Designation: D7582 – 10$^{\varepsilon 1}$

StandardTest Methods for Proximate Analysis of Coal and Coke by Macro Thermogravimetric Analysis[1]

This standard is issued under the fixed designation D7582; 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.

ε^1 NOTE—13.2.3 was editorially corrected in December 2011.

1. Scope

1.1 These instrumental test methods cover the determination of moisture, volatile matter, and ash, and the calculation of fixed carbon in the analysis of coal and coke samples prepared in accordance with Practice D2013 and Practice D346.

1.2 These instrumental test methods are not applicable to thermogravimetric analyzers using microgram size samples.

1.3 Test Methods D3173, D3174, and D3175 shall be considered the referee test methods.

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

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]

D121 Terminology of Coal and Coke
D346 Practice for Collection and Preparation of Coke Samples for Laboratory Analysis
D2013 Practice for Preparing Coal Samples for Analysis
D3173 Test Method for Moisture in the Analysis Sample of Coal and Coke
D3174 Test Method for Ash in the Analysis Sample of Coal and Coke from Coal
D3175 Test Method for Volatile Matter in the Analysis Sample of Coal and Coke
D3176 Practice for Ultimate Analysis of Coal and Coke
D3180 Practice for Calculating Coal and Coke Analyses from As-Determined to Different Bases
D3302 Test Method for Total Moisture in Coal
D5016 Test Method for Total Sulfur in Coal and Coke Combustion Residues Using a High-Temperature Tube Furnace Combustion Method with Infrared Absorption
E691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method

3. Terminology

3.1 For definitions of 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. In *macro thermogravimetric* analysis a sample size of approximately 1 g is used. All mass measurements are conducted by the system. 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. The mass change is recorded repeatedly during the entire procedure. For the thermogravimetric analysis of coal and coke samples the moisture and ash analyses are complete when the sample reaches a constant mass as defined in the instrumental operating parameters. Alternatively, the measurement of moisture and ash can be considered complete after heating the sample for a fixed period of time. In the volatile matter analysis, the samples are weighed after heating to 950°C and held at this temperature for 7 min.

4.2 *Moisture* is determined by measuring the loss in mass of the analysis specimen of coal or coke when heated under specified conditions of temperature, time, atmosphere, specimen mass, and equipment specifications.

4.3 *Volatile matter* is determined by measuring the loss in mass of the analysis specimen of coal or coke when heated under rigidly controlled conditions. The measured mass loss is used to calculate the volatile matter after correcting for the moisture content.

[1] This test method is under the jurisdiction of ASTM Committee D05 on Coal and Coke and is the direct responsibility of Subcommittee D05.21 on Methods of Analysis.

Current edition approved June 1, 2010. Published July 2010. Originally approved in 2009. Last previous edition approved in 2009 as D7582-09. DOI: 10.1520/D7582–10E01.

[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 *Ash* is determined by measuring the mass of the residue remaining after burning the coal or coke specimen under specified conditions of specimen mass, temperature, time, atmosphere, and equipment specifications.

4.5 In these test methods, moisture, volatile matter, and ash can be determined sequentially in a single instrumental procedure. Another procedure allows the moisture and ash to be determined sequentially. Moisture and ash can also be determined in separate determinations. Ruggedness testing and past experiences have shown the volatile matter values determined on samples without first determining the moisture (drying the sample) are always higher than those of the dried samples.

4.6 Good laboratory practice requires checking for biases between analytical methods for contractual compliance. When only a few coal types will be routinely tested, the instrument used in these test methods must be shown to yield results, for the coal(s) to be tested, that are equivalent to those obtained using Test Methods D3173, D3174, and D3175. If they are found to be not equivalent, either the instrument used is calibrated or the instrumental results are adjusted to establish and maintain equivalence. Alternatively, when a broad spectrum of coal types will be tested, the instrument used in these test methods shall be calibrated using certified reference materials of known composition covering the range of parameters being determined. The certified values shall be established using Test Methods D3173, D3174, and D3175. Section 16.2 lists a number of biases that have been shown to exist between instrumental results. Other biases, of unknown magnitude and sign, may exist for other coals.

5. Significance and Use

5.1 *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 *Moisture* can be used in conjunction with the air-dry moisture loss determined by Test Method D3302 to determine total moisture in coal. Total moisture is used for calculating other analytical results to an as-received basis using Practice D3180.

5.3 *Ash yield* is the residue remaining after heating the coal and coke samples (see Note 1).

NOTE 1—The ash obtained differs in composition and amount from the mineral constituents present in the original coal. Combustion causes an expulsion of all water, the loss of carbon dioxide from carbonates, the conversion of iron pyrite into iron oxides and sulfur oxides, and other chemical reactions. Ash yield, as determined by this test method, can differ from the amount of ash produced in furnace operations or other combustion systems because combustion conditions influence the chemistry and amount of ash.

5.4 *Ash yield* is used, *(1)* as a parameter for evaluating sampling procedures and coal cleaning processes, *(2)* in the ultimate analysis calculation of oxygen by difference using Practice D3176, *(3)* in calculations including material balance, reactivity and yields of products relevant to coal conversion processes such as gasification and liquefaction, *(4)* in calculations to estimate the loading on electrostatic precipitators and on the fly ash and bottom ash disposal systems as well as erosion rates on boiler systems.

5.5 *Volatile matter yield*, when determined as herein described, may be used to *(1)* indicate coke yield on carbonization, *(2)* provide the basis for purchasing and selling, or *(3)* establish combustion characteristics.

5.6 *Fixed carbon* is a calculated value. It is the difference between 100 and the sum of the percent moisture, ash, and volatile matter. All percents shall be on the same moisture reference base.

5.7 Moisture, ash, and volatile matter are three of the principal parameters used for assessing the quality of coal.

6. Interferences

6.1 There are no known interferences for these test methods.

7. Apparatus

7.1 *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 (30-45°C/min from ambient 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 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 at least 0.1 mg. 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.

7.2 *Crucibles*—with covers of composition and dimensions specified for the instrument by the instrument manufacturer. The covers shall fit closely enough so that the carbon deposit from bituminous, subbituminous, and lignitic coals does not burn away from the underside of the cover during the determination of the volatile matter

8. Reagents and Materials

8.1 *Drying Gas*—Nitrogen (99.5% purity), Argon (99.5% purity) or air, dried to a moisture content of 1.9 mg/L or less (dew point –10°C or less).

8.2 *Inert Gas*—Nitrogen (99.5% purity) or Argon (99.5% purity).

8.3 *Oxidizing Gas*—Oxygen (99.5% purity) or air.

8.4 *Certified Reference Materials*—Coal or coke material(s) meeting the requirements of 10.1, with a certificate of analysis specifying the reference value and the uncertainty of the reference value. Reference material(s) can be employed to calibrate the instrument for the determination of volatile

matter. Certified reference values shall have been established using Test Methods D3173, D3174, and D3175. Reference materials used for the calibration of volatile matter shall include information on the certificate of analysis detailing the method(s) employed to determine volatile matter of the reference material.

9. Hazards

9.1 The user shall insure 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.

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

10. Analysis Sample

10.1 The analysis sample shall be the material pulverized to pass a 250-µm (No. 60) sieve in accordance with Practice D2013 or Practice D346.

11. Preparation of Apparatus

11.1 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.

11.2 Condition new crucibles and covers for use in these test methods by heating under the same conditions of the test and cool before use.

11.3 The macro TGA system can be programmed to terminate the measurement process when the test specimens and crucibles have reached a constant mass. Crucibles are weighed by the instrument at specified intervals. The analysis is complete when the sample reaches constant mass. Constant mass is defined as a point where the mass change is < or = to 0.05% over a nine-minute period, either by using not less than three successive weighings or a fixed nine-minute period of successive weighings. This mass change of 0.05% is equivalent to 0.0005 g for a 1.0000 g sample. Alternately, the instrument can be programmed to allow for moisture and ash determination by heating the test specimens for the time periods, heating rates and soak temperatures specified in Test Methods D3173 and D3174. The mass measured at the end of the time period is used for calculations.

12. Calibration and Standardization

12.1 The instrument shall be calibrated for the determination of volatile matter employing certified reference materials. The calibration shall be performed at the same furnace ramp temperature as that used for the analysis. Do not use coal reference materials(s) for coke volatile matter calibration. Do not use coke reference material(s) for coal volatile matter calibration. Use coal reference material(s) with a certified reference value and uncertainty based on measurements made employing Test Methods D3173, D3174, and D3175 to calibrate this test method.

13. Procedure

13.1 The determination of moisture, followed by volatile matter followed by ash can be carried out in sequence using the same test specimen. Alternatively, the determination of moisture, volatile matter, or ash can be carried out separately on test specimens of coal or coke.

13.2 *Sequential Determination of Moisture, Volatile Matter and Ash:*

13.2.1 After verifying instrument setup according to Section 11 on the preparation of apparatus, load and tare the crucibles. Add 1 g ± 0.1 g of coal or coke to the crucible in the balance position and weigh immediately before advancing 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.

13.2.2 For moisture determinations, heat the weighed test specimens in crucibles without the covers at 107 ± 3 °C. Use a drying gas flow rate of 0.4 to 1.4 furnace volume changes per minute (see 8.1). Program the instrument to terminate the test when the test specimens and crucibles have reached a constant mass (see 11.3). Alternatively, program the instrument to allow for moisture determination by heating the test specimens for 1 h.

13.2.3 For volatile matter determinations following the moisture analysis, place covers on the crucibles in the TGA carousel (the covers are placed automatically in some systems and manually in others). Program the instrument to reweigh the crucibles, with specimens inside, and covers in place before initiating the volatile matter part of the cycle.

13.2.3.1 To provide an inert atmosphere, use nitrogen or argon with a flow rate of 0.7 to 1.4 furnace volume changes per minute to sweep away the volatile components. Raise the furnace temperature at a rate such that the temperature is raised from 107°C to 950 ± 10°C in a 26-30 min time period (See Note 2). Program the instrument to hold at this temperature for 7 min. The TGA weighs the covered crucibles at regular intervals while the temperature of the furnace is raised. The weights of the crucibles and covers at the end of the 7-min hold period are used in the calculation of the volatile matter.

NOTE 2—It is the nature of resistance furnaces to start heating slowly with a gradual increase in heating rate until the furnace heating element controller reduces the power to moderate the heating rate. As a result, high furnace ramp rates are seldom ever uniform over the temperature range selected. Selecting a heating time (26-30 min) with a high heating ramp rate accomplishes the desired result, to duplicate the conditions (Macro TGA furnaces set at 30-45°C/min ramp rate) that were used by the laboratories in the interlaboratory study. At the same time, it allows the Macro TGA furnaces to moderate the heating rate enough to avoid overshooting the selected high temperature of 950°C.

13.2.3.2 With strongly caking low-volatile and medium-volatile bituminous coals, the coke button can burst as a result of the rapid liberation of volatile matter within the button. This is designated as popping. Such popping can blow the lid off the crucible and cause mechanical loss of the coked material. When evidence of such popping is observed, reject the determination and repeat the test with smaller test specimen sizes until popping is no longer evident. Also, some high swelling coals can expand beyond the volume of the crucible such that

they raise the crucible cover and stick to the underside of the cover. This material can be lost when the crucible cover is removed. For swelling coals examine the crucible covers as they are removed. If carbonaceous material clings to the underside of the cover, reject the determination and repeat the test with smaller test specimen sizes until there is no evidence of carbonaceous material clinging to the underside of the cover.

13.2.4 For ash determinations following the volatile matter determinations program the furnace to cool from 950 to 600°C. Remove the crucible covers. (The crucible covers are removed automatically in some systems and manually in others). Change the furnace atmosphere to oxygen or air. Raise the temperature either to 750 ± 10°C for coals or 950 ± 10°C for coke in one hour. If the oxidizing gas is oxygen adjust the flow rate to 0.4 to 0.5 furnace volume changes per minute. If the oxidizing gas is air adjust the flow rate to 1.3 to 1.4 furnace volume changes per minute. Program the instrument to terminate the test when the test specimens and crucibles have reached a constant weight (See 11.3). Alternatively, program the instrument to allow for ash determination by heating the test specimens for not less than 2 h for coal, and 3 h for coke, after reaching the final hold temperature. If there is evidence of carbonaceous material in the ash reject the determination and repeat the test.

13.3 *Sequential Determination of Moisture and Volatile Matter:*

13.3.1 Follow the instructions in 13.2.1 to set up the instrument.

13.3.2 Follow the instructions in 13.2.2 for moisture determinations.

13.3.3 Follow the instructions in 13.2.3 and 13.2.3.1 for volatile matter determinations.

13.4 *Sequential Determination of Moisture and Ash:*

13.4.1 Follow the instructions in 13.2.1 to set up the instrument.

13.4.2 Follow the instructions in 13.2.2for moisture determinations.

13.4.3 Ash determinations on the residues (dried test specimens) from the moisture determination are made by changing the furnace atmosphere to oxygen or air, and raising the temperature of the furnace at a rate such that it reaches 500 ± 10°C in 1 h and either 750 ± 10°C (for coals) or 950 ± 10°C (for cokes) by the end of the second hour. If the oxidizing gas is oxygen the flow rate is set at 0.4 to 0.5 furnace volume changes per minute. If the oxidizing gas is air the flow rate is set at 1.3 to 1.4 furnace volume changes per minute. Continue to heat and weigh the test specimens at the high temperature until they reach a constant weight (See 11.3). Alternatively, program the instrument to allow for ash determination by heating the test specimens for not less than 2 h for coal, and 3 h for coke, after reaching the final hold temperature. If there is evidence of carbonaceous material in the ash reject the determination and repeat the test (See 13.4.3.1).

13.4.3.1 Gradual heating allows sulfur bearing materials to be oxidized and release sulfur dioxide before calcium carbonate (calcite) decomposes. Some samples can contain a high amount of carbonate minerals or pyrite, or both. In these cases, sulfur retained as sulfates can be highly variable between duplicate runs. In such cases, the sulfate sulfur in the ash can be determined in accordance with Test Method D5016 and the ash yield reduced in proportion to the sulfur trioxide (SO_3) so determined. Then report and designate the ash value both as determined and corrected.

13.5 *Individual Determination of Moisture and Ash:*

13.5.1 To determine each of the parameters, moisture, volatile matter, and ash in separate procedures follow the instructions in 13.2.1 for set up.

13.5.2 For moisture determinations follow the instructions in 13.2.2.

13.5.3 For ash determinations, after transferring the specimens to the crucibles and weighing, set the furnace atmosphere to oxygen or air and follow the instructions given in 13.4.3.

14. Calculation or Interpretation of Results

14.1 With a computer-controlled macro thermogravimetric analyzer, the computer is normally programmed to perform calculations automatically. The equations used in the calculations are listed in the following sections.

14.2 Calculate the percent moisture in the analysis sample, M, as follows:

$$M = [(W - B)/W] \times 100 \quad (1)$$

Where:

W = mass of test specimen used, g, and
B = mass of test specimen after drying in moisture test, g.

14.3 If the volatile matter determination is made with the test specimen used for the moisture determination, then calculate the percent volatile matter in the analysis sample, V, as follows:

$$V = [(B - C)/W] \times 100 \quad (2)$$

Where:

C = mass of test specimen after heating in volatile matter test, g.

14.3.1 If the volatile matter determination is made with a separate test specimen of sample from the analysis sample bottle, then calculate volatile matter as follows:

$$D = (W - C)/W \times 100 \quad (3)$$

Where:

D = mass loss, %.

$$V = D - M \quad (4)$$

14.4 Calculate the ash percent in the analysis sample, A, as follows:

$$A = [(F - G)/W] \times 100 \quad (5)$$

Where:

F = mass of crucible and ash residue, g, and
G = mass of empty crucible, g.

14.5 Calculate the fixed carbon percent in the analysis sample, H, as follows:

$$H = 100 - (M + A + V) \quad (6)$$

Where all values are on the same moisture reference base.