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Standard Test Methods for Proximate Analysis of the Analysis Sample of Coal and Coke by Instrumental Procedures¹

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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 Method D 2013 and Practice D 346. Results obtained through the use of the instrumental tests have been shown to differ from those obtained with Test Methods D 3173, D 3174, and D 3175 on some coals and cokes. Where a relative bias between the instrumental methods and Test Methods D 3173, D 3174, and D 3175 for proximate analysis of coal and coke are shown to exist, the instrumental results shall be corrected or the instrument calibrated using samples of known proximate analysis. Test Methods D 3173, D 3174, and D 3175 shall be considered the referee test methods. The instrumental test methods are not applicable to thermogravimetric analyzers using microgram size samples.

1.2 The moisture value determined is used for calculating other analytical results to a dry basis. When used in conjunction with the air dry loss moisture, as determined in accordance with Method D 2013, Test Method D 3302, or Practice D 346, the calculated total moisture can be used to convert dry basis analytical results to the as-received basis.

1.3 The result of the ash determinations can be applied in the ultimate analysis, Practice D 3176.

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:

D 121 Terminology of Coal and Coke²

D 346 Practice for Collection and Preparation of Coke Samples for Laboratory Analysis²

D 1757 Test Method for Sulfate Sulfur in Ash from Coal and Coke²

D 2013 Practice for Preparing Coal Samples for Analysis²

D 3173 Test Method for Moisture in the Analysis Sample of Coal and Coke²

D 3174 Test Method for Ash in the Analysis Sample of Coal and Coke from Coal²

D 3175 Test Method for Volatile Matter in the Analysis Sample of Coal and Coke²

D 3176 Practice for Ultimate Analysis of Coal and Coke²

D 3180 Practice for Calculating Coal and Coke Analyses from As-Determined to Different Bases²

D 3302 Test Method for Total Moisture in Coal²

3. Terminology

3.1 For definitions of terms used in this test method, refer to Terminology D 121.

4. Summary of Test Methods

4.1 Moisture is determined by establishing the loss in mass of the analysis specimen of coal or coke when heated under rigidly controlled conditions of temperature, time, atmosphere, specimen mass, and equipment specifications.

4.2 Volatile matter is determined by measuring the loss in mass of the moist or dried analysis specimen of coal or coke when

² Annual Book of ASTM Standards, Vol 05.06.

heated under rigidly controlled conditions. If appropriate, the measured mass loss establishes the volatile matter after correcting for the moisture content.

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

4.4 In these test methods, moisture, volatile matter, and ash may be determined sequentially in a single instrumental procedure. With some systems, the procedure consists of simply placing a specimen in the microprocessor-controlled instrument and initiating the automatic process of analyzing the specimen.

4.5 In other systems, the analytical process is manually controlled, although the instruments may have microprocessors to assist in controlling conditions of the instrument and for calculations. The actual analytical process can vary from instrument to instrument, but the overall process shall provide for the determination of moisture, volatile matter, and ash as specified in 4.1, 4.2, and 4.3.

4.6 Different procedures are described to permit conformity with differences in instrument design and for differences in sample behavior.

4.7 Where a relative bias between these test methods and other ASTM test methods for the proximate analysis of coal and coke has been shown to exist (12.23.1), the instrument used in these test methods must be calibrated using specimens of known composition covering the range of parameters being determined.

5. Significance and Use

5.1 Moisture, as determined by the instrumental test method, is used for calculating other analytical results to a moisture-free basis using procedures in Practice D 3180. Moisture percent determined by this test method may be used in conjunction with the air-dry moisture loss determined in Method D 2013 and Test Method D 3302 to determine total moisture in coal. Total moisture is used for calculating other analytical results to an *as-received* basis using Practice D 3180.

5.2 Ash yield, as determined by this test method, is the residue remaining after burning the coal and coke samples.

5.3 Volatile matter yield, when determined as herein described, may be used to (1) establish the rank of coals, (2) indicate coke yield on carbonization, (3) provide the basis for purchasing and selling, or (4) establish burning characteristics.

5.4 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 moisture reference base.

5.5 Moisture, ash, volatile matter, and fixed carbon percents constitute the proximate analysis of coal and coke.

NOTE 1—The ash obtained differs in composition and amount from the mineral constituents present in the original coal. Incineration 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 incineration conditions influence the chemistry and amount of ash.

6. Apparatus

6.1 *Furnace or Oven*—The primary apparatus shall consist of a furnace or oven with a cavity large enough to accept crucibles containing the specimens. The furnace or oven shall be 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 at a rate of 50°C/min from ambient to 950°C.

6.1.1 The temperatures within the cavity shall be monitored and maintained at values that are specific to each of the determinations. Temperatures, as measured in crucibles located throughout the cavity shall be maintained within the following limits:

Determination of	Temperature, °C	
	min	max
Moisture	104	110
Ash-coal	700	750
Ash-coke	900	950
Volatile matter	930	970

6.1.2 Provisions shall be made to introduce a sweep gas or a reactant gas, and to remove products of drying, devolatilization, or combustion. Gases and acceptable flow rates for the different determinations are as follows:

Determination of	Gas	Flow Rate, Furnace Volume per Minute
Moisture	nitrogen or air	2–4
Ash	oxygen	0.4–0.8 ^A
	air	2–4
Volatile matter	nitrogen	2–4

^AThis oxygen flow is chemically equivalent to 2 to 4 volume changes of air per minute.

6.2 *Crucibles*, with covers, of a convenient form that allows the moisture and volatile matter, or moisture and ash, or all three determinations to be made on the same specimen, shall be used. The crucibles may be made of fused silica with self-sealing covers that have ground glass seals or of porcelain with self-sealing covers. The covers shall allow the rapid escape of gases during the determination of volatile matter. All crucibles used shall have the dimensions specified by the instrument manufacturer.

6.3 *Balance*, sensitive to 0.1 mg. The balance may be an internal balance and an integral part of the instrument used for determining the moisture, volatile matter, and ash, or it may be a separate piece of apparatus that may not be interfaced with the instrument.

6.4 The instrumental system in its entirety shall be operated in strict accordance with the manufacturer's operating instructions.

6.5 *Venting Equipment*—Combustion and volatile gases evolved during the test procedures shall be vented from the laboratory and suitable venting equipment shall be installed in the vicinity of the apparatus.

7. Analysis Sample

7.1 Obtain the sample for coal in accordance with Method D 2013 and the sample for coke in accordance with Practice D 346. Obtain the analysis sample by pulverizing the material to a fineness to pass the 250- μm (No. 60) sieve.

8. Reagents and Materials

8.1 *Dry Gas*—Nitrogen (>99.5 % purity) or air, dried to a moisture content of 1.9 mg/L or less (dew point -10°C or less) to be used to purge the drying oven. Any desiccant or drying method capable of achieving this degree of dryness is suitable. (See Reagent section of Test Method D 3173.)

9. Procedure

9.1 Some instruments allow for the determination of moisture, volatile matter, and ash in sequence using the same specimen. Alternatively, some instruments, or components of the instruments, may be used to carry out separate determinations of moisture, volatile matter, or ash using separate specimens of coal or coke.

9.2 Heat new crucibles and covers (see 9.2.1) for use in these test methods under the conditions of the test and cool before use. For each test, weigh a prepared crucible (Note 2). Add approximately 1 g of coal or coke to the crucible and then weigh the crucible and specimen. Make all weighings to the nearest 0.1 mg. Transfer the specimen from the sample bottle to the crucible quickly to minimize the exposure of the specimen to the atmosphere during the weighing process. Use crucible covers to protect the specimen before and after the moisture determination. Use crucible covers during the determination of the volatile matter. Weigh the cover with the crucible and specimen for this test.

9.2.1 The cover shall fit closely enough so that the carbon deposit from bituminous, subbituminous, and lignitic coals does not burn away from the under side of the cover.

NOTE 2—In microprocessor-controlled instruments, the specimen weights are recorded by the microprocessor and retained for further calculations. In instruments with internal balances, or with those interfaced to a balance, these weights are automatically recorded. For some instruments without these features, the specimen weights may be entered manually into the microprocessor memory.

9.3 *Moisture Determination:*

9.3.1 For moisture determinations, heat the weighed samples in crucibles *without the covers* in the drying oven at 104 to 110°C. Various modes of operation are possible depending on the instrument used and the manner in which the determination is completed.

9.3.2 Automated instruments with an internal balance that can weigh the specimen repeatedly during the determination can be programmed to terminate the test when the specimens and crucibles have reached a constant weight. Typically, crucibles are weighed automatically at 3-min intervals, and the analysis is complete when two successive weighings agree within the plateau deviation specified for the instrument. Use nitrogen with a purity >99.5 % and a moisture content of 1.9 mg/L or less (dew point of -10°C or less) as the drying gas in the oven (see 8.1). Some models of this type of instrument also allow for moisture determination by heating the specimen for 1 h at the prescribed temperature limits.

9.3.3 For moisture determinations using instruments that do not have an internal balance, weigh the specimens and place the specimens and crucibles without covers, in the preheated oven (104 to 110°C) through which passes a current of preheated air. Dry the preheated air to a moisture content of 1.9 mg/L or less (dew point -10°C or less). Close the oven quickly and heat for 1 h. Then remove the specimen crucibles, cover quickly, allow to cool to ambient temperature in a desiccator, and weigh as soon as possible.

9.3.3.1 Air with a moisture content of 1.9 mg/L or less (dew point -10°C or less) may be substituted for nitrogen in the moisture and ash analysis, but nitrogen shall always be used in the volatile matter determination.

9.4 *Volatile Matter Determination:*

9.4.1 Volatile matter determinations may be made using the specimens from the moisture determinations. An alternative method is to weigh 1 g (to the nearest 0.1 mg) of analysis sample in a preweighed crucible with self-sealing cover. Place the crucibles in the furnace which is heated at a rate of 50°C/min to 950 \pm 20°C and hold at this temperature for 7 min (see 9.2.1 and Note 3). The furnace shall have an inert atmosphere, preferably nitrogen. After cooling in a desiccator, weigh the crucibles with the specimens and covers.

9.4.2 For instruments with an internal balance, the instrument automatically weighs the crucibles, specimens, and self-sealing covers at the beginning of the analysis. The instrument will then make weighings at regular intervals while the temperature of the furnace is raised at a rate of 50°C/min to 950 \pm 20°C and held for 7 min. The instrument uses the weight of the specimen at the end of the 7-min period in the calculation of the volatile matter.

9.4.3 For instruments without an internal balance, weigh the crucibles, specimens, and covers and then place them in the furnace. Raise the temperature of the furnace at a rate of 50°C/min to 950 \pm 20°C and hold for 7 min. Then remove the crucibles

from the furnace, without disturbing the covers, and allow to cool to ambient temperature in a desiccator. Weigh the crucibles and covers as soon as possible.

NOTE 3—Caution: Warning: With some strongly caking low-volatile and medium-volatile bituminous coals, the coke button may explode as a result of the rapid liberation of volatile matter within the button. This is usually designated as *popping*. Such popping may blow the lid off the crucible and cause mechanical losses of the coked material. When such popping is observed, the determination should be rejected and the test repeated until popping does not occur or Alternative Procedure No. 2 for volatile matter is used (9.5.2).

9.5 Alternative Procedures for Volatile Matter:

9.5.1 *Alternative Procedure No. 1*—Place the weighed crucibles with specimens and self-sealing covers in the furnace preheated to $950 \pm 20^\circ\text{C}$. Leave the crucibles in the furnace for 7 min and then remove and allow to cool without disturbing the covers. Weigh the crucibles with the covers as soon as possible after cooling to ambient temperature in a desiccator.

9.5.2 *Alternative Procedure No. 2*—Use this procedure if Alternative Procedure No. 1 causes excessive swelling, ashing, or mechanical losses of specimens. In this procedure, place the weighed crucibles with specimens and self-sealing covers in the cold furnace and heat to a temperature of 600°C at a rate of $25^\circ\text{C}/\text{min}$. Once this temperature is attained, the furnace is then heated at a rate of $35^\circ\text{C}/\text{min}$ until the maximum temperature of $950 \pm 20^\circ\text{C}$ is attained. Hold the specimens at the final temperature for 6 min and then remove and allow to cool without disturbing the covers. Weigh the crucibles and the covers as soon as possible after cooling to ambient temperature in a desiccator.

9.6 Ash Determination:

9.6.1 Ash determinations may be made on the specimens from the volatile matter determination, the specimens from the moisture determination, or on a separate portion of the analysis sample. The ash in these specimens is then determined in various ways depending on the source of the specimen used and the type of instrument used in the analysis.

9.6.2 Using instruments with an internal balance, if the specimen is from the volatile matter determination, cool the furnace from 950 to 600°C , change the furnace atmosphere to pure oxygen with a flow of oxidant chemically equivalent to two to four volume changes of air per minute, and then gradually raise the temperature to 700 to 750°C . Heat coke samples to a final temperature of 900 to 950°C . The instrument weighs the specimens in the crucibles without covers at regular intervals until they reach a constant weight. If the specimen is from the moisture determination (volatile matter not determined), change the furnace atmosphere to pure oxygen (Note 4), and raise the temperature of the furnace at a rate such that it reaches 450 to 500°C in 1 h and 700 to 750°C in 2 h. Heat coke samples so that a final temperature of 900 to 950°C is reached by the end of the second hour. Continue to heat and weigh at 700 to 750°C until the coal specimens reach a constant weight. Heat coke samples at 950°C until constant weight is achieved (Note 5).

NOTE 4—Air may be substituted for oxygen if the operator is only performing a moisture and ash analysis and the airflow is adjusted to two to four volume changes per minute.

NOTE 5—The gradual heating is done to allow the oxidation of sulfur bearing materials and release of sulfur dioxide before calcium carbonate (calcite) is decomposed. Some specimens contain a high amount of carbonate minerals or pyrite, or both. In such cases, sulfur retained as sulfates can be both unduly high and nonuniform between duplicate specimens. In such cases, determine sulfate sulfur in the ash in accordance with Test Method D 1757 and reduce the ash yield in proportion to the sulfur trioxide (SO_3) so determined. Then report and designate the ash value both as determined and corrected.

9.6.3 For instruments that do not have an internal balance, weigh the crucibles with specimens and no covers, place them in the furnace, and raise the temperature at a rate such that the furnace reaches 450 to 500°C in 1 h and 700 to 750°C in 2 h. Heat coke samples so that a final temperature of 900 to 950°C is reached by the end of the second hour. Maintain the gas flow through the furnace with a flow rate of oxidant chemically equivalent to two to four volume changes per minute during the ashing procedure. Continue the ashing at 700 to 750°C (900 to 950°C for coke) for an additional 2 h (Note 6). Remove the crucibles from the furnace, cool in a desiccator to minimize moisture absorption, and weigh the crucibles as soon as possible.

NOTE 6—While the 4-h interval is sufficient to achieve complete incineration of most coals, certain cokes and nonreactive coals can require additional time. If unburned carbon particles are observed, or if duplicate results are suspect, return the specimen to the furnace for sufficient time to reach a constant weight (± 0.001 g). The 4-h limit may be reduced if the specimen reaches a constant weight at 700 to 750°C (900 to 950°C for coke) in less than 4 h.

10. Calculation

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

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

where:

W = weight of specimen used, g and

B = weight of specimen after drying in moisture test, g.

10.2 If the volatile matter determination is made with the 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 = weight of specimen after heating in volatile matter test, g.

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

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

where:

D = weight loss, %.

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

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

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

where:

F = weight of crucible and ash residue, g and

G = weight of empty crucible, g.

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

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

11. Report

11.1 For reporting analyses to other than the as-determined basis, refer to Practice D 3180.

12. Precision and Bias³

12.1 *Precision*—The relative precision of these test methods for the determination of moisture, volatile matter, and ash was calculated from data obtained from coals with the following concentration ranges:

	Concentration, %
Moisture	from 0.2 to 27.9
Volatile matter (dry basis)	from 1.0 to 50.8
Ash (dry basis)	from 6.0 to 19.6

12.1.1 *Repeatability Limit (r)*—~~The difference, in value below which the absolute value, difference~~ between two test results calculated to a dry basis (Practice D 3180) of separate and consecutive test determinations, carried out on ~~portions of the same analysis specimen, sample of 250 μ m (No. 60) coal and coke~~ in the same laboratory; by the same operator; using the same apparatus, shall not exceed the repeatability interval $I(r)$ in more than 5 % of such paired values (95 % confidence level). ~~When such apparatus on samples taken at random from a difference is found single quantity of homogeneous material, may be expected to exceed the repeatability interval, there is reason to question one, or both, occur with a probability of the test results.~~

12.1.1.1 Calculate the repeatability intervals for moisture, volatile matter, and ash determined by the automated method using the following equations (Note 7):

$$\text{Moisture: } I(r) = 0.20 + 0.012x \quad (7)$$

$$\text{Volatile matter: } I(r) = 0.29 + 0.014x \quad (8)$$

$$\text{Ash: } I(r) = 0.07 + 0.020x \quad (9)$$

where x is the average of the two results for each parameter. For example: Duplicate analyses for moisture by the automated procedure gave values of 5.68 and 5.84 %. The average moisture value from the duplicate analysis is 5.76 % and the calculated repeatability interval $I(r)$ is 0.27 %. The difference between the two values is 0.16 % and does not exceed the $I(r)$ of 0.27 %. Therefore, these two values are acceptable at the 95 % confidence level.

NOTE 7—The reported repeatability and reproducibility data are for instruments run in the constant weight mode as described in 9.3.2.

12.1.1.2 Calculate the repeatability of moisture, volatile matter, and ash determined by the semiautomated method using the following equations (Note 7):

$$\text{Moisture: } I(r) = 0.19 + 0.030x \quad (10)$$

$$\text{Volatile matter: } I(r) = 0.72 + 0.023x \quad (11)$$

$$\text{Ash: } I(r) = 0.38 \quad (12)$$

approximately 95%.

12.1.2 *Reproducibility Limit (R)*—~~The difference, in value below which the absolute value, difference~~ between the averages of duplicate determinations two test results calculated to a dry basis (Practice D 3180) carried out in different laboratories on representative ~~using samples prepared from the same bulk sample after reducing to 100 % through a 250- μ m of 250 μ m (No. 60)~~

³ Supporting data are available from ASTM Headquarters. Request RR:D05-1012.

sieve should not exceed the reproducibility interval $I(r)$ in more than 5 % of such paired values (95 % confidence level). When such coal and coke taken at random from a difference single quantity of material that is found as homogeneous as possible, may be expected to exceed the reproducibility interval, there is reason to question one, or both, occur with a probability of approximately 95%.

12.1.3 Automated Method:

NOTE—where \bar{X} is the average of two single test results:

12.1.2.1 Calculate the reproducibility intervals for moisture, volatile matter, and ash determined by the automated method using the following equations (Note 7):

$$\text{Moisture: } I(R) = 0.24 + 0.034x \quad (13)$$

(13) Moisture: $I(R) = 0.24 + 0.034x$ results

Parameter	Repeatability Limit (r)	Reproducibility Limit (R)
Moisture	$0.2 + 0.012 \bar{X}$	$0.24 + 0.034 \bar{X}$
Volatile matter	$0.29 + 0.014 \bar{X}$	$0.62 + 0.047 \bar{X}$
Ash	$0.07 + 0.020 \bar{X}$	$0.14 + 0.23 \bar{X}$

12.1.4 Semiautomated Method:

NOTE—where \bar{X} is the average of the two results for each parameter. For example, duplicate analyses for moisture by the automated method in one laboratory gave an average value of 5.76 % and a value of 6.08 % was obtained in a different laboratory. The between-laboratory average moisture value is 5.92 %. The calculated reproducibility interval single test results

$I(r)$ is 0.44 % and the difference between the different laboratory values is 0.32 %. Since this difference is less than the $I(r)$, these two values are acceptable at the 95 % confidence level.

12.1.2.2 Calculate the reproducibility for moisture, volatile matter, and ash determined by the semiautomated method using the following equations (Note 7):

Parameter	Repeatability Limit (r)	Reproducibility Limit (R)
Moisture	$0.19 + 0.030 \bar{X}$	$1.95 + 0.028x$
Volatile matter	$0.19 + 0.030 \bar{X}$	1.23
Ash	$0.19 + 0.030 \bar{X}$	1.23

12.2 An interlaboratory study, designed consistent with Practice E 969, was conducted in 1989, ten laboratories participated in this study. Supporting data are available from ASTM Headquarters.⁴

⁴ Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR: D05-1012.

12.3 Bias:

12.23.1 The tests for moisture, ash, and volatile matter in coal and coke samples are empirical. Since no suitable reference material for moisture, ash, and volatile matter in coal and coke samples is currently available, no statement on the absolute bias of these test methods can be made. However, data collected during the development of these test methods have been used to prepare a statement on the relative bias that was found in this round-robin test between these test methods and Test Methods D 3173, D 3174, and D 3175.³ The data collected in the interlaboratory round-robin tests indicated a relative bias exists between the semiautomated method for determining ash and Test Method D 3174, between the automated method for determining volatile matter and Test Method D 3175, and between the semiautomated method for determining volatile matter and Test Method D 3175.

12.23.2 Where a relative bias between two test methods has been shown to exist, the instrument used for the proximate analysis of coal and coke samples must be calibrated using samples of known quality covering the range of parameters being determined.

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