



Designation: E2716 – 23

Standard Test Method for Determining Specific Heat Capacity by Modulated Temperature Differential Scanning Calorimetry¹

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 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 *Units*—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.*

1.6 *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

E473 Terminology Relating to Thermal Analysis and Rheology

E967 Test Method for Temperature Calibration of Differen-

tial 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

E3142 Test Method for Thermal Lag of Thermal Analysis Apparatus

3. Terminology

3.1 *Definitions:*

3.1.1 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 In thermal analysis, a physical property of a material is measured either as a function of time at a specified constant temperature, or more frequently, as a function of temperature under conditions of a fixed rate of temperature change. The measured property is the dependent variable, and the measured temperature is the independent variable.

4.2 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.

4.2.1 Test Method A consists of heating the test specimen in a controlled atmosphere through the temperature region of

¹ This test method is under the jurisdiction of ASTM Committee E37 on Thermal Measurements and is the direct responsibility of Subcommittee E37.01 on Calorimetry and Mass Loss.

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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.

interest, using temperature modulation conditions that are appropriate for the measurement.

4.2.2 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 desired.

4.3 The accuracy of the measured heat capacity 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 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 This test method involves the continuous monitoring of the specimen temperature within the test chamber's enclosed environment of a flowing, static, or self-generated gaseous atmosphere (or vacuum) during execution of the stipulated procedure. In MTDSC apparatus, the sensor employed to measure the specimen temperature is not in direct contact with the specimen but is in fixed close thermal contact assumed to be representative of the specimen, such that the measured temperature is that of the sensor itself and the actual specimen temperature will lag behind this measured temperature during heating or cooling (see Test Method E3142). The magnitude of this temperature offset depends upon a number of systematic and random factors including, but not limited to, type and size of sensor, rate of temperature change, size and thermal conductance of the specimen, specimen container, and thermal contact between the specimen and the specimen container during the measurement. To obtain the correct specimen temperature, the MTDSC apparatus must be temperature calibrated at equivalent experimental conditions so that the recorded temperature correctly indicates the specimen temperature.

6.2 Temperature sensors are subject to degraded performance with age and exposure to the MTDSC test chamber atmosphere. Therefore, it is imperative that the apparatus is temperature calibrated regularly. At a minimum, annual calibration is recommended for all instrument signals.

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

6.4 The occurrence of chemical changes, or mass loss or gain, during the measurement may invalidate the test. Therefore, the temperature range and specimen holder should be chosen to avoid these processes.

7. Apparatus

7.1 *Modulated Temperature Differential Scanning Calorimeter*—Multiple generations of MTDSCs from numerous commercial suppliers, as well as in-house custom apparatus, utilizing a variety of sensor configurations may be available to the user. While all such apparatus capabilities may not be equivalent, for purposes of this test method, any MTDSC that meets the following criteria should be able to generate acceptable results.

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 0.1 mW; 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 capacity of ≥ 100 mg to weigh specimens and/or containers (pans, crucibles, etc.) to ±0.10 µg.

7.3 *Containers* (pans, crucibles, etc.) that are inert to the specimen and are of suitable structural shape and integrity to