. Preparation of Apparatus

11.1 Perform any setup or calibration procedures recommended by the apparatus manufacturer in the operations manual.

12. Calibration and Standardization

12.1 Calibrate the temperature signal from the apparatus in accordance with Test Method E967 using an indium reference material and a heating rate of 10°C/min.

12.2 Calibrate the heat flow signal from the apparatus in accordance with Practice E968 using an indium reference material.

NOTE 4—For both 12.1 and 12.2, another suitable reference material may be used to cover a different temperature range.

12.3 Calibrate the apparatus heat capacity signal(s) for specific heat capacity measurements under temperature modulated conditions in accordance with the instructions of the manufacturer as described in the instrument manual.

12.4 Select the temperature that, for Method A, is the mid-point of the temperature range over which the measurement is to be made, or, for Method B, that is the temperature at which the measurement is to be made, or the midpoint of all the isothermal temperatures used in the measurement, if multiple isothermal temperatures are used.

12.5 Crimp a clean, empty specimen holder plus lid and record the mass to a precision of ±0.01 mg. Place on the reference side of the DSC.

12.6 Weigh a clean, empty specimen holder plus lid to a precision of ±0.01 mg. Encapsulate the sapphire material from 8.1 in this specimen holder. Record the mass of the sapphire standard and specimen holder to a precision of ±0.01 mg, and place on the sample side of the instrument. Apply the following temperature modulation conditions: ±1.0°C amplitude, 100 s period (10 mHz frequency) (if different modulation conditions are used, they shall be reported). Hold the sample isothermal for at least 10 minat the desired temperature and then measure the heat capacity value at the end of the isotherm.

12.7 Calculate the specific heat capacity constant (K_{Cp}) by taking the ratio of the theoretical value of sapphire to the measured value at the test temperature.

NOTE 5—Specific heat capacity values for synthetic sapphire may be found in Table 1 of Test Method E1269.

13. Procedure

13.1 Purge the DSC apparatus with dry nitrogen at a flow rate of 50 ± 10 mL/min throughout the experiment.

13.2 Crimp a clean, empty specimen holder plus lid and place on the reference of the MTDSC apparatus. Record the mass of the specimen holder plus lid to a precision of ±0.01 mg if required for proper operation of the DSC apparatus.

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

13.4 Encapsulate the sample to be studied into the specimen holder plus lid combination and record the mass of the sample plus specimen holder and lid to ±0.01 mg. Calculate the sample mass to ±0.01 mg.

13.5 *Method A:*

13.5.1 Beginning 30°C below the lowest temperature of interest to 10°C above the highest temperature of interest, execute a ramped modulated DSC experiment over the temperature range of interest using the following modulated parameters: ±1.0°C amplitude, 100 s period (10 mHz frequency), and 3°C/min heating rate (if different modulation conditions are used, they should be reported).

13.5.2 Record the amplitude of the modulated heat flow and the amplitude of the modulated temperature continually or at the temperature of interest.

13.5.3 Using the amplitude of the modulated heat flow and amplitude of the modulated temperature from 13.5.2, calculate and report the specific heat capacity at the temperature of interest as described in Section 14.

13.5.4 Re-weigh the specimen holder plus specimen. If a mass loss of 0.3 % or greater occurred with respect to the initial mass, the measurement is invalid. Any change in mass shall be reported.

13.6 *Method B:*

13.6.1 Establish the isothermal test temperature of interest. Initiate a temperature modulation of ±1.0°C amplitude, 100 s period (10 mHz frequency) (if different modulation conditions are used, they should be reported). After 10 minutes of temperature modulation, record and report the heat capacity.

13.6.2 Record the amplitude of the modulated heat flow and the amplitude of the modulated temperature continually or at the temperature of interest.

13.6.3 Using the amplitude of the modulated heat flow and amplitude of the modulated temperature from 13.5.2, calculate and report the specific heat capacity at the temperature of interest as described in Section 14.

13.6.4 Re-weigh the specimen holder plus specimen. If a mass loss of 0.3 % or greater occurred with respect to the initial mass, the measurement is invalid. Any change in mass shall be reported.

14. Calculation or Interpretation of Results

14.1 At the temperatures of interest, measure the amplitude of the modulated heat flow and record to the nearest ±0.01 mW.

14.2 At the same temperatures in 14.1, measure the amplitude of the modulated heating rate to the nearest ±0.01°C/min.

14.3 Calculate the specific heat capacity as follows:

$$C_{p_s} = \left(60s/min \cdot A_{mhf} \cdot K_{C_p}\right)/\left(A_{mhr} \cdot W_s\right) \quad (1)$$

where:

C_{p_s} = Specific heat capacity of the specimen, J/g °C,
A_{mhf} = Amplitude of the modulated heat flow calculated in 14.1, mW,
A_{mhr} = Amplitude of the modulated heating rate calculated in 14.2,°C/min,
W_s = Mass of the sample specimen, mg, and
K_{C_p} = Calibration constant calculated in 12.7.

15. Report

15.1 Report the following information:

15.1.1 Complete identification and description of the material tested, including source, manufacturer code, and any thermal or mechanical pretreatment.

15.1.2 Description of the instrumentation used for the test, such as manufacturer and model number.

15.1.3 Description of calibration procedure including values for calibration constants.

15.1.4 Specific heat capacity at the desired measurement temperatures.

16. Precision and Bias

16.1 An interlaboratory test is planned in 2012 to 2013 to establish within laboratory repeatability, between laboratory reproducibility and bias. Anyone wishing to participate in this interlaboratory test should contact the Committee E37 Staff Manger at ASTM International Headquarters.

16.2 *Precision:*

16.2.1 A limited repeatability study was performed in 2008 using five replicate determinants on a single sample of sapphire and in a single laboratory. The repeatability relative standard deviation of this interlaboratory test was 1.1 %.

16.2.2 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 3.2 % was obtained. The repeatability value estimates the 95 % confidence limit.

17. Keywords

17.1 differential scanning calorimetry; heat capacity; modulated temperature differential scanning calorimetry; specific heat; specific heat capacity; thermal analysis