Designation: D8339 – 20

Standard Test Method for The Analysis of Flue Gas Desulfurization Solids by Macro Thermogravimetric Analysis[1]

This standard is issued under the fixed designation D8339; 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 instrumental test method covers the determination of free moisture, gypsum ($CaSO_4$•$2H_2O$), calcium sulfite hemihydrate ($CaSO_3$•½H2O), calcium hydroxide ($Ca(OH)_2$), calcium carbonate ($CaCO_3$), and ash in flue gas desulfurization solids using a macro thermogravimetric analyzer.

1.2 This instrumental test method is not applicable to thermogravimetric analyzers using microgram size samples.

1.3 *Units*—The values stated in SI units are to be regarded as standard. The values given in parentheses after SI units are provided for information only and are not considered 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, 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]

D121 Terminology of Coal and Coke

D3180 Practice for Calculating Coal and Coke Analyses from As-Determined to Different Bases

D8146 Guide for Evaluating Test Method Capability and Fitness for Use

E177 Practice for Use of the Terms Precision and Bias in ASTM Test Methods

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

E1601 Practice for Conducting an Interlaboratory Study to Evaluate the Performance of an Analytical Method

3. Terminology

3.1 *Definitions of Terms Specific to This Standard:*

3.1.1 *flue-gas desulfurization solids, n*—generally are finely divided materials containing various amounts of free moisture.

3.1.1.1 *Discussion*—The origin of the materials is dewatered slurries resulting from the absorption of sulfur dioxide by slurries of lime or limestone fines in a flue gas desulfurization process.

3.1.2 *free moisture, n*—the moisture that evolves from flue-gas desulfurization solids, clay materials, hydrated lime, and similar materials, when they are heated at temperatures ranging from 45 °C to 60 °C until a constant mass is reached.

3.1.2.1 *Discussion*—Free moisture in these materials is not the same as the free moisture in coal, as defined in Terminology D121.

3.2 For definitions of other terms used in this test method, refer to Terminology D121.

4. Summary of Test Method

4.1 In thermogravimetric analysis, the mass of a sample in a controlled atmosphere is recorded repeatedly as a function of temperature or time, or both. *Macro thermogravimetric analysis* (macro TGA) of flue gas desulfurization solids (FGD-Solids) uses a sample mass of approximately 1 g. In a typical analysis, the temperature is normally ramped from ambient to a specific temperature and held at that temperature for a prescribed length of time, and the correspondent specimen mass is repeatedly recorded by the instrument.

4.2 FGD-Solids components: *free moisture, gypsum, calcium sulfite hemihydrate, calcium hydroxide, calcium carbonate*, and *ash* are sequentially determined in a single multi-step heating program. The analysis of a particular component is complete when the specimen reaches a constant mass or at the end of the step.

4.3 *Free Moisture* is determined by measuring the mass loss, caused by evaporating free water from the analysis specimen when heated to 50 °C.

[1] This test method is under the jurisdiction of ASTM Committee D05 on Coal and Coke and is the direct responsibility of Subcommittee D05.29 on Major Elements in Ash and Trace Elements of Coal.

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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.

4.4 *Gypsum*, $CaSO_4 \cdot 2H_2O$, is determined by measuring the mass loss, caused by removal of gypsum hydrate water from the analysis specimen when further heated to 240 °C.

4.5 *Calcium Sulfite Hemihydrate*, $CaSO_3 \cdot ½H_2O$, is determined by measuring the mass loss, caused by removal of calcium sulfite hydrate water from the analysis specimen when further heated to 400 °C. $CaSO_3$ is subsequently oxidized to $CaSO_4$ prior to the next step.

4.6 *Calcium Hydroxide*, $Ca(OH)_2$, is determined by measuring the mass loss, caused by removal of hydroxide water from the analysis specimen when further heated to 550 °C.

4.7 *Calcium Carbonate*, $CaCO_3$ is determined by measuring the mass loss caused by removal of carbon dioxide from the analysis specimen when further heated to 950 °C.

4.8 *Ash* is determined as the residue from the sequential determination of previously analyzed components.

5. Significance and Use

5.1 *Free Moisture*, as determined by this instrumental test method, is used for calculating other analytical results to a dry basis using procedures in Practice D3180.

5.2 *Gypsum* is the primary product used to assess the quality of the FGD-Solids for industrial purposes, especially construction wallboard. FGD solids are also used in mining applications, cement manufacturing, and for agricultural purposes.

5.3 *Calcium Sulfite Hemihydrate* is used to assess the suitability of some FGD-Solids for industrial uses.

6. Apparatus

6.1 *Macro Thermogravimetric Analyzer (Macro TGA)*—A computer-controlled apparatus consisting of a furnace with a cavity large enough to accept crucibles containing test specimens that meet the minimum mass requirements of the procedure. The macro TGA system can accommodate multiple crucibles, allowing for continuous analysis with one crucible reserved for the blank or reference crucible. The furnace is constructed so the cavity is surrounded by a suitable refractory and insulated so as to develop a uniform temperature in all parts of the cavity, but with a minimum free space. The furnace shall be capable of being heated rapidly (25 °C/min or higher) from ambient temperature to 950 °C. The temperature shall be monitored and maintained at values specified for each determination. The system shall have an integrated balance capable of sequentially weighing the crucibles and test specimens repeatedly throughout the analysis. All mass measurements are conducted and recorded by the system. The sensitivity of the balance shall be 0.1 mg or lower. Provision shall be made to introduce gases specified for this standard and to remove products of drying, devolatilization, and combustion. The macro TGA system shall have a venting fan, tolerant of hot product gases, to efficiently remove the exhaust gases.

6.2 *Crucibles,* of composition and dimensions specified for the instrument by the instrument manufacturer. No crucible lids are required for this method.

7. Reagents and Materials

7.1 *Drying Gases*—Nitrogen (99.5 % purity) or Argon (99.5 % purity).

7.2 *Oxidizing Gas*—Oxygen (99.5 % purity).

8. Hazards

8.1 The user shall ensure acceptable documented safety procedures are in place for the handling of all reagents and test materials and for the operation of laboratory equipment specified for these test methods.

8.2 *Venting Equipment*—Install equipment in the vicinity of the apparatus to vent combustion and volatile gases evolved during the test procedures from the laboratory.

9. Sampling, Test Specimens, and Test Units

9.1 FGD-Solids are generally finely divided materials containing various amounts of free moisture. Since the origin of the materials is slurries, the particle sizes of the solids are generally less than the 250 µm (No. 60 U.S. Standard sieve) material required for the analysis for coal. For some FGD-Solids samples, it may be necessary to pre-dry the samples before analysis to remove excessive free moisture. One should be careful to not over dry the sample, which may affect the sulfite content. (See Note 1.)

NOTE 1—During the ruggedness testing in the development of this test method, it was determined that drying some FGD-Solids in air at 77 °C for 3 h reduced the amount of calcium sulfite hemihydrate ($CaSO_3 \cdot ½H_2O$) in the wet sample by as much as 20 % (relative). Changes to the other components determined in the method were insignificant.

10. Preparation of Apparatus

10.1 Verify the instrument can meet all specifications in the standard with respect to gas flows, heating rates, and balance sensitivity prior to use. Condition the instrument after initial setup, or repairs, by conducting a run through a complete cycle without samples.

10.2 Condition new crucibles for use in these test methods by heating under the same conditions of the test and cooling before use.

11. Procedure

11.1 The determination of free moisture, followed by the determination of gypsum, calcium sulfite hemihydrate, calcium hydroxide, calcium carbonate, and ash, is carried out in multi-step sequence using the same FGD-Solids test specimen.

11.2 Each macro TGA step is complete when the test specimen either reaches constant mass or is held at a fixed temperature for a fixed time. Constant mass is defined as a point where the fractional mass change is less than or equal to 0.05 % over a 9 min period, either confirmed by using not less than three successive weighings, or a fixed 9 min period of successive weighings.

11.3 The heating program for determination of FGD-Solids components is given in Table 1.[3]

[3] Riley, J. T., Marsh, M., and Lawrenz, D., "Analysis of FGD Solids With a Macro TGA System," *J. Testing and Evaluation*, Vol 45, No. 3, 2017, pp. 904–910

TABLE 1 Temperature Program and Conditions for the Macro TGA Analysis of FGD-Solids

Step	Component	T_{start}, °C	T_{end}, °C	Ramp rate, °C/min	Hold time, min[A]	Gas and flow rate, FV/min[B]	Final mass
1	free moisture	ambient	50	1	NA	N_2, 0.4	m_1
2	$CaSO_4$•$2H_2O$	50	240	17	15	N_2, 1.0	m_2
3	$CaSO_3$•½ H_2O	240	400	17	5	N_2, 1.0	m_3
4	$CaSO_3$•½ H_2O	400	400	0	15	O_2, 1.0	m_4
5	$Ca(OH)_2$	400	550	10	25	N_2, 1.0	m_5
6	$CaCO_3$ and Ash	550	950	25	15	N_2, 1.0	m_6

[A] NA = Not applicable
[B] FV = furnace volume change

11.4 *Sequential Determination of Free Moisture, Gypsum, Calcium Sulfite Hemihydrate, Calcium Hydroxide, Calcium Carbonate, and Ash:*

11.4.1 After verifying instrument setup according to Section 10 on the preparation of apparatus, load and tare the crucibles. Add 1 g of the test specimen to the crucible in the balance position and weigh it immediately before advancing to the next crucible. Transfer the test specimen from the sample bottle to the crucible quickly to minimize the exposure of the test specimen to the atmosphere during the initial weighing process. The initial mass of the test specimen is recorded as m_0.

11.4.2 *Step 1*—To determine free moisture, use an inert gas with a flow rate of 0.4 furnace volume changes per minute and heat the weighed test specimen at a rate of 1 °C⁄min. Program the instrument to terminate the test when the specimen has reached a constant mass, m_1 (see 11.2 and Table 1).

11.4.3 *Step 2*—For gypsum determination following the free moisture analysis, maintain an inert gas atmosphere and increase the flow rate to 1.0 furnace volume change per minute, raise the furnace temperature at a rate of 17 °C⁄min to 240 °C, and hold the final temperature for 15 min. Record the specimen mass, m_2, at the end of the hold period.

11.4.4 *Step 3*—For calcium sulfite hemihydrate determination following the gypsum analysis, maintain the inert gas flow rate, raise the furnace temperature at a rate of 17 °C⁄min to 400 °C, and hold the final temperature for 5 min. Record the specimen mass, m_3, at the end of the hold period.

11.4.5 *Step 4*—For the second part of the calcium sulfite hemihydrate determination, change the atmosphere to oxygen with the same flow rate, and hold the furnace temperature at 400 °C for 15 min. Any calcium sulfite in the test specimen will be oxidized and the mass will increase until it becomes stable. Record the specimen mass, m_4, at the end of the hold period.

11.4.6 *Step 5*—For calcium hydroxide determination following the calcium sulfite hemihydrate analysis, change the atmosphere to an inert gas, maintain the same flow rate, raise the furnace temperature at a rate of 10 °C⁄min to 550 °C, and hold the final temperature for 25 min. Record the specimen mass, m_5, at the end of the hold period.

11.4.7 *Step 6*—For calcium carbonate and ash determination following the calcium hydroxide analysis, maintain the inert gas flow rate, raise the furnace temperature at a rate of 25 °C⁄min to 950 °C, and hold at final temperature for 15 min. Record the specimen mass, m_6, at the end of the hold period.

12. Calculation or Interpretation of Results

12.1 With a computer-controlled macro thermogravimetric analyzer, the computer is normally programmed to perform calculations automatically.

12.2 The following formulae are used to calculate the as-determined component mass fractions for the various components in the analyzed FGD-Solids specimen:

12.2.1 Free moisture (as-determined):

$$w_{H_2O,ad} = \frac{m_0 - m_1}{m_0} \quad (1)$$

12.2.2 Gypsum ($CaSO_4$•$2H_2O$) (as-determined):

$$w_{CaSO_4\cdot 2H_2O,ad} = 4.779 \cdot \frac{m_1 - m_2}{m_0} \quad (2)$$

12.2.3 Calcium sulfite hemihydrate ($CaSO_3$•½H_2O) (as-determined):

$$w_{CaSO_3\cdot \frac{1}{2}H_2O,ad} = 14.338 \cdot \frac{m_2 - m_3}{m_0} \quad (3)$$

12.2.4 Lime ($Ca(OH)_2$) (as-determined):

$$w_{Ca(OH)_2,ad} = 4.113 \cdot \frac{m_4 - m_5}{m_0} \quad (4)$$

12.2.5 Calcium carbonate ($CaCO_3$) (as-determined):

$$w_{CaCO_3,ad} = 2.274 \cdot \frac{m_5 - m_6}{m_0} \quad (5)$$

12.2.6 Ash (as-determined):

$$w_{ash,ad} = \frac{m_6}{m_0} \quad (6)$$

12.2.7 Ash (calculated, as-determined):

$$w_{calcd.ash,ad} = 0.7907 \cdot w_{CaSO_4\cdot 2H_2O,ad} + 1.0541 \cdot w_{CaSO_3\cdot \frac{1}{2}H_2O,ad} + 0.7569 \cdot w_{Ca(OH)_2,ad} + 0.5603 \cdot w_{CaCO_3,ad} \quad (7)$$

where:

m_i = the correspondent mass at the end of the step (see Table 1 and 11.4)
$w_{i,ad}$ = the mass fraction of the FGD-Solids component
4.779 = factor to convert hydrate water to $CaSO_4$•$2H_2O$
14.338 = factor to convert hydrate water to $CaSO_3$•½H_2O
4.113 = factor to convert lime water to $Ca(OH)_2$
2.274 = factor to convert carbon dioxide to $CaCO_3$
0.7907 = factor to convert $CaSO_4$•$2H_2O$ to $CaSO_4$

1.0541 = factor to convert the $CaSO_3 \cdot ½H_2O$ to $CaSO_4$
0.7569 = factor to convert the $Ca(OH)_2$ to CaO
0.5603 = factor to convert $CaCO_3$ to CaO

12.3 To convert the as-determined values ($w_{i,ad}$) to the dry basis ($w_{i,d}$), use the following equation:

$$w_{i,d} = \frac{w_{i,ad}}{1 - w_{H_2O,ad}} \quad (8)$$

13. Report

13.1 In addition to the final test results (reported as percent mass fractions), the following information should be reported.

13.1.1 *Free Moisture*—Report the drying gas (nitrogen or argon) used in the determination of free moisture.

13.1.2 Report the percent mass fraction of calcium sulfite hemihydrate ($CaSO_3 \cdot ½H_2O$) determined only in *step three of the analysis*. Although *step four* is a necessary oxidation step in the procedure, the calcium sulfite hemihydrate determined in this step is not a reliable measure of this component.

13.1.3 For reporting analyses to other than the as-determined basis, refer to Practice D3180.

14. Precision and Bias

14.1 The precision of this test method is based on an interlaboratory study of Test Method D8339, conducted in 2019. Eight laboratories tested different splits of the same materials. Every "test result" represents an individual determination, and all participants reported triplicate test results. Practice E691 was followed for the design and analysis of the data; the details are given in ASTM Research Report RR:D05-2000.[4]

14.2 *Precision*—The relative precision of this test method for the determination of free moisture, gypsum ($CaSO_4 \cdot 2H_2O$), calcium sulfite hemihydrate ($CaSO_3 \cdot ½H_2O$), calcium carbonate ($CaCO_3$), and ash in flue gas desulfurization solids is shown in Table 2. The precision characterized by the repeatability (S_r, r) and reproducibility (S_R, R) is described in Tables A1.1-A1.5.

14.2.1 *Repeatability*—The difference between repetitive results obtained by the same operator in a given laboratory applying the same test method with the same apparatus under constant operating conditions on identical test material within short intervals of time would in the long run, in the normal and correct operation of the test method, exceed the following values only in 1 case in 20.

14.2.2 *Repeatability Limit (r)*—The value below which the absolute difference between two test results of separate and consecutive test determinations, carried out on the same sample in the same laboratory by the same operator using the same apparatus on samples taken at random from a single quantity of homogeneous [≤ 250 µm (No. 60 U.S. Standard sieve)] material, may be expected to occur with a probability of approximately 95 %.

14.2.2.1 *Example: Gypsum Repeatability*—Duplicate analyses for gypsum gave values of 95.68 % and 95.84 %. The repeatability interval $I(r)$ for gypsum is 0.39 %. The difference between the two values is 0.16 % and does not exceed the $I(r)$ of 0.39 %. Therefore, these two values are acceptable at the 95 % confidence level and their average should be reported as the final test result.

14.2.3 *Reproducibility Limit (R)*—The value below which the absolute difference between two test results, carried out in different laboratories using samples taken at random from a single quantity of homogeneous [≤ 250 µm (No. 60 U.S. Standard sieve)] material may be expected to occur with a probability of approximately 95 %. As specified in Practice E1601, the condition that the ratio of the Reproducibility Limit to the sample mean value (R/sample mean value) should be less than 50 was used for improving the precision values.

14.2.3.1 *Example: Gypsum Reproducibility*—Duplicate analyses for free moisture in one laboratory gave an average value of 95.76 %, and a value of 96.58 % was obtained in a different laboratory. The reproducibility interval $I(R)$ for gypsum is 0.68 %, and the difference between the different laboratory values is 0.82 %. Since this difference is greater than the $I(R)$ of 0.68 %, these two values are not acceptable at the 95 % confidence level; therefore, each of the laboratories should obtain an additional test result for comparison.

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

14.3 *Scope Limits for a Test Method*—Guide D8146 offers techniques for evaluating the statistical capability and fitness for use in standard test methods. Scope limits is one such technique.

14.3.1 The lower scope limit of a test method is the larger of [lowest sample mean tested in the Interlaboratory Study (ILS)] or [the test level where the ratio of the test level to the within

[4] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D05-2000. Contact ASTM Customer Service at service@astm.org.

TABLE 2 Percent Mass Fractions Ranges and Limits for Repeatability (r), Reproducibility (R), and Precision Ratio (PR) for Various Parameters

Parameter[A]	Mass Fraction Range, %	r	R	PR
Free Moisture	0.12 to 12.04	0.25	0.43	2.6
Gypsum	64.34 to 97.90	0.39	0.68	2.6
Calcium Sulfite Hemihydrate	2.08 to 3.58	0.35	0.75	2.0
Calcium Carbonate	0.41 to 15.78	0.23	0.38	2.0
Ash	78.26 to 79.71	0.14	0.33	2.3

[A] Calcium hydroxide, $Ca(OH)_2$, can be determined as outlined in this procedure. The percent mass fraction of calcium hydroxide determined in this study was 0.21 % to 0.69 % for the 10 samples. However, the high variability of the reported results did not allow for statistically correct calculation of acceptable repeatability and reproducibility limits.

laboratory standard deviation (S_r) is ten]. The latter is conveniently calculated from the relationship expressing the repeatability limit for the test method as r_{int} /(0.28 - r_{sl}). A regression line of the repeatability limit (r) versus average test value for the samples used in the ILS establishes the values of the intercept (r_{int}) and the slope (r_{sl}). The lower scope limits, or analytical parameter values (APV_r), for the five parameters in Table 2 were calculated using the r_{int} /(0.28 – r_{sl}) concept. The APV_r value for free moisture was used for the Mass Fraction Range in Table 2. The APV_r values for the other four parameters in Table 2 were all less than the lowest sample mean in the interlaboratory study (ILS).

14.3.2 Additionally, the upper scope limit of a test method is set to a value that does not exceed the parameter value of the test material with the highest value used in the ILS. The upper scope limits for the five parameters in Table 2 are the highest sample means in the ILS.

14.4 Precision Ratio (*PR*) is the ratio between the reproducibility and repeatability (*R/r*) and can be used to determine whether a test method is sufficiently robust. Generally, a *PR* value between 2 and 4 indicates the test method appears to adequately control between-laboratory common cause variability. The *PR* values for the five parameters determined in this study are listed in Table 2.

14.5 *Bias:*

14.5.1 SRM 2429 was used as one of the samples in the interlaboratory study (ILS) that produced the data for this precision statement. Table 3 shows a comparison of the ILS averages and the "information values" for some of the parameters determined in this test method. An SRM information value may be of interest to the SRM user but does not have an associated uncertainty.

14.5.2 Since no reference materials provide certified values for free moisture, gypsum ($CaSO_4$•$2H_2O$), calcium sulfite hemihydrate ($CaSO_3$•$½H_2O$), calcium carbonate ($CaCO_3$), or ash in flue gas desulfurization solids, no statement on the absolute bias of these test methods can be made.

15. Keywords

15.1 ash; coal; FGD solids; flue-gas desulfurization; free moisture; gypsum product; macro-TGA; macro thermogravimetric analysis

TABLE 3 Comparison of Interlaboratory Study Values of FGD-Solids Materials with Information Values for NIST SRM 2429 and Determined Values for Pure Calcium Carbonate

FGD-Solids Material	Average of ILS Reported Values Mass Fraction, %	Standard Deviation *s*	NIST SRM 2429 Information Values Mass Fraction, %
Gypsum	97.90	0.171	97.41
Calcium Sulfite Hemihydrate	1.67	0.428	1.01
Calcium Carbonate	0.41	0.076	0.79
	Average of 10 separate runs on 10 different days	Sandard Deviation *s*	ACS Analytical Reagent Calcium Carbonate
Pure Calcium Carbonate	99.97	0.215	100.0