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Standard Test Methods for
Determination of Carbon, Hydrogen and Nitrogen in Analysis Samples of Coal and Carbon in Analysis Samples of Coal and Coke[1]

This standard is issued under the fixed designation D5373; 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.

ε1 NOTE—Updated research report footnote in Section 11 editorially in March 2015.

1. Scope

1.1 Test Method A covers the determination of carbon in the range of 54.9 % to 84.7 %, hydrogen in the range of 3.25 % to 5.10 %, and nitrogen in the range of 0.57 % to 1.80 % in the analysis samples (7.1) of coal.

1.1.1 Test Method B covers the determination of carbon in analysis samples of coal in the range of 58.0 % to 84.2 %, and carbon in analysis samples of coke in the range of 86.3 % to 95.2 %.

NOTE 1—The coals included in the interlaboratory study employed to derive the precision statement for this standard cover ASTM rank lignite A to low volatile bituminous. Additional information concerning the composition of these coals appears in Annex A5. The cokes used in the interlaboratory study employed to derive the precision statement for coke included an equal number of met cokes and pet cokes.

1.2 All percentages are percent mass fractions unless otherwise noted.

1.3 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this 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 and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]
D346/D346M 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
D3176 Practice for Ultimate Analysis of Coal and Coke
D3180 Practice for Calculating Coal and Coke Analyses from As-Determined to Different Bases
D5865 Test Method for Gross Calorific Value of Coal and Coke
D7582 Test Methods for Proximate Analysis of Coal and Coke by Macro Thermogravimetric Analysis
2.2 *ISO Standard:*
ISO 5725-6 Accuracy (Trueness and Precision) of Measurement Methods and Results Part 6: Use in Practice of Accuracy Values[3]

3. Summary of Test Methods

3.1 In Method A, carbon, hydrogen and nitrogen in coal are determined concurrently in a single instrumental procedure using a furnace operating at temperatures in the range of 900 °C to 1050°C. The quantitative conversion of the carbon, hydrogen and nitrogen into their corresponding gases (CO_2, H_2O, and NO_x) occurs during combustion of the sample at an elevated temperature in an atmosphere of oxygen. Combustion products which can interfere with the subsequent gas analysis are removed. Oxides of

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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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[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.

[3] Available from American National Standards Institute (ANSI), 25 W. 43rd St., 4th Floor, New York, NY 10036, http://www.ansi.org.

nitrogen (NO_x) are reduced to N_2 before detection. The carbon dioxide, water vapor and elemental nitrogen in the gas stream are determined by appropriate instrumental detection procedures.

3.2 In Method B, carbon in coal and coke is determined by combusting the sample in a 1350°C furnace. The H_2O in the combustion gases is removed and CO_2 is determined by infrared absorption.

4. Significance and Use

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

4.2 Carbon and hydrogen determinations can be used in calculations including material balance, reactivity and yields of products relevant to coal conversion processes such as gasification and liquefaction.

4.3 Carbon and nitrogen values can be used in material balance calculations employed for emission accounting purposes.

NOTE 2—The bulk composition of coal changes at a rate that varies from coal to coal during storage. As a result using coal for calibration can yield incorrect estimates of carbon, and hydrogen content in particular.

5. Apparatus

5.1 *Analytical Instrument for CHN Analysis (Method A)*—An instrument capable of analyzing a test portion of 6 mg or greater. It includes a furnace capable of maintaining a temperature (900°C to 1050°C) in the range to ensure quantitative recovery of carbon, hydrogen and nitrogen in coal as their corresponding gases (CO_2, H_2O, and NO_x). The combustion gases or a representative aliquot shall be treated to remove, separate out or convert any components that can interfere with the measurement of carbon dioxide, water vapour or nitrogen. The detection system shall include provisions for evaluating the response in a manner that correlates accurately with the carbon dioxide, water vapour and nitrogen present in the treated combustion gases.

5.2 *Analytical Instrumentation for Carbon in Coal and Coke Analysis (Method B)*—An instrument with a furnace capable of maintaining a temperature of at least 1350°C at all times during the analysis. The high temperature helps ensure the quantitative recovery of carbon from cokes. The infrared absorption detection system shall include provisions for evaluating the response in a manner that correlates accurately with the carbon dioxide present in the dry combustion gases. Follow the manufacturer's recommendations for sample mass (typically 50 mg to 300 mg).

5.3 *Balance*—A stand-alone balance or a balance integrated with the instrument, with a resolution of at least 0.1 % relative of the test portion mass.

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.[4] 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 *Carrier Gas,* as specified for the instrument by the manufacturer.

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

6.4 *Additional Reagents,* of types and qualities as specified for the instrument by the manufacturer.

6.5 *Calibration Materials*—Calibration materials shall be accompanied by a certificate of analysis stating the purity of the material. If the certificate of analysis does not provide assigned values for carbon, hydrogen or nitrogen use the purity as stated on the certificate to establish carbon, hydrogen and nitrogen from the theoretical values. Store these pure substances in a desiccator under conditions that maintain the compounds in a dry state.

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[4] *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.

TABLE 1 Calibration Materials and Their Theoretical Contents of Carbon, Hydrogen and Nitrogen (Method A)

Name	Formula	C %	H %	N %
EDTA	$C_{10}H_{16}N_2O_8$	41.1	5.5	9.6
Phenylalanine	$C_9H_{11}NO_2$	65.4	6.7	8.5
Acetanilide	C_8H_9NO	71.1	6.7	10.4
BBOT	$C_{26}H_{26}N_2O_2S$	72.5	6.1	6.5
Graphite	C	100.0		

6.6 *Reference Materials*—Certified reference material (CRM) coal(s) prepared by a recognized authority to monitor changes in instrument response that can be affected by constituents not present in the calibration materials (Note 3) and to verify the acceptability of nitrogen results. Coal(s) traceable to a certified reference material (CRM) coal(s) can also be used. Follow instructions on the reference material certificate with respect to storage of the reference material and use of assigned values. Use only those carbon, hydrogen and nitrogen values that have an assigned uncertainty or are traceable to a value with an assigned uncertainty.

Note 3—Coal contains mineral constituents as well as acid gas forming constituents that can affect the performance of chemicals used to ensure the consistent and uniform conversion and recovery of carbon, hydrogen and nitrogen.

Note 4—The amount of nitrogen in the majority of coal employed for power production purposes is in the range of 0.5 % to 1.8 % . None of the calibrants yields percent nitrogen values within the ranges expected for coal. For this reason reference material (RM) coal is used to check the acceptability of nitrogen results.

7. Preparation of Analysis Sample

7.1 The sample shall be the analysis sample prepared to a top size of less than 250 μm (60 mesh). Coal samples shall be prepared in accordance with Practice D2013. Coke samples shall be prepared in accordance with Practice D346/D346M.

8. Instrument Preparation

8.1 *Instrument Set-Up*—Verify all instrument operating parameters meet the specifications in the instrument operating manual. Verify the condition and quantities of all chemicals currently in use are satisfactory for the number of samples to be analyzed. Prior to any analysis, check for and, if necessary correct any leaks in the combustion system, and the carrier gas system.

8.2 *Blank Analyses*—Perform blank analyses to establish carbon, hydrogen and nitrogen levels in the combustion and carrier gases as required by the specific method. The level of carbon, hydrogen or nitrogen in these gases shall not exceed 1 % relative of the instrument response for the lowest mass of calibration material (8.4) for each analyte. Re-determine blank analyses whenever the carrier gas or oxygen supplies are changed or any chemicals are renewed.

8.3 *Conditioning*—Select a conditioning sample in the range of 75 % (or more) carbon dry basis. It is recommended that the moisture content be less than 3 %. Carry out four determinations on the conditioning sample. Discard the first determination. If the range of the three retained determinations for either carbon, hydrogen or nitrogen values exceed 1.2*r* where *r* is the repeatability of this standard, instrument stability is suspect. In this case take corrective action before proceeding with calibration.

8.4 *Calibration*—If the instrument has been previously calibrated in accordance with Annex A1, determinations can proceed provided the calibration is verified in accordance with Annex A2. Otherwise calibrate the instrument as described in Annex A1.

8.4.1 *Calibration for Carbon in Coal and Coke at 1350°C (Method B)*—Use pure graphite to calibrate instruments operating at 1350°C that are used for determining carbon in coal and coke analysis samples.

9. Procedure

9.1 *Determination:*

9.1.1 Carry out a determination of the moisture content of each analysis sample or each reference material coal, or both, in accordance with Test Method D3173 or Test Methods D7582 within 48 h of the determination of carbon, hydrogen and nitrogen on each analysis sample.

9.1.2 Carry out the determination by weighing out a test portion of each analysis sample within a mass range recommended by the manufacturer. Conduct determinations on consecutive test portions of an analysis sample as needed to meet quality control requirements.

9.1.3 Verify the calibration upon completion of all test determinations and as needed to meet quality control requirements according to Annex A2.

9.1.4 Prior to conducting any test determinations, upon completion of all test determinations and as needed to meet quality control requirements conduct determinations on consecutive test portions of a reference material (RM) coal (6.6). Verify the acceptability of results for the RM coal in accordance with Annex A3.

Note 5—Appendix X2 provides guidance on the selection of the mass of a test portion that will yield for a mass of carbon similar to the mid range mass of the calibration material.

TABLE 2 Concentrations Range and Limits for Repeatability and Reproducibility for Carbon, Hydrogen, and Nitrogen in Coal (Method A)

Element	Concentration Range, %	Repeatability Limit, *r* %	Reproducibility Limit, *R* %
Carbon	54.9 to 84.7	0.45	1.00
Hydrogen	3.25 to 5.10	0.10	0.25
Nitrogen	0.57 to 1.80	0.05	0.15

TABLE 4 Comparison of Reference EDTA and Reference Phenylalanine Certificate of Analysis Values with Interlaboratory Values for Carbon, Hydrogen, and Nitrogen

Reference Pure Substance	Phase	Parameter	Number of Results	Certificate of Analysis Value	Interlaboratory Study Value	Bias	Significant (95 % Confidence)
EDTA	1B	Carbon	34	41.09	41.10	0.01	no
EDTA	1C	Carbon	24	41.09	40.99	-0.10	no
Phenylalanine	1B	Carbon	32	65.43	65.49	0.06	no
Phenylalanine	1C	Carbon	22	65.43	65.37	-0.06	no
EDTA	1B	Hydrogen	33	5.52	5.52	0.00	no
EDTA	1C	Hydrogen	24	5.52	5.54	0.02	no
Phenylalanine	1B	Hydrogen	32	6.71	6.72	0.01	no
Phenylalanine	1C	Hydrogen	24	6.71	6.71	0.00	no
EDTA	1B	Nitrogen	32	9.59	9.55	-0.04	yes
EDTA	1C	Nitrogen	21	9.59	9.54	-0.05	no
Phenylalanine	1B	Nitrogen	32	8.48	8.46	-0.02	no
Phenylalanine	1C	Nitrogen	21	8.48	8.45	-0.03	no

10. Calculation

10.1 Record the total carbon, hydrogen and nitrogen as analyzed as a percentage by mass. Report the results on dry basis to the nearest 0.1 % for carbon, 0.01 % for hydrogen and to the nearest 0.01 % for nitrogen.

10.2 Use the following equations for the calculation to dry basis:

10.2.1 For the carbon content:

$$C_d = C_{ad} \times \frac{100}{100 - M_{ad}} \tag{1}$$

10.2.2 For the nitrogen content:

$$N_d = N_{ad} \times \frac{100}{100 - M_{ad}} \tag{2}$$

10.2.3 For the hydrogen content:

$$H_d = \left(H_{ad} - 0.1119 \times M_{ad}\right) \times \frac{100}{100 - M_{ad}} \tag{3}$$

where:

d	=	dry basis,
ad	=	as determined (as analyzed) basis,
C	=	content of carbon, %,
N	=	content of nitrogen, %,
H	=	content of hydrogen, %, and
M_{ad}	=	moisture content of the sample as analyzed, %.

11. Precision and Bias[5]

11.1 The precision data for Test Method A for the determination of carbon, hydrogen, and nitrogen in coal are shown in Table 2. The precision data for Test Method B for the determination of carbon in coal and coke are shown in Table 3.

TABLE 3 Concentration Range and Limits for Repeatability and Reproducibility for Carbon in Coal and Coke Determined Using 1350°C Combustion (Method B)

Element	Concentration Range, %	Repeatability Limit, r %	Reproducibility Limit, R %
Carbon in Coke	86.3 to 95.4	0.87	1.68
Carbon in Coal	57.7 to 84.0	0.55	2.31

11.1.1 *Repeatability Limit (r)*—The value below which the absolute difference between two test results calculated to a dry basis (Practices D3180 and D3176) 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 material, may be expected to occur with a probability of approximately 95 %.

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[5] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D05-1034 and ~~RR:D05-1042~~RR:D05-1046.

11.1.2 *Reproducibility Limit (R)*—The value below which the absolute difference between two test results calculated to a dry basis (Practices D3180 and D3176), carried out in different laboratories, using samples taken at random from a single quantity of material that is as homogeneous as possible, may be expected to occur with a probability of approximately 95 %.

NOTE 6—Additional information concerning precision statistics appears in Annex A4 as well as the composition of the coals employed carbon, hydrogen, and nitrogen in the interlaboratory study (RR:D05–1034) that appears in Annex A5. Additional information collected during the determination of carbon in coal and coke at 1350°C interlaboratory study (RR:D05–1042)(RR:D05–1046) appears in Annex Annex A6.

11.2 *Bias*—Two materials, EDTA and phenylalanine, distributed from a common source were included in the carbon, hydrogen and nitrogen interlaboratory study (Method A) as reference pure substances. Each participating laboratory calibrated their instrument using one or more of the pure substances (6.5) obtained from a different source. The reference pure substances were analyzed in two phases of the study conducted one year apart. A comparison of the certificate of analysis values and those obtained in the interlaboratory study for the reference pure substances are shown in Table 4.

11.2.1 During the interlaboratory study for the determination of carbon in coke (Method B) the ruggedness testing showed the analyses at 1350°C are biased high when compared to analyses at either 1150°C or 950°C. The average values of these biases are shown in Table 5 and both biases are significant at the 95 % confidence level. The ruggedness testing was done with a carbon analyzer using ceramic boats in an open combustion tube. No accelerants or combustion aids, such as those used in some analyzers, were used. The carbon values from this study are shown in Annex Annex A6.

NOTE 7—Guidelines for reporting test sample results that do not meet the repeatability requirements of this standard when all calibration verification and reference material check sample acceptance requirements are met are provided in Appendix X3.

12. Calculation to Other Bases

12.1 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 D3176 and D3180.

TABLE 5 Relative Biases for Carbon in Coke Determined for 10 Coke Samples at Different Combustion Temperatures

Parameter	Test Condition 1 Combustion Temperature	Test Condition 2 Combustion Temperature	Average Bias % (Absolute)	Significant (95 % Confidence)
Carbon in Coke	1350°C	1150°C	0.44	yes
Carbon in Coke	1350°C	950°C	0.96	yes

NOTE 1—Test Condition 2 is biased lower.

ANNEXES

(Mandatory Information)

A1. NUMBER OF CALIBRATION POINTS FOR METHODS A AND B

A1.1 To meet the precision requirements of this method 6 calibration points are required for a linear fit and 8 calibration points are required for a non linear fit. These requirements are summarized for various fits in Table A1.1. A calibration point consists of a determination on a single test portion of calibration material.

NOTE A1.1—The interlaboratory study employed to validate the precision of this test method required laboratories to employ 6 calibration points for a linear fit and 8 for a non linear fit. Additional calibration points can be used.

A1.2 Guidance on the selection of masses of pure substance for calibration is given in Appendix X1.

A1.3 Verify the calibration according to Annex A2.

A2. CALIBRATION VERIFICATION FOR CARBON, HYDROGEN AND NITROGEN (METHOD A)

A2.1 Some instruments allow for calibration drift correction. Verify the acceptability of a drift correction immediately after conducting the drift correction.

A2.2 Verify the acceptability of the calibration by determining the carbon, hydrogen and nitrogen in % of a calibration material (6.5) not used for calibration. Appendix X1 provides guidance on selection of the mass of verification material.

A2.3 Table A2.1 lists the relative percentages the verification determinations shall agree with the values of the carbon, hydrogen and nitrogen from the certificate of analysis.

NOTE A2.1—These limits are from the calibration data supplied by the 14 laboratories that took part in the interlaboratory study (ILS) employed to validate this standard. The calibration data includes results from the pure substances listed in 6.5 and five instrument configurations covering two phases of the ILS conducted 1 year apart. These limits can serve as reasonable performance criteria for calibrations conducted in the same or different laboratories over an extended period of time.

A2.4 If any verification determination does not agree within the limits specified in Table A2.2, conduct three additional verification determinations. Use masses of verification calibrant that yield a mass of carbon within 5 mg of the calibration masses at the lower extreme, mid-point and upper extreme of the calibration (see Appendix X1). If the additional verification determinations agree with the values from the certificate of analysis within the limits specified in Table A2.2 then it is acceptable to continue with determinations on the analysis samples. Otherwise reject the calibration as well as all determinations back to the last acceptable verification. Check instrument set-up (8.1), conduct blank analyses (8.2) and condition the instrument (8.3). Calibrate the instrument according to Annex A1 before proceeding with analysis.

TABLE A1.1 Minimum Number of Calibration Points for Common Regressions

Regression	Number of Calibration Points Required
Linear	6
Quadratic	8
Power	8