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Standard Test Method for Thermal Lag of Thermal Analysis Apparatus[1]

This standard is issued under the fixed designation E3142; 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.

INTRODUCTION

In thermal analysis, the temperature of a test specimen is changed while a physical property is measured. The measured physical property is the dependent variable and temperature (also measured) is the independent variable. In the majority of thermal analysis apparatus, temperature sensors cannot be attached directly to the specimen but can only touch the surface or be placed adjacent or close to the specimen such that the indicated temperature will be different to that of the specimen itself. In consequence the specimen temperature will lag the indicated temperature upon heating and cooling due to thermal resistance between sensor and specimen. The larger the test specimen, the greater the thermal lag is likely to be. To obtain the correct specimen temperature, thermal analysis apparatus is temperature calibrated so that the recorded temperature correctly indicates the specimen temperature. Such temperature calibration compensates for the temperature offset (τ) between the specimen temperature and that of the temperature sensor. This temperature offset changes linearly with temperature rate-of-change (β) (heating or cooling). The slope of this linear relationship is known as "thermal lag" ($\Delta T/\Delta\beta$). Knowing the thermal lag for an apparatus permits temperature calibration determined at one temperature rate-of-change to be adjusted to that at other rates. It is the purpose of this standard to aid the user to determine the thermal lag for an apparatus and to apply that thermal lag to measurements made at temperature rates-of-change different from that at which the temperature calibration is performed.

1. Scope

1.1 This test method addresses the dependence of temperature calibration on the temperature rate-of-change. This test method describes the determination of the thermal lag of thermal analysis apparatus and its application to the modification of the temperature calibration for that apparatus obtained at alternative linear temperature rates-of-change.

1.2 This test method is applicable, but not limited to, the temperature calibration of differential thermal analyzers (DTAs), differential scanning calorimeters (DSCs), thermogravimetric analyzers (TGAs), thermomechanical analyzers (TMAs), and dynamic mechanical analyzers (DMAs).

1.3 This test method is applicable only to apparatus demonstrating a linear relationship between indicated temperature and temperature rate-of-change.

1.4 The values stated in SI units are to be regarded as the 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, health, and environmental 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

[1] This test method is under the jurisdiction of ASTM Committee E37 on Thermal Measurements and is the direct responsibility of Subcommittee E37.10 on Fundamental, Statistical and Mechanical Properties.

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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.

E698 Test Method for Kinetic Parameters for Thermally Unstable Materials Using Differential Scanning Calorimetry and the Flynn/Wall/Ozawa Method
E967 Test Method for Temperature Calibration of Differential Scanning Calorimeters and Differential Thermal Analyzers
E1142 Terminology Relating to Thermophysical Properties
E1363 Test Method for Temperature Calibration of Thermomechanical Analyzers
E1582 Test Method for Temperature Calibration of Thermogravimetric Analyzers
E1867 Test Methods for Temperature Calibration of Dynamic Mechanical Analyzers
E1970 Practice for Statistical Treatment of Thermoanalytical Data
E2069 Test Method for Temperature Calibration on Cooling of Differential Scanning Calorimeters

3. Terminology

3.1 *Definitions:*

3.1.1 Terms applicable to this test method and can be found in Terminologies E473 and E1142 and include the terms *calorimeter, differential, differential scanning calorimeter, differential thermal analysis, dynamic mechanical analysis, temperature, thermal analysis, thermogravimetric analysis*, and *thermomechanical analysis*.

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *temperature offset, n*—the difference between the actual specimen temperature and that reported by a temperature sensor.

3.2.2 *thermal lag, n*—the change in indicated temperature offset with temperature rate-of-change.

4. Summary of Test Method

4.1 Following apparatus temperature calibration with a reference material at an identified temperature rate-of-change, the temperature offset of the apparatus is measured with that sample reference material as a function of additional temperature rates-of-change. A display of temperature (T) versus temperature rate-of-change (β) produces a linear relationship from which the slope ($\Delta T/\Delta\beta$) may be obtained. This slope value is known as thermal lag.

4.1.1 The thermal lag may be used to modify the temperature calibration of an apparatus at temperature rates-of-change other than at which it is calibrated.

4.1.2 The thermal lag of an apparatus may change with experimental conditions such as temperature, purge gas pressure, purge gas thermal conductivity, or other experimental conditions or instrument properties. Thermal lag shall be determined under the same experimental conditions as that of the test specimen.

4.1.3 Thermal lag calculations shall not be used for temperature rate-of-change values greater than 10 K/min.

4.1.4 Thermal lag is known to vary with temperature. If a multipoint temperature calibration is used, then thermal lag shall be determined at each calibration temperature.

5. Significance and Use

5.1 Differing temperature rates-of-change may be required for different measurements (for example, Test Method E698). Temperature calibration changes as a function of temperature rate-of-change. The use of the known thermal lag of an apparatus may be used to adjust the temperature calibration of the apparatus obtained at one temperature rate-of-change with that at another required for a given applications. This adjustment procedure for temperature calibration is described in 8.1.

5.2 This test method may be used in research, quality assurance, and specification acceptance.

6. Interferences

6.1 Thermal lag on heating may differ from that on cooling.

6.2 Where thermal lag is examined upon cooling, the reference material shall be selected to show no supercooling. Liquid crystal materials and adamantane are examples of materials without supercooling (see Test Method E2069).

7. Procedure

7.1 Select the appropriate ASTM standard for temperature calibration of the apparatus (Test Method E967 for differential scanning calorimeters or differential thermal analyzers, Test Method E1582 for thermogravimetric analyzers, Test Method E1363 for thermomechanical analyzers, or Test Methods E1867 for dynamic mechanical analyzers).

7.2 Perform the procedure described in the calibration standard and record the determined temperature as T_1 and the observed temperature rate-of-change as β_1.

NOTE 1—The temperature rate-of-change shall be measured. Use of the programmed temperature rate-of-change is not satisfactory.

7.3 Perform the procedure described in the calibration standard at two additional heating rates other than β_1 representing the low, medium, and high heating rate capability of the apparatus. Record these additional data pair values as T_2 and β_2, and T_3 and β_3.

NOTE 2—The reliability of the results of this determination increases as temperature rate-of-change increases.

7.4 Prepare a display of the values for 7.2 and 7.3, with T-values on the Y-axis and the corresponding β-values on the X-axis.

NOTE 3—The display shall approximate a straight line. If not, then this test method is not applicable.

7.5 Using linear regression (see Practice E1970), determine and report the slope ($\Delta T/\Delta\beta$) and its standard deviation ($\sigma\Delta T/\Delta\beta$) of the best-fit straight line for these three points.

NOTE 4—The appropriate SI units for this value is seconds. However, it is easier to leave this value in the units of minutes for the purpose of its application. Alternatively, one may use the conversion factor of 1 min = 60 s in the calculations.

NOTE 5—The thermal lag is known to vary with temperature. If a multipoint temperature calibration is used, then thermal lag shall be determined at each calibration temperature.

NOTE 6—For the purpose of this test method, a goodness-of-fit R^2 value greater than 0.95 is considered acceptable.

8. Calculation and Interpretation of Results

8.1 The value of the thermal lag ($\Delta T/\Delta \beta$) determined in 7.5 may be used to determine the off-set value applied to the transition temperature obtained at temperature rates-of-change other than that specified in the corresponding temperature calibration standard using Eq 1 and Eq 2.

$$\tau = (\Delta T / \Delta \beta) \times (\beta_s - \beta_o) \quad (1)$$

$$T_t = T_o + \tau \quad (2)$$

where:

β_s = the temperature rate-of-change at which the apparatus was temperature calibrated, K/min,
β_o = the temperature rate-of-change for the observed measurement, K/min,
τ = temperature offset due to thermal lag, K
$\Delta T/\Delta \beta$ = thermal lag, min, obtained from linear regression,
T_o = observed transition temperature, K, and
T_t = true transition temperature, K.

NOTE 7—The values for β have direction. Heating rates are positive and cooling rates are negative. This convention gives direction to τ as well.

9. Report

9.1 Report thermal lag ($\Delta T/\Delta \beta$) and its imprecision ($\sigma\Delta T/\Delta \beta$) or relative imprecision ($\sigma\Delta T/\Delta \beta/(\Delta T/\Delta \beta)$).

10. Precision and Bias

10.1 This standard is used to determine the bias introduced by the thermal lag effect of a thermal analysis measurement and to correct for that effect. The precision of temperature offset may be estimated by the principal of propagation of uncertainties by the relative standard deviation of the thermal lag.

$$\sigma\Delta\beta \approx \sigma\beta \quad (3)$$

$$\sigma\tau = [(\sigma \Delta T / \Delta \beta \times \Delta \beta)^2 + (\Delta T / \Delta \beta \times \sigma \Delta \beta)^2]^{1/2} \quad (4)$$

$$\sigma T_t = [(\sigma T_o)^2 + (\sigma \tau)^2]^{1/2} \quad (5)$$

where:

T_o = the observed transition temperature, K,
σT_o = standard deviation of the absolute temperature measurement, K (obtained from the precision state of the respective calibration standard in 7.1),
$\Delta T/\Delta \beta$ = thermal lag, min,
$\sigma\Delta T/\Delta \beta$ = the thermal lag standard deviation, min, obtained from linear regression, $\Delta\beta = \beta_s - \beta_o$,
$\sigma\Delta\beta$ = standard deviation of $\Delta\beta$, and
$\sigma\beta$ = standard deviation of the temperature rate-of-change measurement.

10.1.1 The value of $\sigma\tau$ is often much smaller than σT and so the imprecision in the corrected temperature T_t is equivalent to the imprecision of the uncorrected temperature T_o.

10.2 An interlaboratory study is planned from 2018–2023 to establish within laboratory repeatability, between laboratory reproducibility, and bias. Anyone wishing to participate in this interlaboratory study should contact the Committee E37 Staff Manager at ASTM International Headquarters.

10.3 *Precision:*

10.3.1 A limited repeatability study was performed in using four calibration materials in a single laboratory. The results of that study are presented in Table 1 and have been filed at ASTM Headquarters.[3]

10.3.2 Within laboratory variability may be described using he repeatability value (r) obtained by multiplying the standard deviation by 2.8. The repeatability value estimates the 95 % confidence limit. That is, two results obtained in the same laboratory (using the same apparatus, on the same specimen by the same operator, closely spaced in time) have a 95 % probability of being within the repeatability value of each other.

10.3.3 Between laboratory variability may be described using the reproducibility value (R) obtained by multiplying the reproducibility standard deviation by 2.8. The reproducibility value estimates the 95 % confidence limit. That is, two results obtained in different laboratories, or using different apparatus, or by different operators, or at different times, have a 95 % probability of being within the repeatability value of each other.

10.3.4 The reproducibility of this test method has not yet been determined (see 10.2).

10.4 *Bias:*

10.4.1 Bias is the difference between a mean determined value and an acceptable reference value.

10.4.2 The bias of this test method has not been determined (see 10.2).

11. Keywords

11.1 calibration; differential scanning calorimetry; differential thermal analysis; dynamic mechanical analysis; temperature calibration; thermal lag; thermogravimetric analysis; thermomechanical analysis

[3] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:E37-1051. Contact ASTM Customer Service at service@astm.org.

TABLE 1 Single Laboratory Repeatability for Differential Scanning Calorimetry

Material	T °C	$\Delta T/\Delta\beta$ min^{-1}	$\sigma\Delta T/\Delta\beta$ min^{-1}
Indium	157	0.071519	0.00091
Tin	232	0.053441	0.00172
Lead	327	0.041801	0.000215
Zinc	420	0.070282	Not available