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Standard Test Methods for Instrumental Determination of Carbon, Hydrogen, and Nitrogen in Laboratory Samples of Coal and Coke¹

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¹ These test methods are under the jurisdiction of ASTM Committee D05 on Coal and Coke and are the direct responsibility of Subcommittee D05.21 on Methods of Analysis.

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1. Scope

1.1 These test methods cover the instrumental determination of carbon, hydrogen, and nitrogen in laboratory samples of coal and coke prepared in accordance with Test Methods D 2013 and D 346.

1.2 Within the limitations outlined below, these test methods are applicable to either the air-dry or moisture-free laboratory sample, or both.

1.2.1 For instrumental systems in which the moisture and waters of hydration in the sample are liberated with (and only with) the oxidation products upon combustion, the analyses can be performed on a test specimen of the air-dry sample (Note 1). Concentrations determined on this air-dried basis represent the total carbon (including that present as carbonate), total hydrogen (including that present as water), and total nitrogen.

NOTE 1—These systems are also satisfactory for determining the subject materials in the moisture-free sample.

1.2.2 For systems in which the moisture and hydrates are otherwise liberated, the analysis shall be performed on the moisture-free sample. Values obtained on this basis represent the total carbon, organic hydrogen, and total nitrogen.

1.3 These test methods can be used to provide for the requirements specified in Practice D 3176 for the ultimate analysis.

1.4 The values stated in SI units shall be regarded as the 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.* Specific precautionary statements are given in 8.3.1.

2. Referenced Documents

2.1 ASTM Standards:

D 346 Test Method for Collection and Preparation of Coke Samples for Laboratory Analysis²

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 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 4621 Guide for Quality Management in an Organization That Samples or Tests Coal and Coke²

D 5142 Test Methods for the Proximate Analysis of the Analysis Sample of Coal and Coke by Instrumental Procedures²

3. Summary of Test Methods

3.1 Carbon, hydrogen, and nitrogen are determined concurrently in a single instrumental procedure. In some systems, the procedure consists of simply weighing a test specimen, placing the test portion into the instrument, and initiating the (subsequently automatic) analytical process. In other systems, the analytical process may be controlled manually to some degree.

3.2 The actual process can vary substantially from instrument to instrument because a variety of means can be used to effect the primary requirements of the test methods. These test methods provide for the following: (1) conversion of the subject materials in an oxygen stream in their entirety to carbon dioxide, water vapor, nitrogen oxides, and ash, respectively; and (2) subsequent, quantitative determination of the gases in an appropriate reference gas stream.

² Annual Book of ASTM Standards, Vol 05.06.

3.2.1 The conversion of the subject materials to their corresponding gases occurs largely during combustion of the sample at an elevated temperature in an atmosphere of purified oxygen. The gases that are produced include the following:

3.2.1.1 Carbon dioxide from the oxidation of organic and elemental carbon and the decomposition of carbonate minerals;

3.2.1.2 Hydrogen halides from organic halides (and organic hydrogen, as required);

3.2.1.3 Water vapor from the oxidation of (the remaining) organic hydrogen and the liberation of moisture and waters of hydration;

3.2.1.4 Nitrogen and nitrogen oxides from the oxidation of organic nitrogen and the decomposition of nitrates; and

3.2.1.5 Sulfur oxides from the oxidation of organic sulfur, and the decomposition of sulfide and sulfate minerals.

(I) In some systems, sulfurous and sulfuric acids can also be obtained from a combination of the sulfur oxides and the water vapor.

3.2.2 For hydrogen and nitrogen, the required conversion is completed in a two-step process consisting of the following:

3.2.2.1 Removal of the halides and sulfur oxides and liberation of the associated hydrogen (as water), by conducting the combustion gases through a series of absorption traps containing appropriate absorbing materials.

3.2.2.2 Reduction of the nitrogen oxides to elemental nitrogen (see Note 2) by passing the resultant gases over copper at an elevated temperature. The carbon dioxide, water vapor, and nitrogen may then be determined via one of several satisfactory detection schemes.

NOTE 2—In this process, residual oxygen is also removed.

3.2.3 In one configuration, the gases are conducted through a series of thermal conductivity detectors and gas absorbers aligned so that, at the water vapor detector level, the gases pass through the sample side of the detector, a water vapor absorber, and the reference side of the detector. At the carbon dioxide detector level, the gases are then conducted through the sample side of the detector, a carbon dioxide absorber, and the reference side of the detector. Finally, the resultant gases, which contain only nitrogen and the carrier gas, pass through the sample side of the nitrogen detector and are vented. At this detector level, high-purity carrier gas is used as the reference gas. In these ways, the detectors determine the thermal conductivities solely of the specified components.

3.2.4 In a second configuration, the carbon dioxide and water vapor are determined by infrared detection, using an aliquot of the combustion gases from which only the halides and sulfur oxides have been removed. These detectors determine the infrared absorption of the pertinent gases at precise wavelength windows so that the absorbances result from only the specified components. In these systems, nitrogen is determined by thermal conductivity, using a second aliquot of the gases, additionally treated to also reduce the nitrogen oxides to nitrogen and to remove the residual oxygen, carbon dioxide, and water vapor.

3.2.5 In a third configuration, which is essentially a modified gas chromatographic system, the nitrogen, carbon dioxide, and water vapor in the treated combustion gases are eluted from a chromatographic column and determined (at appropriate retention times) by thermal conductivity detection.

3.3 In all cases, the concentrations of carbon, hydrogen, and nitrogen are calculated as functions of the following:

3.3.1 Measured instrumental responses,

3.3.2 Values for response per unit mass for the elements (established via instrument calibration), and

3.3.3 Mass of the sample.

3.4 Or to the following: the instrument response is proportional to the gas density, which has been calibrated against a gas density of known concentration.

3.5 A capability for performing these computations automatically can be included in the instrumentation used for these test methods.

4. Significance and Use

4.1 Carbon and hydrogen values are used to determine the amount of oxygen (air) required in combustion processes and for the calculations of efficiency of combustion processes.

4.2 Carbon and hydrogen determinations are used in material balance calculations on coal conversion processes; also, one or the other is used frequently in correlations of chemical and physical properties, such as yields of products in liquefaction reactivity in gasification and the density and porosity of coal.

4.3 Nitrogen data are required to fulfill the requirements of the ultimate analysis, Practice D 3176. Also, the data obtained can be used to evaluate the potential formation of nitrogen oxides as a source of atmospheric pollution.

4.4 Nitrogen data are used for comparing coals and in research. If the oxygen content of coal is estimated by difference, it is necessary to make a nitrogen determination.

5. Apparatus

5.1 Because a variety of instrumental components and configurations can be used satisfactorily for these test methods, no specifications are presented here with respect to overall system design.

5.2 Functionally, however, the following requirements are specified for all approved instruments (Note 3):

NOTE 3—The approval of an instrument with respect to these functions is paramount to these test methods, since such approval tacitly provides approval of both the materials and the procedures used with the system to provide for these functions.

5.2.1 The conditions for combustion of the sample shall be such that (for the full range of applicable samples) the subject components shall be converted completely to carbon dioxide, water vapor (except for hydrogen associated with volatile halides), and nitrogen or nitrogen oxides. Generally, instrumental conditions that effect complete combustion include (1) availability of the oxidant, (2) temperature, and (3) time.

5.2.2 Representative aliquots of the combustion gases shall then be treated for the following reasons:

5.2.2.1 To liberate (as water vapor) hydrogen present as hydrogen halides and sulfur oxyacids; and

5.2.2.2 To reduce (to the element) nitrogen present as nitrogen oxides.

(1) The water vapor and nitrogen so obtained shall be included with the materials originally present in these aliquots.

5.2.3 Additional treatment of the test specimens (prior to detection) depends on the detection scheme used for the instrument (Note 4).

NOTE 4—The additional treatments can be provided by the instrumental components used to satisfy 5.2.2.

5.2.3.1 For the configuration described in 3.2.3, the halides proper, sulfur oxides, and residual oxygen shall be removed from the single test specimen in which the water vapor, carbon dioxide, and nitrogen are determined sequentially.

5.2.3.2 For the configuration described in 3.2.4, the test specimen in which the water vapor and carbon dioxide are determined, only the halides and sulfur oxides shall be removed from the gas stream in which the water vapor and carbon dioxide are determined. For combusted gases in which the nitrogen is determined, the water, carbon dioxide, and residual oxygen shall also be removed.

5.2.3.3 For the configuration described in 3.2.5, the halides and sulfur oxides shall be removed from the combusted gases obtained from the single test specimen.

5.2.4 The detection system (in its full scope) shall determine the analytical gases individually and without interference. Additionally, for each analyte, either of the following applies:

5.2.4.1 The detectors themselves shall provide linear responses that correlate directly to concentration over the full range of possible concentrations from the applicable samples, or

5.2.4.2 The system shall include provisions for evaluating nonlinear responses appropriately so that the nonlinear responses can be correlated accurately with these concentrations.

(1) Such provisions can be integral to the instrumentation, or they can be provided by (auxiliary) computation schemes.

5.2.5 Finally, except for those systems in which the concentration data are output directly, the instrument shall include an appropriate readout device for the detector responses.

6. Reagents

6.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.³ Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

6.2 *Helium, Carrier Gas*, as specified by the instrument manufacturer.

6.3 *Oxygen*, as specified by the instrument manufacturer.

6.4 *Additional Reagents*, as specified by the instrument manufacturer. This specification refers to the reagents used to provide for the functional requirements cited in 5.2.2-5.2.3.3. These reagents can vary substantially for different instruments; in all cases, however, for systems that are functionally satisfactory (and therefore approved), the reagents recommended by the manufacturer are also tacitly approved. Consequently, these reagents shall be those recommended by the manufacturer.

7. Preparation of Analysis Sample

7.1 The samples shall initially be prepared in accordance with Test Methods D 2013 or D 346.

7.2 If required by characteristics of the instrumental system, reduce the air-dry samples (7.1) typically to pass 75 μm (No. 200 U.S.A. Standard Sieve Series) to obtain test units of the analysis sample in the size range recommended by the instrument manufacturer. If required by characteristics of the instrumental system, as specified in 1.2.2, treat the test specimens in accordance with Test Method D 3173 to provide moisture-free materials solely appropriate for these systems. In this and all subsequent sample handling steps, exercise care to minimize changes in moisture content resulting from exposure to the atmosphere.

8. Instrument Preparation

8.1 Assemble the instrumental system in accordance with the manufacturer's instructions.

8.2 *Adjustment of Response of Measurement System*—Weigh an appropriate test portion of standard reference material (SRM), calibrating agent, or reference coal. Analyze the test portion (see 9.1). Repeat this procedure. Adjust instrument response, as recommended by the manufacturer, until the absence of drift is indicated.

³ *Reagent Chemicals, American Chemical Society Specifications*, American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Analar Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmaceutical Convention, Inc. (USPC), Rockville, MD.

8.3 *Calibration*—Select coal SRMs or other calibrating agents and materials specified by the manufacturer that have certified carbon, hydrogen, and nitrogen values in the range of samples to be analyzed. At least three such SRMs or calibrating agents are recommended for each range of carbon, hydrogen, and nitrogen values to be tested. When possible, two of the SRMs or calibrating agents shall bracket the range of carbon, hydrogen, and nitrogen to be tested, with the third falling within the range.

8.3.1 All coal SRMs should be in accordance with 7.1 and shall be supplied by or have traceability to an internationally recognized certifying organization. (**Warning**—An indicated problem with linearity of the instrument during calibration can result from contamination of the SRM or calibrating agent as the container becomes depleted. It is therefore recommended that the SRM or calibrating agent be discarded when less than five grams remain in the container.)

8.3.2 *Calibration Procedure*—Analyze, as samples, portions of an SRM, reference coal, or calibrating agent chosen to represent the level of carbon, hydrogen, and nitrogen in the samples to be tested. If not required by the characteristics of the instrumental system, use the “as-determined” carbon, hydrogen, and nitrogen values for calibration. These values must have been calculated previously from the certified “dry basis” carbon, hydrogen, and nitrogen values and residual moisture determined using either Test Methods D 3174 or D 5142. Continue analyzing until the results from five consecutive determinations fall within the repeatability interval (see 12.21.1) of these test methods. Calibrate the instrument according to the manufacturer’s instructions using these values. Analyze, as samples, two SRMs reference coals or calibrating agents that bracket the range of values to be tested. The results obtained for these samples must be within the stated precision limits of the SRM, reference coal, or calibrating agent, or the calibration procedure must be repeated. Records for all calibrations must be in accordance with Guide D 4621.

8.3.3 *Periodic Calibration Verification and Recalibration*—In accordance with Guide D 4621, analyze a control sample on a periodic basis. Results obtained for the control sample must be within established limits, or all results obtained since the last successful control check must be rejected and the calibration procedure repeated.

9. Procedure

9.1 Analyze a test specimen of the analysis sample in accordance with the manufacturer’s instructions.

10. Calculation

10.1 Calculate the concentrations of carbon, hydrogen, and nitrogen, on the appropriate sample basis, as follows:

$$A = \frac{(B \times C)}{D} \times 100 \quad (1)$$

where:

A = % of the analyte,

B = detector response for that analyte,

C = unit mass per detector response established for the analyte during calibration, and

D = mass of test specimen, g.

The calculations can be provided automatically by the instrumental system used for these test methods.

11. Report

11.1 Report results from the carbon, hydrogen, and nitrogen determinations on any of the several common bases that differ solely with respect to moisture. Procedures for converting the as-determined concentrations to the other bases are specified in Practices D 3176 and D 3180.

12. Precision and Bias

~~12.1 These test methods are highly dependent on the calibration of the equipment.~~

~~12.2 The~~

~~12.1 The precision of these this test methods for the determination of e Carbon, h Hydrogen, and nitrogen was calculated from data obtained from coal and coke with the following concentration ranges: carbon (dry-basis) from 48.6 to 90.6 %, hydrogen (dry-basis) from 0.14 to 5.16 %, and nitrogen (dry-basis) from 0.69 to 1.57 %.~~

~~12.2.1 Repeatability—The difference, Nitrogen in absolute value, between two test results, conducted on portions of the same analysis sample, 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 a difference is found to exceed the repeatability interval, there is reason to question one, or both, of the test results. The repeatability intervals for carbon, hydrogen, and nitrogen coal are given shown in Table 1.~~

~~12.2.2 Example—Duplicate analyses for carbon exhibited values of 73.26 and 73.62 %. The~~

~~12.1.1 Repeatability Limit (*r*)—The value below which the absolute difference between the two test results is 0.36 %. Since this value does not exceed the *I*(*r*) value calculated to a dry basis (Practice D 3180) of 0.64 %, these duplicate analyses are acceptable at separate and consecutive test determinations, carried out on the 95 % confidence level.~~

~~12.2.3 Reproducibility—The difference, same sample, in absolute value, between the averages of duplicate determinations conducted in different laboratories same laboratory, by the same operator, using the same apparatus on representative samples prepared taken at random from the same bulk sample after reducing to 100 % through a 250 Mm (No. 60 U.S.A. Standard Sieve~~

TABLE 1 Concentrations Range and Limits for Repeatability and Reproducibility for Carbon, Hydrogen, and Nitrogen in Coal

Element	Concentration Range, % Dry Basis	$\frac{1}{2}$ Repeatability Limit, r	$\frac{1}{2}$ Reproducibility Limit, R
Carbon	0.64		2.54
Carbon	48.6 to 90.6	0.64	2.51
Hydrogen	0.46		0.30
Hydrogen	0.14 to 5.16	0.16	0.30
Nitrogen	0.44		0.17
Nitrogen	0.69 to 1.57	0.11	0.17

Series) sieve shall not exceed the reproducibility interval $I (R)$ in more than 5 % single quantity of such paired values (95 % confidence level). When such a difference is found homogeneous material, may be expected to exceed the reproducibility interval, there is reason to question one, or both, of the test results. The reproducibility intervals for carbon, hydrogen, and nitrogen are given in Table 1.

12.2.4 *Example*—Duplicate analysis for hydrogen in one laboratory revealed an average value of 5.15 %, and occur with a value probability of 4.93 % was obtained in a different laboratory. The difference between the different laboratory approximately 95 %.

12.1.2 *Reproducibility Limit (R)*—The value is 0.22 %. Since below which the laboratory absolute difference is less than the $I (R)$, the between two laboratory test results calculated to a dry basis (Practice D 3180), carried out in different laboratories, using samples taken at the 95 % confidence level.

12.3 random from a single quantity of material that is as homogeneous as possible, may be expected to occur with a probability of approximately 95 %.

12.2 *Bias*—Bias is eliminated when the apparatus instrument is calibrated properly calibrated against certified reference standards. Proper calibration includes comparison of test data on NIST SRM 1632 or other reagents and materials that have instrumental results to certified carbon, hydrogen, and nitrogen values. Results for certified standards above and below anticipated analysis sample results should be within certified precision levels for all standards over the calibration range of the instrument.

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