Designation: E2402 – 11

Standard Test Method for Mass Loss and Residue 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

1.1 This method provides procedures for validating mass loss and residue measurements by thermogravimetric analyzers (TGA) and analytical methods based upon the measurement of mass loss or residue content. Performance parameters determined include mass loss and residue 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 method.

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.*

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 Practice for Calibration of Temperature Scale for Thermogravimetry

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

2.2 *Other Standard:*

United States Food and Drug Administration, 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.

3.2 *Definitions of Terms Specific to This Standard:*

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

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

3.2.3 *residue*—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.

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 method based upon mass loss and residue measurements may be performed using a specific test specimen as the analyte.

[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.

[3] Available from Food and Drug Administration (FDA), 10903 New Hampshire Ave., Silver Spring, MD 20993-0002, http://www.fda.gov.

4.4 The mass loss of three or more specimens (nominally representing the maximum, midpoint and minimum of the range of the 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 correlation of the results from measurements of the three or more specimens.

4.4.2 Mass loss and residue detection limit and quantitation limit 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.

5. Significance and Use

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

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

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

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

6. Interferences

6.1 This 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 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 and at a constant rate between 5 and 25 °C/min.

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

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

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 to 100 ± 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 to 25 °C/min to within ± 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.

7.2 Graduated micropipettes with a capacity of 20 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 over the temperature range of 25 to 200 °C.

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

8.2 *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) for the components of the Mass Loss 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 Practices E1582 and E2040, respectively, using the same purge gas, purge flow rate and heating rate (here 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 quantities of each of the reference specimens covering the mass loss range of the test. Nominal mass values might be 2, 50, and 98 mass 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 to 40 µL ± 1 µL of largest mass loss specimen (for example, the 98 mass 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 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 from 25 to 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. 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 $[\Delta M_{min}(1)]$.

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 $[\Delta M_{max}(2)$ and $\Delta M_{max}(3)]$.

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

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

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 $M_r(3)]$.

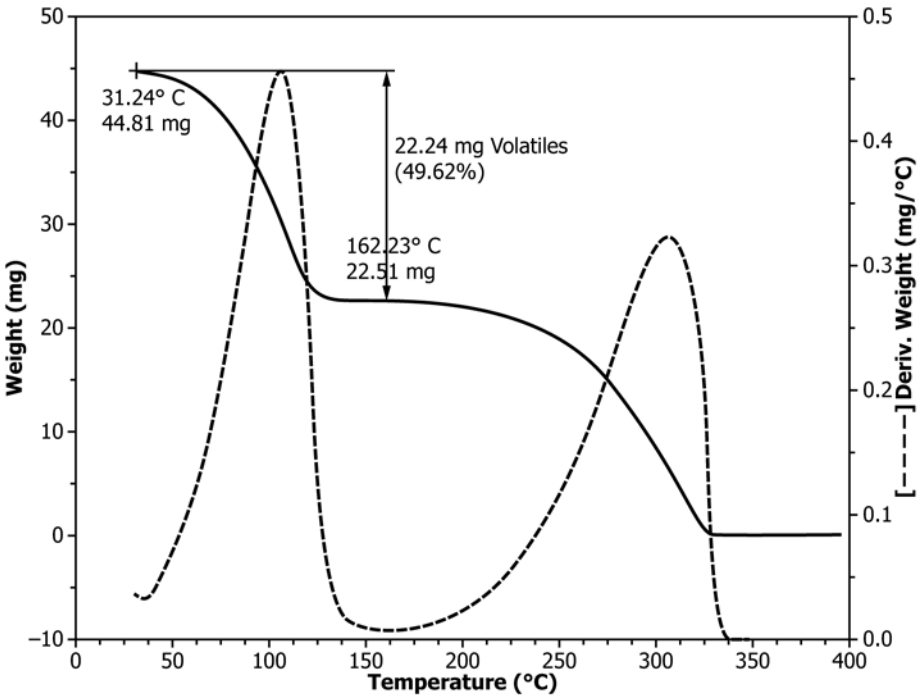

FIG. 1 Determination of Mass Loss for Medium Mass Loss Material

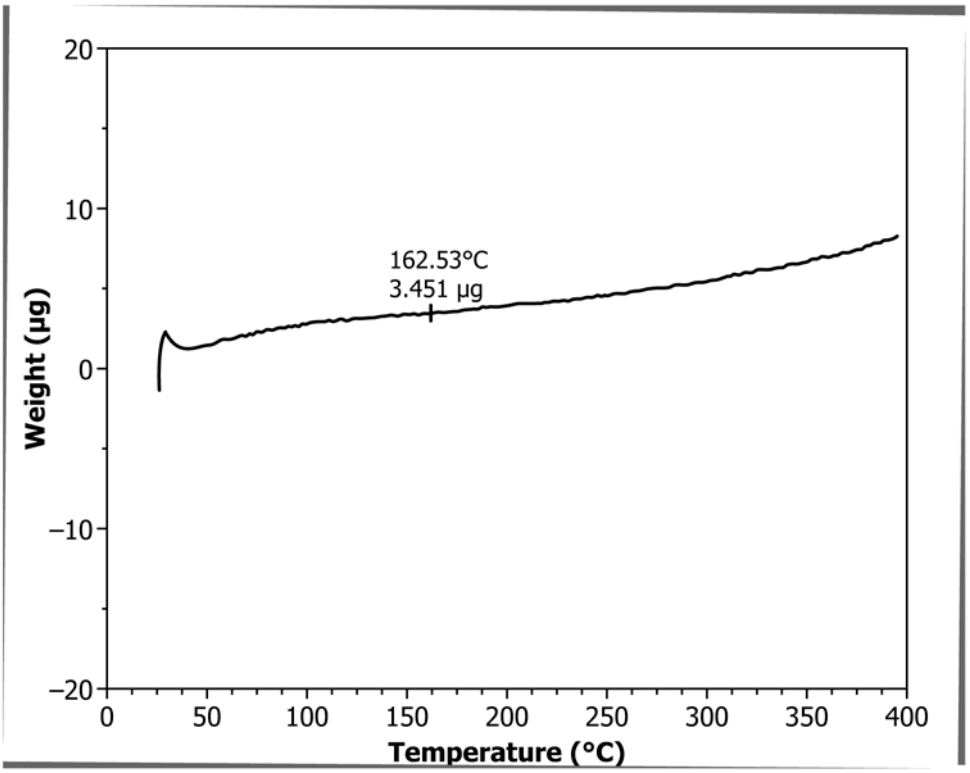

FIG. 2 Blank Determination of Residue

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 and residue detection limit (DL) and quantitation limit (QL) 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_{min} obtained in 11.16 (see Practice E1970). Report this value as the mass loss repeatability value (r) in mass %.

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 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. Calculation

12.1 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.

12.2 Residue is calculated by Eq 1.

$$R = M_2 \times 100\,\%/M_o \tag{1}$$

where:

R = residue, mass %,
M_2 = mass at the higher temperature, mg, and
M_o = mass at the beginning of the experiment, mg.

12.3 Mass loss is calculated using Eq 2.

$$\Delta M = (M_1 - M_2) \times 100\,\%/M_o \tag{2}$$

where:

ΔM = mass loss, mass %, and
M_1 = mass at the lower temperature, mg.

12.4 Mass loss detection limit is calculated using Eq 3.

$$DL = 3.3\, s_r \tag{3}$$

where:

DL = mass loss detection limit, mg, and
s_r = blank mass loss standard deviation, mg,

12.5 Mass loss quantitation limit is calculated using Eq 4:

$$QL = 10\, s_r \quad (4)$$

where:

QL = mass loss quantitation limit, mg.

12.6 Linearity is calculated using Eq 5.

$$L = \left[\frac{|\, largest\ \delta Y\, |}{m \times X_{max} + b} \right] 100\,\% \quad (5)$$

where:

L = linearity, mass %,
m = slope, dimensionless, (from 11.19),
b = intercept, mass %, (from 11.19),
M_o = original mass of the sample, mg, and
$|largest\ \delta Y|$ = absolute value of the largest deviation from the best-fit straight line.

12.7 Bias (*Bias*) for the residue and mass loss measurements are equal in magnitude but are opposite in sign. Bias, M_r, is measured in mg. Bias may be calculated in %, relative to the initial mass loss, using Eq 6.

$$Bias\ (mass\ loss) = -M_r \times 100\,\%/M_o \quad (6)$$

$$Bias\ (residue) = M_r \times 100\,\%/M_o$$

12.8 Detection limit (*DL*) and Quantitation limit (*QL*) may also be reported as a percent of the analyte mass at the beginning of the experiment, M_o, using the equations:

$$DL = 100\,\% \times 3.3\, s_r/M_o \quad (7)$$

and

$$QL = 100\,\% \times 10\, s_r/M_o \quad (8)$$

12.9 *Example Calculations:*

12.9.1 For the example calculations described below, the following experimental data is used:

M_o = 40.0 mg
ΔM_{max} = 99.075 mass %
ΔM_{mid} = 49.645 mass %
ΔM_{min} = 2.544 mass %
M_r = 0.01227 mg ⇒ 0.03068 mass %
n_{max} = 3
n_{mid} = 3
n_{min} = 3
n_o = 3
s_{max} = 0.0320 mass %
s_{mid} = 0.2614 mass %
s_{min} = 0.1424 mass %
s_r = 0.00304 mg ⇒ 0.00760 mass %
X_{max} = 98.76 mass %
X_{mid} = 50.25 mass %
X_{min} = 2.30 mass %

where:

n = number of replicate determinations, and
X = the known volatile matter values for the mass loss reference materials.

12.9.2 Example calculation of mass loss detection limit:

DL = 3.3 × 0.00304 mg = 0.0100 mg
⇒ 3.3 × 0.00760 mass % = 0.0251 mass %

12.9.3 Example calculation of mass loss quantitation limit:

QL = 10 × 0.00304 mg = 0.0304 mg
⇒ 10 × 0.00760 mass % = 0.0761 mass %

12.9.4 Example calculation for repeatability:

$$r = \left[\frac{2 \times 0.0320^2 + 2 \times 0.2614^2 + 2 \times 0.1424^2}{2+2+2} \right]^{1/2}$$
$$= \left[\frac{0.002048 + 0.1367 + 0.04056}{6} \right]^{1/2}$$
$$= 0.173\ \text{mass}\,\%$$

12.9.5 Example calculation of linearity:

12.9.5.1 From the best-fit to the *max*, *mid*, and *min* data (see Practice E1970):

m = 1.000771537
b = –0.054247100 mass %

12.9.5.2 From the best-fit straight line:

$\delta Y_{max} = \Delta M_{max} - (m \times X_{max} + b)$ = (99.075 – 98.782) mass %
δY_{max} = 0.2931 mass %
δY_{mid} = –0.5895 mass % ← largest deviation from best-fit line
δY_{min} = –0.2965 mass %

12.9.5.3 Example calculation of linearity:

$$L = \frac{|-0.5895|}{98.7820}\, 100\,\% = 0.597\,\%$$

12.9.6 Example calculation of bias:

Bias (mass loss) = –0.01227 mg, or
–100 % × 0.01227 mg /
40.0 mg = –0.0307 mass %
Bias (residue) = 0.01227 mg, or 0.0307 mass %

13. Report

13.1 Manufacturer and model of TGA apparatus.

13.2 Some or all of the performance parameters described by this method are useful for the application at hand including:

13.2.1 Range (ΔM_{min} to $\Delta\ M_{max}$),
13.2.2 Mass loss detection limit (*DL*),
13.2.3 Mass loss quantitation limit (*QL*),
13.2.4 Linearity (*L*),
13.2.5 Bias (mass loss) and Bias (residue), and
13.2.6 Repeatability (*r*).

13.3 The specific dated version of the method used.

14. Precision and Bias

14.1 Precision and bias are determined by the procedures in this document. No separate precision and bias information is required.

15. Keywords

15.1 detection limit; linearity; precision; quantitation limit; range; repeatability; thermal analysis; thermogravimetric analysis; validation