



Designation: **E1582—17** **E1582 – 21**

## Standard Test Method for Temperature Calibration of Thermogravimetric Analyzers<sup>1</sup>

This standard is issued under the fixed designation E1582; 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 ( $\epsilon$ ) indicates an editorial change since the last revision or reapproval.

### 1. Scope\*

1.1 This test method describes the temperature calibration of thermogravimetric analyzers over the temperature range from 25 °C to 1500 °C and is applicable to commercial and custom-built apparatus. This calibration may be accomplished by the use of either melting point standards or magnetic transition standards.

1.2 The weight change curve in thermogravimetry results from a number of influences, some of which are characteristic of the specimen holder assembly and atmosphere rather than the specimen. The variations from instrument to instrument occur in the point of measurement of the temperature, the nature of the material, its size and packing, the geometry and composition of the specimen container, the geometry and design of the furnace, and the accuracy and sensitivity of the temperature sensor and displaying scales. These all contribute to differences in measured temperatures, which may exceed ~~20 °C~~ 20 °C. In addition, some sample holder assemblies will show variations of measured temperature with sample size or heating/cooling rate, or both. Since it is neither practical nor advisable to standardize sample holders or thermobalance geometries, instruments may be calibrated by measurement of the deviation of a melting or magnetic (Curie Point) point transition temperature from the standard reference temperature. This deviation can be applied as a correction term to subsequent measurements.

1.3 This test method assumes that the indicated temperature of the instrument is linear over the range defined by a two-point calibration and that this linearity has been verified. These two calibration temperatures should be as close to the experimental measurements to be made as possible.

1.4 This test method describes two procedures for temperature calibration of thermogravimetric analyzers using any type balance. Procedure A uses melting point standards for calibration. Procedure B uses magnetic transition standards for calibration.

1.5 The data generated by these procedures can be used to correct the temperature scale of the instrument by either a positive or negative amount using either a one- or two-point temperature calibration procedure.

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

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, health, and environmental practices and determine the applicability of regulatory limitations prior to use.*

1.8 *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.*

<sup>1</sup> 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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\*A Summary of Changes section appears at the end of this standard

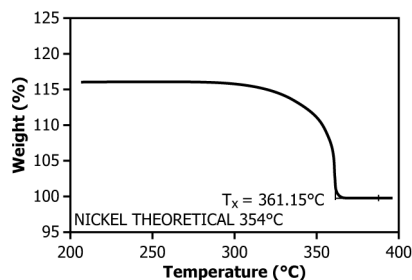


FIG. 1 Magnetic Reference Temperature

## 2. Referenced Documents

### 2.1 ASTM Standards:<sup>2</sup>

E473 Terminology Relating to Thermal Analysis and Rheology

E691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method

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

E1142 Terminology Relating to Thermophysical Properties

E2040 Test Method for Mass Scale Calibration of Thermogravimetric Analyzers

## 3. Terminology

3.1 *Definitions*—Technical terms used in this document are defined in Terminologies E473 and E1142, including *Celsius*, *Curie temperature*, *derivative*, *Kelvin*, *magnetic transformation*, *onset point*, *thermogravimetry*, *thermogravimetric analyzer*, and *thermogravimetric analyzer:thermomagnetometry*.

3.1.1 *magnetic reference temperature, n*—the observed temperature at which a change in the magnetic properties of a material in a magnetic field produces an apparent mass change. This temperature is read from the dynamic thermogravimetry curve as the point of intersection of the extrapolated higher temperature portion of the base line with a tangent drawn to the point of greatest slope of apparent mass-change curve. This temperature most closely represents the Curie Point, point, that point on the mass change curve where the magnetic effect of the standard material has disappeared completely (see Fig. 1).

### 3.1.1.1 Discussion—

The position of the magnet and the design of the instrument will affect the direction of the mass change.

## 4. Summary of Practice

4.1 This test method provides a set of different procedures since thermogravimetric apparatus is often of significantly differing design.

### 4.2 Calibration of Analyzers Using Magnetic Transition Standards:

4.2.1 In this procedure, the apparent mass change of one or more of the magnetic transition standards is obtained under the normal operating conditions of the instrument. The extrapolated endpoint temperature (see Fig. 1) is determined and compared with the established transition temperature for the material. The difference provides an adjustment or calibration that may be applied to the temperature scale of the instrument.

4.2.2 The apparent mass change of the magnetic transition materials is caused by the magnetic (ferromagnetic) to nonmagnetic (paramagnetic) transition in the presence of a magnetic field. This process is known as thermomagnetometry.

4.3 *Calibration of Analyzers That Have Simultaneous Thermogravimetry-Differential Scanning Calorimeter or Thermogravimetry-Differential Thermal Analysis Capability*—These instruments may be calibrated using melting temperature standards following Practice E967.

<sup>2</sup> 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.

## 5. Significance and Use

5.1 Thermogravimetric analyzers are used to characterize a broad range of materials. In most cases, one of the desired values to be assigned in thermogravimetric measurements is the temperature at which significant changes in specimen mass occur. Therefore, the temperature axis (abscissa) of all apparent-mass-change curves must be calibrated accurately, either by direct reading of a temperature sensor, or by adjusting the programmer temperature to match the actual temperature over the temperature range of interest. In the latter case, this is accomplished by the use of either melting point or magnetic transition standards.

5.2 This test method permits interlaboratory comparison and intralaboratory correlation of instrumental temperature scale data.

## 6. Interferences

6.1 The reference metals are sensitive to impurities and may oxidize at elevated temperatures. All runs shall be conducted in an oxygen-free inert purge gas of the same type to be used in the experimental procedures.

6.2 Care must be taken to stay below temperatures at which the magnetic transition standard will react with the specimen or its holder.

6.3 The atmosphere, purge gas type, purge gas flow rate, and heating rate will affect the calibration. These rates and conditions must be the same for both calibration and analysis. In addition, high heating rates should be avoided, if possible. Due to the differing heat exchange (emissivity and heat capacity) during the calibration and analysis, higher heating rates increase the error in the temperature measurement.

## 7. Apparatus

7.1 *Thermogravimetric Analyzer*—A system of related instruments that are capable of continuously measuring the mass of a specimen in a controlled atmosphere and in a controlled temperature environment ranging from ambient to at least  $25^{\circ}\text{C}$ – $25^{\circ}\text{C}$  above the temperature range of interest over a selected time period. This instrument shall consist of the following:

7.1.1 *Thermobalance*, composed of:

7.1.1.1 *Furnace*, to provide uniform controlled heating of a specimen from  $25^{\circ}\text{C}$  to a constant temperature or at a constant rate within the applicable temperature range of this test method.

7.1.1.2 *Temperature Sensor*, to provide an indication of the specimen/furnace temperature to  $\pm 0.1^{\circ}\text{C}$ .

7.1.1.3 A continuously recording *Balance*, to measure the specimen apparent mass with a minimum capacity of 50 mg and a sensitivity of  $\pm 5\ \mu\text{g}$ .

7.1.1.4 A means of maintaining the specimen/container under *Atmospheric Control*, of nitrogen or other inert gas of 99.9+%/99.9+ % purity at a purge rate of 50 mL/min to 100 mL/min constant to within  $\pm 5\ \text{mL/min}$ .

7.1.2 A *Temperature Controller*, capable of executing a specific temperature program by operating the furnace between selected temperature limits at a specified heating rate between  $0.50.5^{\circ}\text{C}/\text{min}/\text{min}$  to  $2020^{\circ}\text{C}/\text{min}/\text{min}$  constant to within  $\pm 0.1 \pm 0.1^{\circ}\text{C}/\text{min}/\text{min}$  or to an isothermal temperature that is maintained constant to  $\pm 0.5^{\circ}\text{C}/\pm 0.5^{\circ}\text{C}$  for a minimum of 10 min.

7.1.3 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 thermogravimetry are weight, temperature, and time.

7.1.4 *Containers (pans, crucibles, and the like)*, that are inert to the specimen and will remain dimensionally stable within the temperature limits of this test method.

7.2 For the Magnetic Transition Method, a means of applying a *magnetic field* sufficient to produce a 2 % weight change in the test specimen.

**TABLE 1 Recommended Melting Temperature Standards**

| Calibration Material   | Melting Temperature, °C (K) |
|------------------------|-----------------------------|
| Indium <sup>A</sup>    | 156.5985 (429.7485)         |
| Tin <sup>A</sup>       | 231.928 (505.078)           |
| Zinc <sup>A</sup>      | 419.527 (692.677)           |
| Aluminum <sup>A</sup>  | 660.323 (933.473)           |
| Silver <sup>A</sup>    | 961.78 (1234.93)            |
| Gold <sup>A</sup>      | 1064.18 (1337.33)           |
| Copper <sup>A</sup>    | 1084.62 (1357.77)           |
| Nickel <sup>B</sup>    | 1455 (1728)                 |
| Palladium <sup>B</sup> | 1554.8 (1828.0)             |
| Platinum <sup>B</sup>  | 1768.2 (2041.3)             |

<sup>A</sup> Primary fixed points, ITS-90 (1).

<sup>B</sup> Secondary reference points, ITS-90 (2).

## 8. Calibration and Standardization

8.1 *Calibration of Apparatus*—If necessary, calibrate the mass base and temperature sensors of the instrument at room temperature using the procedure described in the instrument manual or Test Method E2040.

### 8.2 Calibration Materials:

8.2.1 *Melting Point Standards*—For the temperature range covered by many applications, the melting transition of the 99.9+%/99.9+ % pure materials listed in Table 1 may be used for calibration.

NOTE 1—The values in Table 1 were determined using special 99.9999 %–99.9999 % pure materials and highly accurate steady-state conditions that are not attainable with this test method. The actual precision of this test method is given in Section 13.

### 8.2.2 Magnetic Transition Standards.

NOTE 2—Materials with known magnetic transitions determined with high precision are required (3).<sup>3</sup> For sources of materials of known or certified Curie transition temperatures, contact the ASTM Information Center. The values for Curie transition temperatures differ from lot to lot of the material. Curie point temperatures given in Table 2 were obtained from Ref. (4).

## 9. Procedure A—Melting Point Standard Calibration

### 9.1 Positioning of the Temperature Sensor (Thermocouple):

9.1.1 The temperature sensor is an integral part of the sample holder and cannot be adjusted.

### 9.2 Standard Preparation Procedure:

9.2.1 Press the metal standard flat and place it in the middle of the crucible. Place the sample/crucible on the center of the sample holder (sensor), see Fig. 2.

9.2.2 Close the balance assembly. Purge the balance and furnace tube with the desired atmosphere and at the selected flow rate. Select the heating rate that will be used in subsequent analyses. See 6.3.

9.2.3 Adjust the balance so that it now gives a zero mass signal.

9.2.4 Open the system and carefully suspend a platinum mass of approximately 50 mg from the end of the wire standard.

9.2.4.1 Close the system.

9.2.5 Rapidly heat the system to 50 °C below the theoretical melting temperature, and allow the system to equilibrate for 5

<sup>3</sup> The boldface numbers in parentheses refer to a list of references at the end of this standard.

TABLE 2 Curie Temperature Standards<sup>A,B,C</sup>

| Metal                           | Curie Point (Magnetic) Transition, °C |
|---------------------------------|---------------------------------------|
| ALUMEL (trademark) <sup>A</sup> | 152.6                                 |
| Alumel <sup>A,C</sup>           | 153.9                                 |
| Nickel <sup>B</sup>             | 358.2                                 |
| Nickel (83 %)-Cobalt (17 %)     | 554.4                                 |
| Nickel (63 %)-Cobalt (37 %)     | 746.4                                 |
| Iron <sup>C</sup>               | 771.4                                 |
| Nickel (37 %)-Cobalt (63 %)     | 930.8                                 |
| Cobalt                          | 1116                                  |

<sup>A</sup> Available from TA Instruments, 109 Lukens Drive, New Castle, DE., the only known source of certified and traceable Curie Temperature Reference Materials. Interested parties are invited to submit information regarding the identification of acceptable alternatives to the Committee on Standards, ASTM International Headquarters, 100 Barr Harbor Drive, West Conshohocken, PA 19428-2959. If you are aware of alternative suppliers, please provide this information to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee,<sup>1</sup> which you may attend.

<sup>B</sup> From Ref. (4).

<sup>C</sup> From Ref. (5).

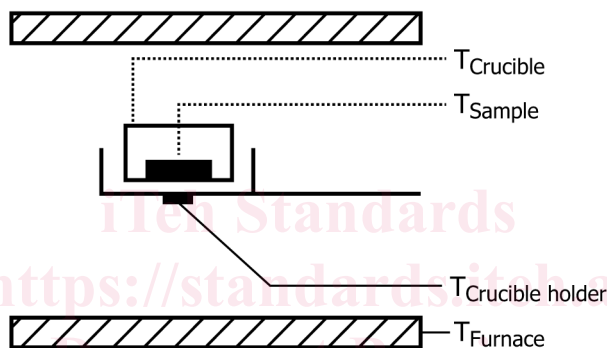


FIG. 2 Sample Positioning for Procedure A

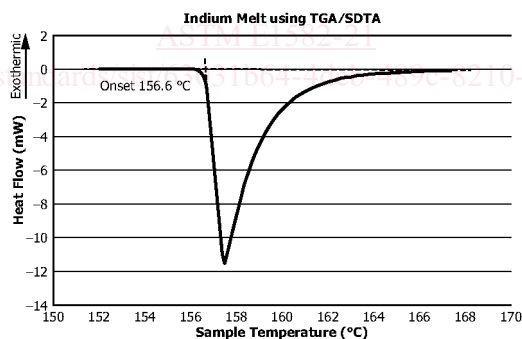


FIG. 3 Heat Flow Curve for Procedure A

minutes. Then heat at the selected programmed rate up through the melting temperature of the standard. When the standard melts, the heat flow signal will show an endothermic peak as is typically seen with a traditional. A typical curve is shown in Fig. 3.

9.2.6 Measure the onset temperature of the endothermic heat flow peak.

## 10. Procedure B—Magnetic Transition Standard Calibration

10.1 For those systems using internal microfurnaces with an adjustable temperature sensor, it shall be adjusted so that it is just beneath (but not touching) the thermogravimetric analyzer specimen container (see Figs. 4 and 5).

10.2 Close the system, adjust the atmospheric flow rate to the selected rate, and zero the balance and chart recorder if used.

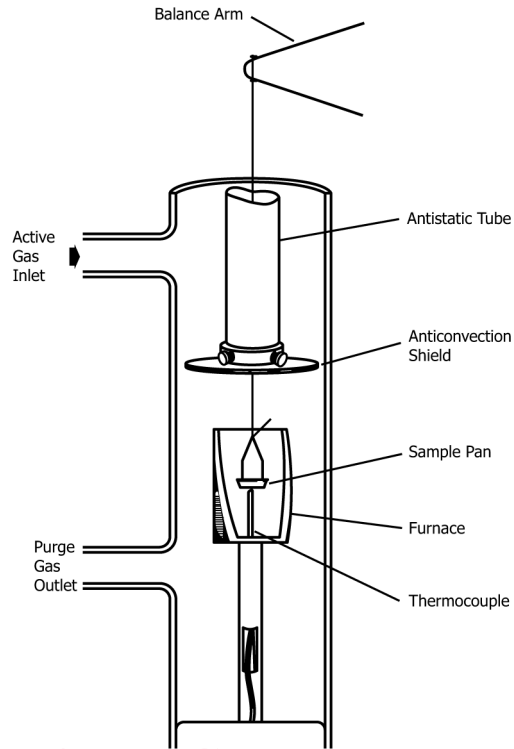


FIG. 4 Positioning of the Temperature Sensor (Thermocouple)

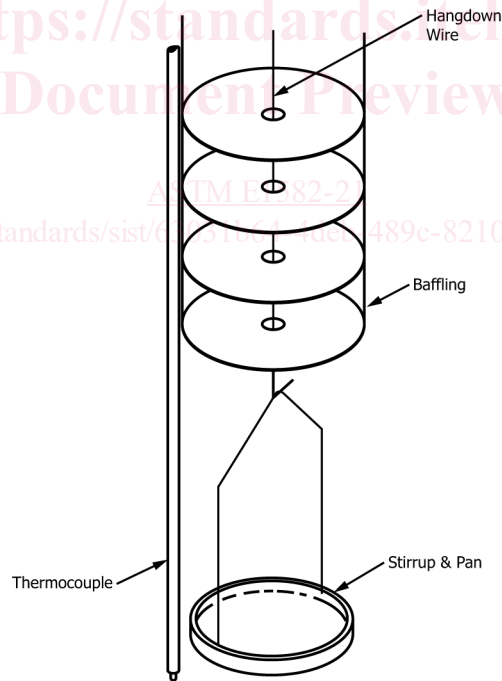


FIG. 5 Positioning of the Temperature Sensor (Thermocouple)

10.3 Open the system and place a specimen of the magnetic transition material in the specimen container in the same position as that in which one would place a specimen. Close the system.

10.4 Place a permanent magnet or electromagnet outside the furnace in a position as close to the furnace and specimen container

as is practical in order to affect an apparent mass change at the reference material transition temperature. Remove (or turn off) the magnet to ascertain whether a conveniently measurable apparent mass change occurs.

NOTE 3—The choice of magnets or magnetic fields should be so that an apparent mass change of up to 2 % is observed by turning the field on and off.

10.4.1 Adjust the specimen size or mass loss sensitivity, if necessary, and replace (or turn on) the magnet.

10.5 Rapidly heat the magnetic transition standard to a temperature at least 50 °C below the transition temperature of the standard and hold that temperature for 5 min.

10.6 Heat the test specimen at the desired heating rate through the transition temperature region until an apparent mass change has been observed ( $T_x$ , Fig. 1).

NOTE 4—To allow full ramp equilibration prior to the transition, the scanning ramp should extend at least 5 min prior to the observed transition (hence, the 50 °C mentioned would be appropriate for scanning rates below 10 °C/min).

NOTE 5—More than one reference material can be used in one run. If the magnetic reference temperature of the reference material is sufficiently different from the mass change region of the test substance that the apparent and real mass changes do not interact, the reference material may be used during measurements on the test substance. Chemical interaction of any type with the sample may alter the temperature of the magnetic transition.

NOTE 6—The same specimen container and heating rates should be used in both the calibration procedures and the analytical determinations. See 6.3.

10.7 Determine the magnetic transition temperature by observing that point on the mass change curve that most closely agrees with that of  $T_x$  of Fig. 1. Computer or hand-made determination of this point can be made.

## 11. Calculation

11.1 For the purposes of these procedures, it is assumed that the relationship between observed temperature ( $TO$ ) and actual specimen temperature ( $T$ ) is a linear one governed by the following equation:

$$T = (TO \times S) + I \quad (1)$$

where:

$S$  and  $I$  = slope and intercept, respectively.

(See 11.2 for the means to calculate  $S$  and  $I$ , used in (Eq 1).)

NOTE 7—For some instruments, the assumption of a linear relation between observed and actual specimen temperature may not hold. Under such conditions, calibration temperatures sufficiently close together shall be used so that the instrument calibration is achieved with a series of linear relations.