



Standard Test Method for Humidity Calibration (or Conformation) of Humidity Generators for Use with Thermogravimetric Analyzers¹

This standard is issued under the fixed designation E2551; 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 test method describes the humidity calibration (or conformance) of humidity generators for use with thermogravimetric analyzers and other thermal analysis apparatus. The humidity range covered is 5 to 95 % relative humidity (% RH) and the temperature range is 0 to 80°C.

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

1.3 There are no ISO equivalents to this standard.

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

2. Referenced Documents

2.1 *ASTM Standards:*²

[D1193 Specification for Reagent Water](#)

[E177 Practice for Use of the Terms Precision and Bias in ASTM Test Methods](#)

[E473 Terminology Relating to Thermal Analysis and Rheology](#)

[E691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method](#)

[E1142 Terminology Relating to Thermophysical Properties](#)

[E1582 Practice for Calibration of Temperature Scale for Thermogravimetry](#)

3. Terminology

3.1 Specific technical terms used in this standard are defined in Terminologies [E473](#) and [E1142](#). These terms include *thermal curve* and *thermogravimetric analysis*.

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.

3.2 Definitions of Terms Specific to This Standard:

3.2.1 *relative humidity, n*—the ratio of actual partial pressure of water to the saturated water vapor pressure at the same temperature, expressed as a percentage.

3.2.2 *water activity, n*—the ratio of actual partial pressure of water to the saturated water vapor pressure at the same temperature, expressed as a decimal fraction.

3.2.2.1 *Discussion*—Water activity is also known as relative pressure in some applications areas.

3.2.3 *first-deviation-from-baseline, n*—the relative humidity or water activity at which a deflection from the established baseline is first observed.

4. Summary of Test Method

4.1 Humidity generators are devices aimed at producing a specific level of humidity in the purge gas used by thermogravimetric analyzers or other thermal analysis apparatus. The requested humidity levels may be held constant (isohum) or increased or decreased in a continuous or stepped fashion.

4.2 The humidified purge gas is submitted to a thermogravimetric analyzer in which the weight of a hygroscopic material is observed. The relative humidity (or activity) of the moisture in the purge gas is stepped or scanned through a humidity range. At a fixed humidity of the purge gas, the test specimen deliquesces and gains weight. In Test Method A, the humidity of the onset of this weight gain is taken as the humidity calibration point. In Methods B and C, the rate of weight change is zero at the humidity calibration point.

5. Significance and Use

5.1 This test method calibrates or demonstrates conformity of the humidity level in a purge gas generated by a humidity generator at a fixed temperature. Such calibration or demonstration of conformity may be required by quality initiatives.

5.2 Conformance demonstrates that the humidified purge gas is within some established limits.

5.3 Calibration provides an offset and or slope value that may be used for establishing the relative humidity scale of the apparatus.

6. Interferences

6.1 Temperature regulation of any solution-head space environment to within $\pm 0.1^\circ\text{C}$ is essential for realizing generated relative humidity values stable to within $\pm 1\%$ RH (expected).

7. Apparatus

7.1 The humidity generator that is the focus of this standard may be an accessory providing a humidified purge gas to some other thermal analysis apparatus (typically a thermogravimetric analyzer) or it may be part of a self-contained instrument that includes both the humidity generator and the thermal analysis apparatus. In the former case, some of the components described below may be redundant.

7.2 *Humidity Generator*—The essential instrumentation required to provide the minimum humidity generator capability for this method includes:

7.2.1 *Temperature Sensor*—to provide an indication of the purge gas temperature readable to within $\pm 0.1^\circ\text{C}$.

7.2.2 *Temperature Controller*—capable of executing a specific temperature program by operating heaters or coolers between selected temperature limits at a rate of temperature change of $0.5^\circ\text{C}/\text{min}$ constant to $\pm 0.1^\circ\text{C}/\text{min}$ or at an isothermal temperature constant to within $\pm 0.1^\circ\text{C}$.

7.2.3 *Humidity Sensor*—capable of indicating the humidity of the purge gas over the range of 5 to 95 % relative humidity (% RH) readable to within $\pm 0.1\%$ RH.

7.2.4 *Humidity Controller*—capable of executing a specific humidity program by operating purge gas humidifiers between selected humidity limits at a rate of humidity change of 0.5% RH/min constant to within $\pm 0.1\%$ RH or at an isohum relative humidity to within $\pm 0.1\%$ RH.

7.2.5 *Purge Gas Flow Sensor*—capable of measuring purge gas flow readable to within $\pm 0.1\text{ mL}/\text{min}$.

7.2.6 *Purge Gas Flow Controller*—capable of controlling purge gas flow readable to within $\pm 0.1\text{ mL}/\text{min}$.

7.2.7 *Humidifier element*—capable of generating purge gases with relative humidity continuously over the range of 5 to 95 % RH.

7.3 *Thermogravimetric Analyzer (TGA)*—The essential instrumentation required to provide the minimum thermogravimetric analytical capability for this method includes:

7.3.1 A *furnace* to provide uniform controlled heating or cooling of a specimen to a constant temperature or at a constant rate within the applicable temperature range of this method.

7.3.2 A *temperature sensor* to provide an indication of the specimen or furnace temperature to within $\pm 0.1^\circ\text{C}$.

7.3.3 A continuously recording balance to measure the specimen weight with a minimum capacity of 100 mg and sensitivity of $\pm 10\ \mu\text{g}$.

7.3.4 A means of maintaining the specimen/container under atmospheric control at a purge rate of 10 to 200 mL/min $\pm 10\text{ mL}/\text{min}$ or 1 %, whichever is greater.

7.3.5 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 $0.5^\circ\text{C}/\text{min}$ constant to within $\pm 0.1^\circ\text{C}/\text{min}$ or to an isothermal temperature that is maintained constant to within $\pm 0.1^\circ\text{C}$ for a minimum of 100 h.

7.3.6 *Containers* (pans, crucibles, etc.) that are inert to the specimen and that will remain gravimetrically stable within the temperature limits of this method.

7.3.7 *Data storage* capable of storage of the weight and relative humidity signals.

7.3.8 A *display* capable of plotting a thermal curve with weight on the ordinate (Y-axis) and relative humidity (or activity) on the abscissa (X-axis) with a sensitivity of $10\ \mu\text{g}$ for weight and 0.1 % RH, respectively.

8. Reagents and Materials

8.1 One or more inorganic salts taken from [Table 1](#) selected to provide the humidity range of interest.

8.2 *Purity of Reagents*—Reagent grade chemicals (or better) shall be used for preparation of all standard solutions.

8.3 *Purity of Water*—Reagent water produced by distillation or by ion exchange, or reverse osmosis followed by distillation shall be used (see Specification [D1193](#)).

TABLE 1 Humidity Fixed Points

Greenspan, L., “Humidity Fixed Points of Binary Saturated Aqueous Solutions,” *Journal of Research of the National Bureau of Standards — A. Physics and Chemistry*, Vol 81A, No. 1, 1977, pp. 89–96.

Temperature (°C)	Lithium Chloride	Potassium Acetate	Magnesium Chloride	Potassium Carbonate	Magnesium Nitrate	Sodium Bromide	Strontium Chloride	Sodium Chloride	Potassium Chloride
10	11.3	23.7	33.5	43.1	57.4	62.2	75.66	75.7	86.8
15	11.3	23.4	33.3	43.2	55.9	60.7	74.13	75.6	85.9
20	11.3	23.1	33.1	43.2	54.4	59.1	72.52	75.5	85.1
25	11.3	22.5	32.8	43.2	52.9	57.6	70.85	75.3	84.3
30	11.3	21.6	32.4	43.2	51.4	56.0	69.12	75.1	83.6
35	11.3	...	32.1	...	49.9	54.6	...	74.9	83.0
40	11.2	...	31.6	...	48.4	53.2	...	74.7	82.3
45	11.2	...	31.1	...	46.9	52.0	...	74.5	81.7
50	11.1	...	30.5	...	45.4	50.9	...	74.4	81.2
55	11.0	...	29.9	50.2	...	74.4	80.7
60	11.0	...	29.3	49.7	...	74.5	80.3
65	10.9	...	28.5	49.5	...	74.7	79.9
70	10.8	...	27.8	49.7	...	75.1	79.5
75	10.6	...	26.9	50.3	...	75.6	79.2
80	10.5	...	26.1	51.4	...	76.3	78.9

9. Hazards

9.1 Salt solutions are extremely corrosive to apparatus if spilled. Care shall be taken in their preparation and handling to prevent contact with apparatus.

10. Preparation of Apparatus

10.1 Perform any setup or calibration procedures recommended by the apparatus manufacturer in the operations manual.

10.2 *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.

11. Calibration and Standardization

11.1 Calibrate the temperature display of the apparatus according to Test Method E1582 using a heating rate of $0.5 \pm 0.2^\circ\text{C}/\text{min}$.

12. Procedure

12.1 Close the system, adjust the atmospheric flow rate of the purge gas to the selected rate, and zero (tare) the balance.

12.2 Open the system and place 5 to 10 mg of the reference material in the specimen container in the same position as would be placed for a test specimen. Close the system.

12.3 Measure the weight of the reference material and report its value.

12.4 Test Method A:

12.4.1 Equilibrate the humidity for 60 min at a value that is 5 % RH below the anticipated deliquescence point described in Table 1.

NOTE 1—Other humidity starting points may be used but shall be reported.

12.4.2 Initiate either a humidity program with either 0.2 % RH steps and 12 min soak times or 1 % RH/hr linear increase to an ending humidity value that is 5 % RH higher than the anticipated deliquescence point in Table 1.

NOTE 2—Other humidity ending points and rate of humidity change may be used but shall be reported.

12.4.3 Plot the results as weight of the reference material on the ordinate (Y-axis) and the relative humidity on the abscissa (X-axis) of a thermal curve.

12.4.4 Determine the first-deviation-from-baseline as the deliquescence point of the reference material (see Fig. 1). Report the corresponding humidity as M_i .

NOTE 3—The rate of weight gain will increase with relative humidity above the humidity at which the initial weight gain is observed. There is no inflection point. The use of extrapolate onset values shall not be used.

12.5 Test Method B:

12.5.1 Equilibrate the humidity for 60 min at 5 % RH above the anticipated deliquescence point described in Table 1.

NOTE 4—Other humidity starting points and equilibrium times may be used but shall be reported.

12.5.2 Initiate decreasing humidity program with either 0.2 % RH steps and 12 min soak times or a linearly decreasing

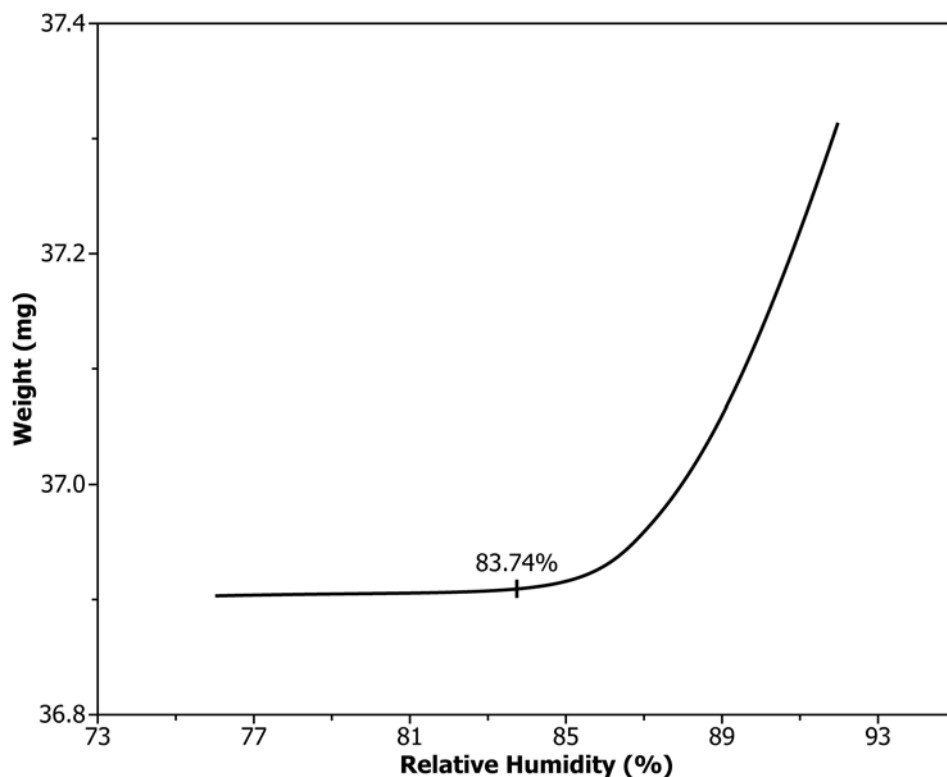


FIG. 1 First-Deviation-From-Baseline as the Deliquescence Point of the reference material

at 1 % RH/hr to an ending value that is 5 % RH lower than the anticipated deliquescence point in **Table 1**.

NOTE 5—Other humidity ending points and rates of change may be used but shall be reported.

12.5.3 Create a plot of the weight of the reference material on the ordinate (Y-axis) versus the relative humidity on the abscissa (X-axis).

12.5.4 Determine the relative humidity at the peak of the deliquescence curve (see **Fig. 2**). Report this value as *M_p*.

12.6 *Test Method C:*

12.6.1 Equilibrate the humidity for 60 min at 5 % RH above the anticipated deliquescence point described in **Table 1**.

NOTE 6—Other humidity starting points and equilibrium times may be used but shall be reported.

12.6.2 Initiate a decreasing humidity program with either a 0.2 % RH steps and 12 min soak times or a linearly decreasing program at 1 % RH/hr to an ending value that is 5 % RH lower than the anticipated deliquescence point in **Table 1**.

NOTE 7—Other humidity ending points and rates of change may be used but shall be reported.

12.6.3 Create a plot of the rate of weight change as a function of a change in humidity (dm/dRH) of the reference material on the ordinate (Y-axis) versus the relative humidity on the abscissa (X-axis).

12.6.4 Determine the relative humidity at the point where dm/dRH = 0 (see **Fig. 3**). Report this value as *M_z*.

13. Calculation or Interpretation of Results

13.1 Conformance (*C*) is the percent relative humidity difference between an observed deliquescence value and that of the reference material (*M_s*) taken from **Table 1** and is given by **Eq 1**. *M_i* or *M_p* are taken as *M_o* for Methods A and B, respectively,

$$C = M_o - M_s \text{ or } C = M_p - M_s \text{ or } C = M_z - M_s \quad (1)$$

NOTE 8—The conformance estimation is essentially an estimate of bias and is suitable only for those humidities in the vicinity of the deliquescent of the reference material. More than one determination of conformance may need to be performed to describe the humidity range from 5 to 95 % RH.

14. Report

14.1 Report the following information:

14.1.1 A complete identification and description of the reference material used for calibration.

14.1.2 Description of the humidity generator and thermogravimetric analyzer used.

14.1.3 Experimental conditions including initial specimen weight, initial and final relative humidities and the rate of humidity change.

14.1.4 The values for *M_i* or *M_p* or both.

15. Precision and Bias

15.1 The precision of these test methods are based on an interlaboratory study conducted in 2011. Three laboratories analyzed a total of three powdered compounds by three unique

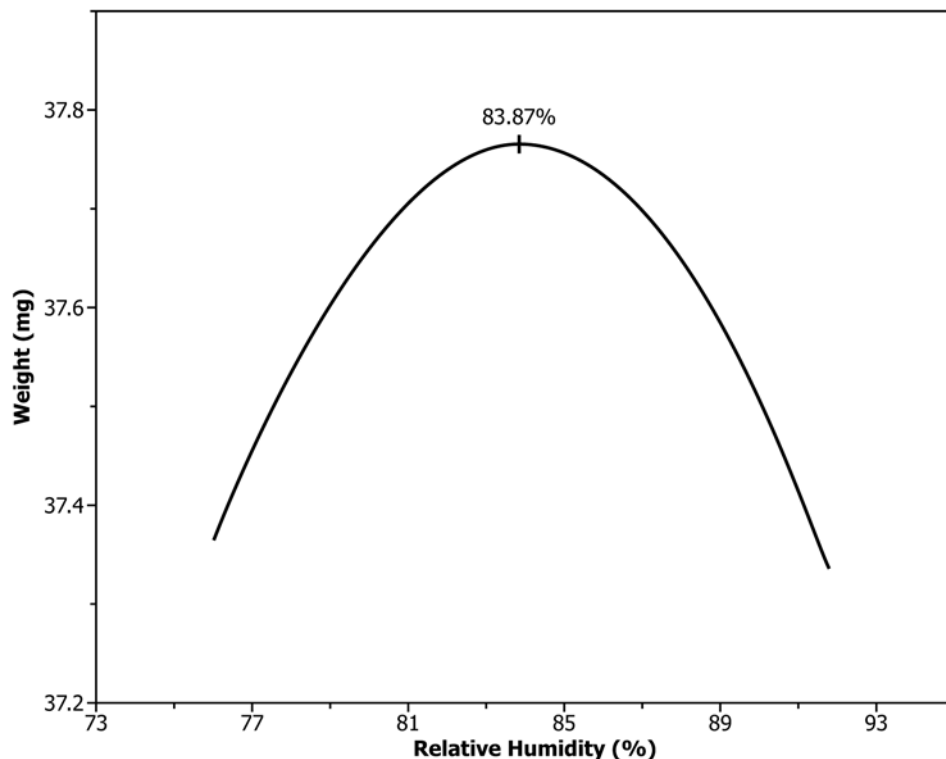


FIG. 2 Relative Humidity at the Peak of the Deliquescence Curve

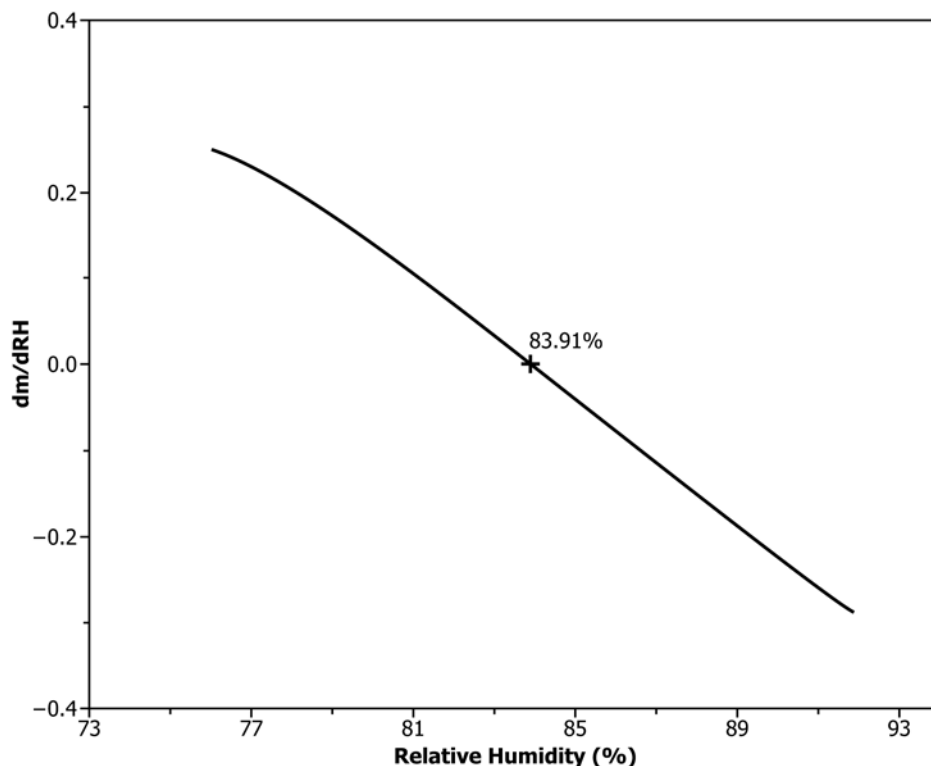


FIG. 3 Relative Humidity at the Point where $dm/dRH = 0$

methods as part of this study. Every test result represents an individual determination, and each lab was asked to report triplicate results for each compound. Practice E691 was followed for the design and analysis of the data; the details are given in ASTM Research Report No. E37-1042.³

15.1.1 *Repeatability Limit (r)*—Two test results obtained within one laboratory shall be judged not equivalent if they differ by more than the “*r*” value for that material; “*r*” is the interval representing the critical difference between two test results for the same material, obtained by the same operator using the same equipment on the same day in the same laboratory.

15.1.1.1 Repeatability limits are listed in Tables 2-4.

15.1.2 *Reproducibility Limit (R)*—Two test results shall be judged not equivalent if they differ by more than the “*R*” value for that material; “*R*” is the interval representing the critical difference between two test results for the same material, obtained by different operators using different equipment in different laboratories.

15.1.2.1 Reproducibility limits are listed in Tables 2-4.

15.1.3 The above terms (repeatability limit and reproducibility limit) are used as specified in Practice E177.

15.1.4 Any judgment in accordance with statements 15.1.1 and 15.1.2 would have an approximate 95 % probability of being correct.

15.2 *Bias*—Bias is the difference between a mean measured result and an accepted value. In this study, the accepted values for results may be found in Table 1. Bias may be determined by comparing the experimental results in Tables 2-4 with these accepted values.

³ Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:E37-1042. Contact ASTM Customer Service at service@astm.org.

TABLE 2 Test Method A — % Relative Humidity at $23 \pm 1^\circ\text{C}$

Material ID	Average ^A	Repeatability Standard Deviation	Reproducibility Standard Deviation	Repeatability Limit	Reproducibility Limit
	\bar{x}	s_r	s_R	<i>r</i>	<i>R</i>
Lithium Chloride (LiCl), powder	10.801	0.128	1.005	0.359	2.814
Potassium Carbonate (K ₂ CO ₃), powder	42.179	0.457	1.755	1.279	4.913
Sodium Chloride (NaCl), powder	75.153	0.184	0.797	0.517	2.233

^A The average of the laboratories' calculated averages.

TABLE 3 Test Method B — % Relative Humidity at 23 ± 1°C

Material ID	Average ^A	Repeatability Standard Deviation	Reproducibility Standard Deviation	Repeatability Limit	Reproducibility Limit
	\bar{x}	S_r	S_R	r	R
Lithium Chloride (LiCl), powder	11.110	0.126	0.358	0.352	1.002
Potassium Carbonate (K ₂ CO ₃), powder	44.474	0.679	0.825	1.901	2.309
Sodium Chloride (NaCl), powder	75.944	0.121	0.165	0.338	0.462

^A The average of the laboratories' calculated averages.

TABLE 4 Test Method C — % Relative Humidity at 23 ± 1°C

NOTE 1— S_r and S_R are reported as the same value. This is in accordance with Practice E691 – 12, Appendix X1, Section X1.1.2.2, “When S_R calculates to less than S_r , S_R is set equal to S_r .” As a result, r and R also obtain the same value according to Equations 10 and 11 in the same document.

Material ID	Average ^A	Repeatability Standard Deviation	Reproducibility Standard Deviation	Repeatability Limit	Reproducibility Limit
	\bar{x}	S_r	S_R	r	R
Lithium Chloride (LiCl), powder	11.02	0.684	0.684	1.916	1.916
Potassium Carbonate (K ₂ CO ₃), powder	44.414	0.685	0.833	1.918	2.331
Sodium Chloride (NaCl), powder	75.919	0.096	0.200	0.268	0.561

^A The average of the laboratories' calculated averages.

15.3 The precision statement was determined through statistical examination of 81 results, determined using three methods, on three different study materials.

16. Keywords

16.1 humidity; moisture; thermal analysis; thermogravimetric analysis

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