



Designation: D8339 – 20

Standard Test Method for The Analysis of Flue Gas Desulfurization Solids by Macro Thermogravimetric Analysis¹

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 reappraisal. A superscript epsilon (ϵ) indicates an editorial change since the last revision or reappraisal.

1. Scope

1.1 This instrumental test method covers the determination of free moisture, gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), calcium sulfite hemihydrate ($\text{CaSO}_3 \cdot \frac{1}{2}\text{H}_2\text{O}$), calcium hydroxide ($\text{Ca}(\text{OH})_2$), 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](#)

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.

[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.

4.4 *Gypsum*, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, 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*, $\text{CaSO}_3 \cdot \frac{1}{2}\text{H}_2\text{O}$, 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*, $\text{Ca}(\text{OH})_2$, 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 ($\text{CaSO}_3 \cdot \frac{1}{2}\text{H}_2\text{O}$) 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. 16, No. 1, pp. 90-93, 1989.

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 ₂ O	50	240	17	15	N ₂ , 1.0	m_2
3	CaSO ₃ •½ H ₂ O	240	400	17	5	N ₂ , 1.0	m_3
4	CaSO ₃ •½ H ₂ O	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):

$$w_{\text{H}_2\text{O,ad}} = \frac{m_0 - m_1}{m_0} \quad (1)$$

12.2.2 Gypsum (CaSO₄•2H₂O) (as-determined):

$$w_{\text{CaSO}_4 \cdot 2\text{H}_2\text{O,ad}} = 4.779 \cdot \frac{m_1 - m_2}{m_0} \quad (2)$$

12.2.3 Calcium sulfite hemihydrate (CaSO₃•½H₂O) (as-determined):

$$w_{\text{CaSO}_3 \cdot \frac{1}{2}\text{H}_2\text{O,ad}} = 14.338 \cdot \frac{m_2 - m_3}{m_0} \quad (3)$$

12.2.4 Lime (Ca(OH)₂) (as-determined):

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

12.2.5 Calcium carbonate (CaCO₃) (as-determined):

$$w_{\text{CaCO}_3\text{,ad}} = 2.274 \cdot \frac{m_5 - m_6}{m_0} \quad (5)$$

12.2.6 Ash (as-determined):

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

12.2.7 Ash (calculated, as-determined):

$$w_{\text{calcd,ash,ad}} = 0.7907 \cdot w_{\text{CaSO}_4 \cdot 2\text{H}_2\text{O,ad}} + 1.0541 \cdot w_{\text{CaSO}_3 \cdot \frac{1}{2}\text{H}_2\text{O,ad}} + 0.7569 \cdot w_{\text{Ca(OH)}_2\text{,ad}} + 0.5603 \cdot w_{\text{CaCO}_3\text{,ad}} \quad (7)$$

where:

m_i = the correspondent mass at the end of the step (see Table 1 and 11.4)

$w_{i,\text{ad}}$ = the mass fraction of the FGD-Solids component

4.779 = factor to convert hydrate water to CaSO₄•2H₂O

14.338 = factor to convert hydrate water to CaSO₃•½H₂O

4.113 = factor to convert lime water to Ca(OH)₂

2.274 = factor to convert carbon dioxide to CaCO₃

0.7907 = factor to convert CaSO₄•2H₂O to CaSO₄



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