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Standard Practice for Calibration of Temperature Scale for Thermogravimetry[1]

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 (ε) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This practice describe the temperature calibration of thermogravimetric analyzers over the temperature range from 25 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 mass 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. 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) transition temperature from the standard reference temperature. This deviation can be applied as a correction term to subsequent measurements.

1.3 This practice 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.

~~1.4This practice describes three procedures for temperature calibration of thermogravimetric analyzers using any type balance. Procedures A and B use melting point standards with vertical and horizontal balances. Procedure C uses magnetic transition standards for calibration. Procedure A is designed specifically for use with horizontal-type balances using external furnaces. Procedure B is designed specifically for use with vertical hang-down balances using either internal or external furnaces. No procedure is restricted to the use of the furnace type described in that procedure.~~

1.4 This practice describes three procedures for temperature calibration of thermogravimetric analyzers using any type balance. Procedures A and B use melting point standards with vertical and horizontal balances. Procedure C uses magnetic transition standards for calibration. Procedure A is designed specifically for use with horizontal-type balances. Procedure B is designed specifically for use with vertical hang-down balances.

1.5 Computer or electronic-based instruments, techniques, or data treatment equivalent to this procedure may be used. ~~Note1—Since all electronic data treatments are not equivalent, the user shall verify equivalency prior to use.~~

1.6 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 two-point temperature calibration procedure or a multi-point temperature calibration with best line fit for the generated data.

NOTE ~~2—A~~ 1—A single-point calibration may be used where this is the only procedure possible or practical. The use of a single-point procedure is not recommended.

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

1.8 This practice is related to ISO 11358 but provides information and methods not found in ISO 11358.

1.9 *This standard does not purport to address all of the safety problems, 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] This practice 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. Referenced Documents

2.1 *ASTM Standards:*[2]

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

[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.

2.2 *Other Standards:*

ISO 11358 ~~Thermogravimetry (TG) of Polymers — General Principles~~ Plastics — Part 4: Thermogravimetry (TG) of Polymers — General Principles[3]

3. Terminology

3.1 *Definitions*—Technical terms used in this document are defined in Terminology E473 and E1142.

3.1.1 *magnetic reference temperature*—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 TG 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, that point on the mass change curve where the magnetic effect of the standard material has disappeared completely (see Fig. 1).

NOTE ~~3—The~~ 2—The position of the magnet and the design of the instrument will affect the direction and the magnitude of the mass change.

4. Summary of Practice

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

4.2 *Calibration of Analyzers Using Melting Point Standards*—The calibration material is heated at a controlled rate in a controlled atmosphere through its melting region. The temperature of the standard is monitored and recorded continuously. In this practice, a small platinum mass is suspended within a thermogravimetric analyzer specimen boat or pan from a fusible link of the standard calibration material. As the standard specimen is heated through the melting region, the platinum mass is released. The mass is either caught in the specimen boat or pan, producing an "action/reaction" blip on the thermal curve, or is allowed to drop through a hole in the bottom of the specimen boat or pan, producing a sharp, discontinuous mass loss. These events may be used to calibrate the thermogravimetric analyzer for the experimental conditions used.

4.3 *Calibration of Analyzers Using Magnetic Transition Standards*:

4.3.1 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.

4.3.2 The apparent mass change of the magnetic transition materials is caused by the magnetic to nonmagnetic transition in the presence of a magnetic field.

4.4 *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.

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.

[3] Available from American National Standards Institute (ANSI), 25 W. 43rd St., 4th Floor, New York, NY 10036, http://www.ansi.org.

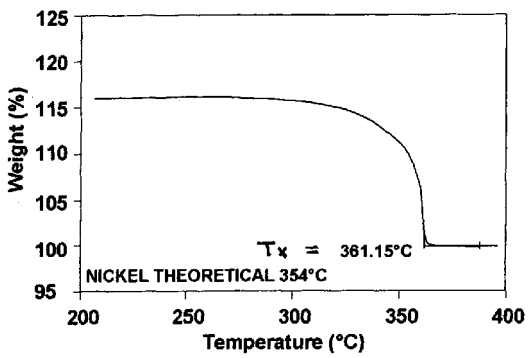


FIG. 1 Magnetic Reference Temperature

5.2 This practice 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. The ICTAC Sixth International Test Program **(1)**[4] warns that heating rates above 6°C/min can produce errors in the temperature calibration.

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 °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 °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 ± 0.1 °C.

7.1.1.3 A continuously recording *Balance,* to measure the specimen weight with a minimum capacity of 50 mg and a sensitivity of ± 5 µg.

7.1.1.4 A means of maintaining the specimen/container under *Atmospheric Control,* of nitrogen or other inert gas of 99.9 +% purity at a purge rate of 50 to 100 mL/min constant to within ±5 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 0.5 to 20°C/min constant to within ± 0.1°C/min or to an isothermal temperature that is maintained constant to ± 0.5°C for a minimum of 10 min.~~ capable of executing a specific temperature program by operating the furnace between selected temperature limits at a specified heating rate between 0.5 to 20 °C/min constant to within ±0.1 °C/min.

7.1.3 A *Recording Device,* capable of recording and displaying any fraction of the specimen weight (TGA thermal curve) including the signal noise, on the *Y*-axis versus any fraction of temperature, including signal noise, on the *X*-axis.

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.

8. Calibration and Standardization

8.1 *Calibration of Apparatus*—If necessary, calibrate the temperature sensor of the instrument at room temperature using the procedure described in the instrument manual.

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+ % pure materials listed in Table 1 may be used for calibration.

NOTE ~~4—It is recommended that the size of the wire used be 0.25 mm in diameter. For sources of very pure fine metal wire, contact the ASTM Information Center.~~ 3—It is recommended that the size of the wire used be 0.25 mm in diameter. Sources of very pure fine metal wire may be found

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

TABLE 1 Recommended Melting Temperature Standards

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

[A] Primary fixed points, ITS-90 **(2)**.
[B] Secondary reference points, ITS-90 **(3)**.

by contacting the Goodfellow Corporation[5] or by contacting the ASTM Information Center.

NOTE5—The 4—The melting temperatures of the first seven materials given in this table are taken from Mangum and Furukawa **(2)** and have been selected as primary fixed points for the International Temperature Scale of 1990. The remaining melting temperatures give in this table are taken from Bedford, Bonnier, Mass, and Pavese **(3)**.

8.2.2 *Magnetic Transition Standards*.

NOTE 65—Materials with known magnetic transitions determined with high precision are required **(4)**. 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 the table were obtained from Refs. **(5)**.

9. Procedure A—Melting Point Standard Test for Horizontal Balance Types

9.1 *Positioning of the Temperature Sensor*—If the system employs a temperature sensor that is movable, it shall be located as close to the specimen as possible without touching it or the balance pan. In addition, it must be located in exactly the same position during calibrations as used during analytical determinations.

NOTE7—This 6—This position may be inside or outside the balance pan.

9.2 *Action-Reaction Procedure*:

9.2.1 Flatten one end of a fine platinum wire (approximately 0.34- mm diameter and 2 cm in length), and spot weld it to the outside of a specimen container as shown in Fig. 2. Carefully bend the wire into a U shape so that the cantilevered end is located in the center of the specimen container.

9.2.2 Suspend this specimen container from the balance mechanism so that it hangs freely, and locate the temperature sensor as outlined in 9.1.

9.2.3 Bend a 5-mm length (0.25-mm diameter) of the wire temperature standard into a sigmoid shape, and suspend it from the end of the platinum wire in the middle of the specimen container.

NOTE8—The 7—The selection of wire standard depends on the part of the temperature axis that is to be calibrated. Two or more standards may be run consecutively to enable one to obtain a calibration curve.

9.2.4 Close the balance assembly, and purge the system with the desired atmosphere at the selected rate. Select the appropriate heating rate.

9.2.5Zero the balance and the recorder.

9.2.6

[5] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:E37-1017.

[5] Available from Goodfellow Corporation, 305 High Tech Drive, Oakdale, PA 15071-3911, http://www.goodfellow.com.

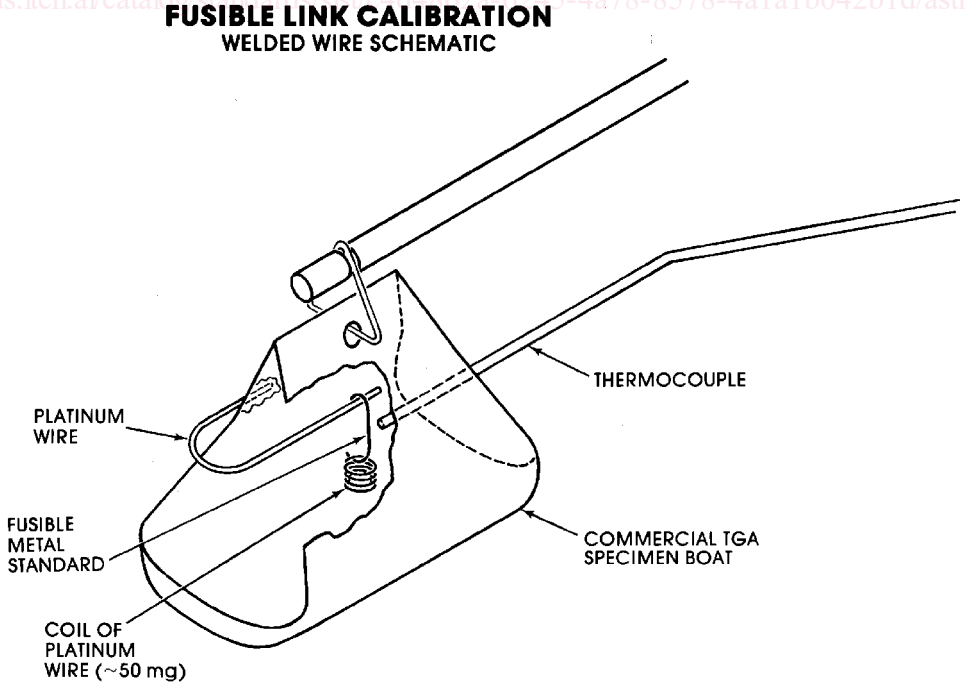


FIG. 2 Fusible Link Calibration; Welded Wire Schematic

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

NOTE9—This 8—This mass can be prepared by tightly winding approximately 50 mm of 0.25- mm diameter platinum wire and distending one loop of the wire to provide a convenient connecting loop.

9.2.65.1 Close the system.

9.2.7For analog systems using a chart recorder, adjust the *y*-axis pen recorder control sensitivity so that the pen is located about the middle of the chart paper.

9.2.89.2.6 Rapidly heat the system to 50 °C below the theoretical melting temperature, and allow the system to equilibrate for 5 min. Then heat at the selected programmed rate up through the melting temperature of the standard. When the standard melts, the platinum mass falls into the specimen boat or pan. This produces an action-reaction blip on the recorded thermal curve without any mass loss. A typical thermal curve is shown in Fig. 3.

NOTE10—The recorder action is fast and must ordinarily be observed at high sensitivity and data acquisition rates. The measurement of the transition temperature for the action-reaction blip is usually determined by manual means, since data analysis programs typically treat events of this nature as noise.

NOTE11—Alloying of silver and gold with a platinum support and specimen boat or pan occurs over time, ultimately making the holder unusable.

9.2.9 9—Alloying of silver and gold with a platinum support and specimen boat or pan occurs over time, ultimately making the holder unusable.

9.2.7 Measure the temperature of the peak of the blip.

9.3 *Drop Procedure*:

9.3.1 Pierce a hole on both sides of the specimen container far up on the sides using a needle. Thread a short length of small diameter quartz rod (1 mm) or platinum wire through these holes so that the rod or wire is horizontal when the container is suspended. Alternatively, the container prepared in 9.2.1 may be used.

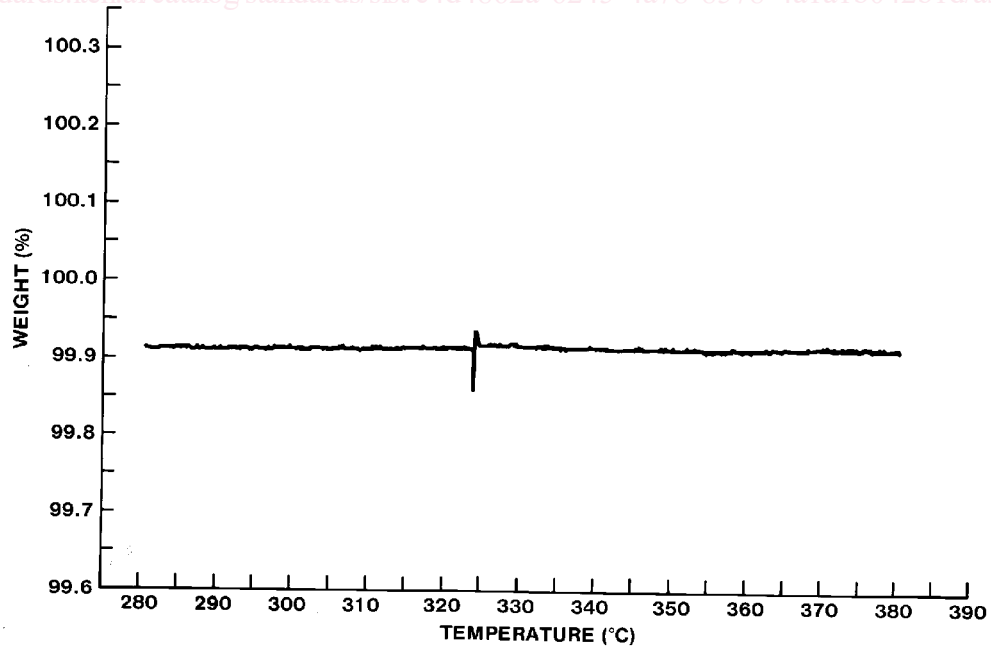
9.3.2 Cut a hole in the bottom of the specimen container, from the inside out, by placing it onto a soft surface and using a razor blade or sharp knife. See Fig. 4.

9.3.3 Suspend this specimen container from the balance mechanism so that it hangs freely, and locate the specimen temperature sensor as outlined in 9.1. See Note 7Note 6.

9.3.4 Bend a 5-mm length of the wire temperature standard into a sigmoid shape, and suspend it from the middle of the rod or wire. See Note 8 Note 7 (9.2.3).

9.3.5 Continue as directed in 9.2.4-9.2.79.2.4-.

9.3.6 Continue as directed in 9.2.89.2.6. When the standard melts, the platinum mass falls through the bottom of the boat or pan, causing a large mass loss (100 %). A typical thermal curve obtained using this experimental arrangement is shown in Fig. 5. The transition temperature may be found by determining the extrapolated onset temperature of the curve. Record this as the melting temperature of the standard material.



NOTE—Sample: TGA STD LEAD CAL; Size: 44.55 mg; Rate: °C/min; N_2 at 50mL/min.

FIG. 3 Typical Thermal Curve