Standard Test Method for
Mass ~~Loss~~ Loss, Residue, and ~~Residue~~Temperature Measurement Validation of Thermogravimetric Analyzers[1]

This standard is issued under the fixed designation E2402; 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~~ Scope*

1.1 This test method provides procedures for validating mass ~~loss~~ loss, residue, and ~~residue~~temperature measurements by thermogravimetric analyzers ~~(TGA)~~(TGAs) and analytical methods based upon the measurement of mass loss or residue ~~content.~~ content or temperature. Performance parameters determined include mass ~~loss~~ loss, residue, and ~~residue~~temperature repeatability (precision), detection limit, quantitation limit, linearity, and bias.

1.2 Validation of apparatus performance and analytical methods is requested or required for quality initiatives or where results may be used for legal purposes.

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

1.4 ~~There is no ISO standard equivalent to this test method.~~

1.4 *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.*

1.5 *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]
E177 Practice for Use of the Terms Precision and Bias in ASTM Test Methods
E473 Terminology Relating to Thermal Analysis and Rheology
E1142 Terminology Relating to Thermophysical Properties
E1582 Test Method for Temperature Calibration of Thermogravimetric Analyzers
E1970 Practice for Statistical Treatment of Thermoanalytical Data
E2040 Test Method for Mass Scale Calibration of Thermogravimetric Analyzers
E2161 Terminology Relating to Performance Validation in Thermal Analysis and Rheology

2.2 *~~Other Standard:~~*
~~U.S. FDA Q2B Validation of Analytical Procedures: Methodology, 62 FR 27464, May 19, 1997~~[3]

3. Terminology

3.1 Technical terms used in this standard are defined in Practice E177 and in Terminologies E473, E1142, and E2161~~,~~ including *analyte, bow, calibration, Celsius, certification, certified reference material, Curie temperature, derivative, detection limit, extrapolated onset value, linearity, magnetic transformation, onset point, plateau, precision, quantification limit, reference material, repeatability, slope, standard deviation, thermogravimetry, thermogravimetric analysis, temperature,* and *validation.*

3.2 *Definitions of Terms Specific to This Standard:*

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[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.

*A Summary of Changes section appears at the end of this standard.

3.2.1 *highly volatile matter—matter, n—*materials (such as moisture, plasticizer, residual solvent, etc.) that boil at temperatures below ~~200°C.~~200 °C.

3.2.2 *mass loss plateau, n—*a region of a thermogravimetric curve with a relatively constant mass (that is, accompanied by a minima in the first derivative of mass with respect to time).

3.2.3 *medium volatile matter—matter, n—*materials (such as oil and polymer degradation products) that boil in the temperature range between 200 °C and ~~400°C.~~400 °C.

3.2.4 *residue—residue, n—*material remaining (such as metal components, filler content or inert reinforcing materials) after more volatile components are vaporized.

~~3.2.4 *mass loss plateau—a region of a thermogravimetric curve with a relatively constant mass (that is, accompanied by a minima in the first derivative of mass with respect to time).*~~

4. Summary of Test Method

4.1 Mass is the primary dependent parameter and temperature is the primary independent parameter measured by ~~TGA.~~thermogravimetric analysis.

4.2 Mass loss and residue measurements are validated by their direct measurement using thermogravimetric apparatus over a specified temperature range using reference materials of known volatiles content as an analyte.

4.3 Alternatively, validation of a ~~TGA~~thermogravimetic method based upon mass loss and residue measurements may be performed using a specific test specimen as the analyte.

4.4 The mass loss of three or more specimens (nominally representing the maximum, midpoint, and minimum of the range of this test method) is measured at least in triplicate. A fourth blank specimen, containing no analyte, is also measured at least in triplicate.

NOTE 1—Repeatability is determined by performing a sufficient number of determinations to calculate statistically valid estimates of the standard deviation or relative standard deviation of the measurements.

4.4.1 Mass loss and residue linearity and bias are determined from the ~~best-fit straight-line~~ linear regressions (best-fit straight line) correlation of the results from measurements of the three or more specimens.

4.4.2 Mass loss and residue detection ~~limit and quantitation limit~~ limit, quantitation limit, and repeatability are determined from the standard deviation of the blank specimen measurements.

4.4.3 Mass loss and residue repeatability are determined from the repeatability measurements of the three or more analyte-containing specimens.

4.5 Temperature measurement is validated using three or more temperature calibration materials (nominally representing the minimum, midpoint, and maximum of the range of the test method) that are measured at least in triplicate.

4.5.1 Temperature linearity, bias, detection limit, quantitation limit, and repeatability are determined from the standard deviation of these measurements.

5. Significance and Use

5.1 This test method may be used to validate the performance of a specific ~~TGA apparatus.~~thermogravimetric analyzer.

5.2 This test method may be used to validate the performance of a specific method based upon a ~~TGA~~thermogravimetry mass loss or residue measurement.

5.3 This test method may be used to determine the repeatability of a specific apparatus, operator, or laboratory.

5.4 This test method may be used for specification and regulatory compliance purposes.

6. Interferences

6.1 This test method depends upon distinctive thermal stability ranges of the measured components as a principle of the test. For this reason, impurities or other materials that have no well-defined thermally stable range, or the thermal stability of which are the same as other components, may create interferences.

7. Apparatus

7.1 *Thermogravimetric Analyzer (TGA)—*The essential instrumentation required to provide minimum thermogravimetry capability for this test method includes:

7.1.1 A thermobalance composed of:

7.1.1.1 A furnace to provide uniform controlled heating of a specimen to a constant temperature of ~~400°C~~at least 400 °C and at a constant rate between 5 °C/min and ~~25°C/min.~~25 °C/min.

7.1.1.2 A temperature sensor to provide an indication of the specimen/furnace temperature readable to ~~±0.1°C.~~±0.1 °C.

7.1.1.3 A continuous recording balance (thermobalance) with a minimum capacity of 100 mg and a sensitivity of ±10 µg to measure the specimen mass.

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7.1.1.4 A means of maintaining the specimen/container under a controlled atmosphere using an inert gas of 99.9+ % purity at a purge rate of 50 mL/min to 100 mL/min ± 5 mL/min.

NOTE 2—Excessive purge rates should be avoided as they may introduce interferences due to turbulence effects and temperature gradients.

7.1.2 A temperature controller capable of executing a specific temperature program by operating the furnace between selected temperature limits at a rate of temperature change of 5 °C/min to ~~25°C/min~~ 25 °C/min to within ± ~~0.5°C/min.~~ 0.5 °C/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 mass, temperature, and time.

7.1.4 Containers (pans, crucibles, etc.) that are inert to the specimen and that will remain gravimetrically stable up to ~~450°C.~~ 450 °C.

7.2 Graduated micropipettes with a capacity of 20 μL to 40 μL measurable to within ±1 μL.

8. Reagents and Materials

8.1 *Mass Loss Reference Materials,* preferably certified for mass loss covering a range of ~~2, 50, and 98 % mass loss~~ nominally 2 %, 50 %, and 98 mass loss % over the temperature range of 25 °C to ~~200°C.~~ 200 °C.

NOTE 3—Materials with other mass loss values may be used but shall be reported.

8.2 *Temperature Calibration Materials,* preferably certified for transition temperature, representing the minimum, midpoint and maximum of the applicable temperature range of the thermogravimetric analyzer (see Test Method E1582).

8.3 *Nitrogen* (or other inert purge gas) of 99.9+ % purity.

9. Hazards

9.1 During the course of these experiments, organic vapors are evolved from the specimen and will exhaust from the instrument. A ventilation system shall be used to ensure that the operator is not exposed to these vapors.

9.2 Review the ~~Material~~ Safety Data Sheets (~~MSDS~~)(SDS) for the components of the mass loss reference materials and the temperature reference materials for additional safety information.

10. Calibration and Standardization

10.1 After turning the power on, allow the instrument to equilibrate for at least one hour prior to any measurement.

10.2 Perform any cleaning and calibration procedures described by the manufacturer in the apparatus operator's manual.

10.3 If not previously established, perform temperature and mass calibrations according to Test Methods E1582 and E2040, respectively, using the same purge gas, purge flow rate, and heating rate (here ~~10°C/min~~ 10 °C/min) to be used for validation experiments.

11. Procedure for Determining Mass Loss and Residue Measurement Repeatability, Detection Limit, Quantitation Limit, Linearity, and Bias

11.1 This process involves characterizing, in triplicate, specimens with no mass loss and at least three or more test specimens taken to represent the low, medium, and high extremes of the range over which performance is to be validated.

NOTE 4—The details of this procedure are written using mass loss reference materials as an analyte, and with a generic set of experimental conditions. For validation of a specific mass loss method, specimens of the analyte should be prepared to represent the range of the intended test method, and steps 11.2 to 11.20 replaced with the specific mass loss procedure (that is, sample size, heating rate, purge gas, purge flow rate, etc.).

11.2 Prepare at least ~~150 mg~~ 150-mg quantities of each of the reference specimens covering the mass loss range of the test. Nominal mass values might be ~~2, 50,~~ 2 %, 50 %, and 98 mass ~~loss %.~~ loss %.

NOTE 5—Most thermoanalytical methods cover 1.5 to 2 decades of range. The mass values selected should approximate the anticipated range. Other masses losses and mass ranges may be used but shall be reported.

11.3 Tare the empty sample pan.

11.4 Using a micropipette, load 20 μL to 40 μL ± 1 μL of the largest mass loss specimen (for example, the 98 mass ~~loss %~~ loss % reference material) onto the sample container. Close the apparatus in preparation for conducting the experiment. Weigh and record the test specimen mass as $M_o(1)$. Purge the sample chamber with dry nitrogen (or other inert gas) at a flow rate of 50 mL/min to 100 mL/min ± 10 % throughout the experiment.

NOTE 6—Other specimen volumes may be used but shall be reported.

11.5 Heat the test specimen at ~~10°C/min~~ 10 °C/min from 25 °C to ~~400°C~~ 400 °C and record the thermal curve.

NOTE 7—Other heating rates may be used but shall be reported. Higher rates, however, may reduce the resolution between high volatility and medium volatility component leading to poorer detection and quantitation limits.

11.6 Cool the test specimen to ~~25°C.~~ 25 °C. The thermal curve need not be recorded.

11.7 Select a point on the mass loss thermal curve from 11.5 before and another on the mass loss plateau immediately after the first mass loss. These temperature points are identified at T_1 and T_2, respectively. Record the masses at these two points as $M_1(1)$ and $M_2(1)$ (see Fig. 1).

NOTE 8—The valley of the first derivative curve may be useful in identifying T_2 the point of maximum resolution between the lower (high volatility) and higher temperature (medium volatility) mass loss regions.

NOTE 9—It is common to select T_1 to be ambient temperature and $M_1(1)$ to be $M_o(1)$

11.8 Determine the mass loss between $M_1(1)$ and $M_2(1)$ as mass loss $[\Delta M_{max}(1)]$ according to Eq 2.

11.9 Repeat steps 11.3 through 11.8 for the medium mass loss test specimen from step 11.2. Use the same measurement limits (T_1 and T_2) determined in step 11.7. Record this mass loss $[\Delta M_{mid}(1)]$.

11.10 Repeat steps 11.3 through 11.8 for the low mass loss test specimen from step 11.2 Use the same measurement limits (T_1 and T_2) determined in step 11.7. Record the mass loss $[\Delta M_{\overline{min}\text{min}}(1)]$.

11.11 Repeat steps 11.3 through 11.8 for an empty container in which no test specimen is used. This is the blank determination. Use the same measurement limits (T_1 and T_2) determined in step 11.7 (Fig. 2). Record the mass remaining ($M_r(1)$) in mg.

NOTE 10—Observe and record the sign of the value for M_r. It may be positive (apparent weight gain) or negative (apparent mass loss).

11.12 Repeat steps 11.3 through 11.8 two more times for the large mass loss specimen. Record these values as mass losses $[\Delta M_{\overline{max}\text{max}}(2)$ and $\Delta M_{\overline{max}\text{max}}(3)]$.

11.13 Repeat steps 11.3 through 11.8 two more times for the medium mass loss specimen. Record these values as mass losses $[\Delta M_{\overline{mid}\text{mid}}(2)$ and $\Delta M_{\overline{mid}\text{mid}}(3)]$.

11.14 Repeat steps 11.3 through 11.8 two more times for the low mass loss specimen. Record these values as mass losses $[\Delta M_{\overline{min}\text{min}}(2)$ and $\Delta M_{\overline{min}\text{min}}(3)]$.

11.15 Repeat steps 11.3 through 11.7 two more times for the blank (no test specimen) case. Record these values as residue $[M_r(2)$ and $M_r(3)]$.

11.16 Calculate the means (M_r and ΔM), and standard deviations (s) for the mass losses, respectively, from the replicate determinations made on each of the three blank and mass loss specimens (see Practice E1970). Record these values as M_r, ΔM_{max}, ΔM_{mid}, ΔM_{min}, s_r, s_{max}, s_{mid}, and s_{min}.

11.17 Using the standard deviation for the mass loss of the blank (s_r) from 11.16, determine and report the mass loss $(DL)_m$ and residue detection limit $(DL)_r$ and mass loss $(QL)_m$ and residue quantitation limit $(QL)_r$ using Eq 3 and Eq 4, respectively.

11.18 Calculate the pooled relative standard deviation for the mass loss from the s_{max}, s_{mid}, and $s_{\overline{min}\text{min}}$ obtained in 11.16 (see Practice E1970). Report this value as the mass loss repeatability value (r) in mass %.

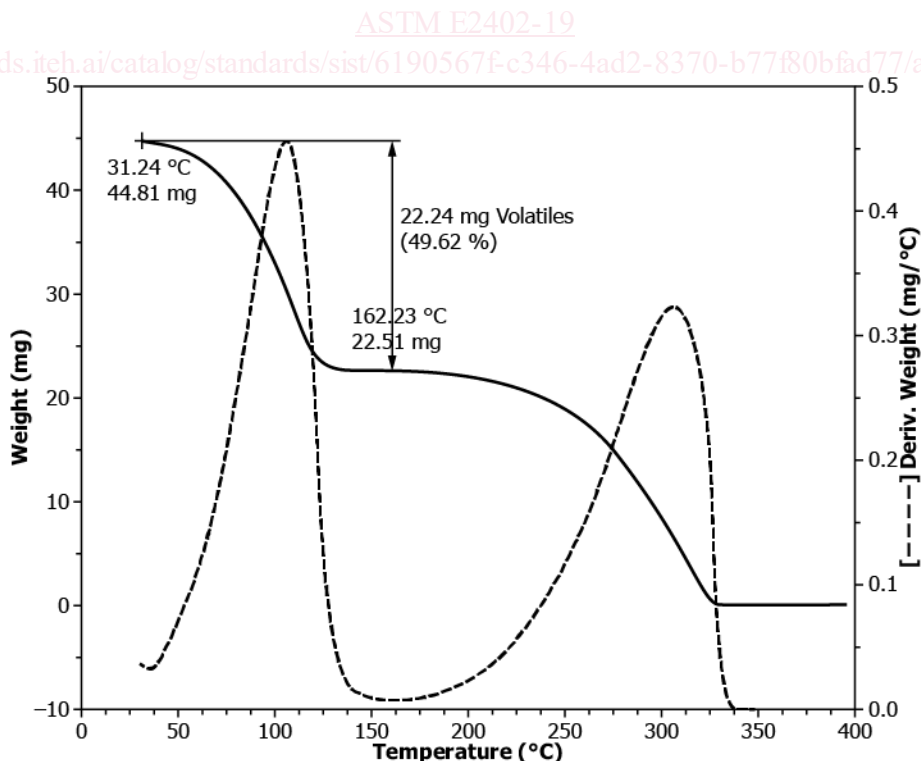FIG. 1 Determination of Mass Loss for Medium Mass Loss Material
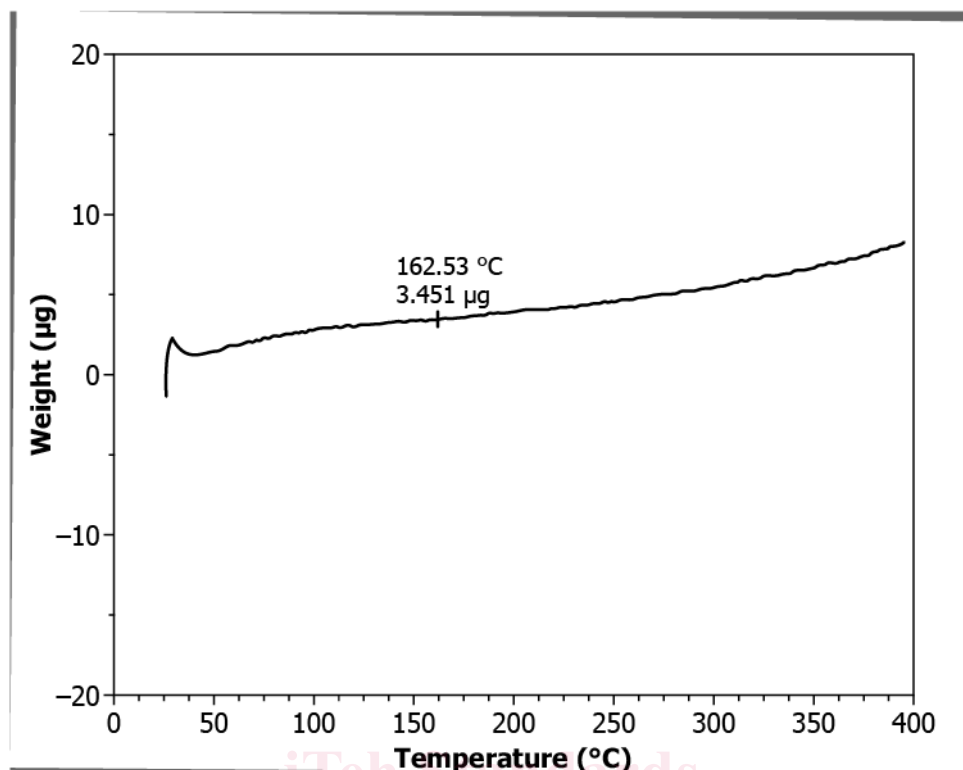
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162.53 °C
3.451 µg

FIG. 2 Blank Determination of Residue

11.19 Using the known mass loss values from step 11.2 as the independent (*X*) values and the mean values for mass loss from step 11.16 as the dependent (*Y*) values, determine ~~the least squares~~ by linear regression the (least squares) best-fit values for the slope (*m*) and intercept (*b*) (see Practice E1970).

11.20 Calculate the linearity (*L*) from the values in 11.19 using Eq 5.

11.21 Report the measurement bias as *M*, in mg. The measurement bias may be expressed as mass % for comparison purposes to the other validation parameters using Eq 6.

12. Procedure for Determining Temperature Repeatability, Detection Limit, Quantitation Limit, Linearity, and Bias

12.1 This process involves characterizing, in triplicate, three (or more) test materials taken to represent the low, medium, and high extremes of the temperature range over which performance is to be validated.

12.2 Select a test method for temperature calibration of the thermogravimetric analyzer such as Test Method E1582.

12.3 Select calibration materials at the minimum, medium-range, and maximum temperatures to be characterized.

12.4 Prepare three test specimens of the low temperature calibration material.

12.5 Using one of the test specimens from 12.4, determine the transition temperature as *T*(low)1 at 10 °C/min. Cool the test specimen to ambient temperature at any convenient rate.

NOTE 11—Other heating rates may be used but shall be reported.

12.6 Prepare three medium-range temperature test specimens.

12.7 Using one of the test specimens from 12.6, determine the transition temperature as *T*(med)1 at the same heating rate used in 12.5.

12.8 Prepare three high temperature test specimens.

12.9 Using one of the test specimens from 12.8 determine the transition temperature as *T*(high)1 at the same heating rate used in 12.5.

12.10 Repeat steps 12.5, 12.7, and 12.9 two more times each for the low, medium-range, and high temperature calibration materials of 12.4, 12.6, and 12.8. Record the transition temperature values as *T*(low)2, *T*(med)2, *T*(high)2, *T*(low)3, *T*(med)3, and *T*(high)3, respectively.

12.11 Calculate (see Practice E1970) the mean (T) and standard deviation (s) for the transition temperatures for the low, medium-range, and high transition materials as T(low), T(med), T(high), s(low), s(med), and s(high) in degrees Celsius.

12.12 Pool (see Practice E1970) the three standard deviation value from step 12.14 and record as s_T.

12.13 Using the pooled standard deviation s_T from 12.12, determine the temperature detection limit $(DL)_T$ and quantitation limit $(QL)_T$ in degrees Celsius as calculated in Eq 3 and Eq 4.

12.14 Using the three literature values for low, medium, and high the transition temperature reference material as the independent (X) value and the three (or more) mean values for the observed temperature values from step 12.11, as the dependent (Y) values, determine by linear regression (least squares best-fit) the slope (m_T) and intercept (b_T) (see Practice E1970).

NOTE 12—The temperature units for m_T will be dimensionless and b_T will be degrees Celsius.

12.15 Calculate the temperature percent linearity $(L)_T$ of the temperature determination from the values in step 12.14 and Eq 5.

12.16 Compare the slope (m_T) from step 12.14 to the anticipated value of 1.00000 using Eq 6. Report this value as the temperature bias ($TBias$).

13. Calculation

13.1 When performing these calculations, retain all available decimal places in the measured values and in intermediate calculated values. The final result should be rounded to three significant figures.

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