Designation: D5373 – 16

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.

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 (8.1) of coal and of carbon in analysis samples of coke in the range of 86.6 % to 97.9 %.

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 for Method A included five each metallurgical (met) cokes and seven each petroleum (pet) cokes, and Method B included an equal number (five each) 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]

D121 Terminology of Coal and Coke
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. Terminology

3.1 For definitions of terms used in this standard, refer to Terminology D121.

4. Summary of Test Methods

4.1 In Method A, carbon, hydrogen, and nitrogen in coal or carbon in coke are determined in a single instrumental procedure using a furnace operating at temperatures in the range of 900 °C to 1050 °C for carbon, hydrogen and nitrogen in coal or 950 °C to 1150 °C for carbon in coke. 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 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.

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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.

4.2 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.

5. Significance and Use

5.1 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.

5.2 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.

5.3 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.

6. Apparatus

6.1 *Analytical Instrument for CHN Analysis in Coal or Carbon in Coke (Method A)*—An instrument capable of analyzing a test portion of 6 mg or greater. For coal, it includes a furnace capable of maintaining a temperature in the range of 900 °C to 1050 °C to ensure quantitative recovery of carbon, hydrogen, and nitrogen as their corresponding gases (CO_2, H_2O, and NO_x). For coke, it includes a furnace capable of maintaining a temperature in the range of 950 °C to 1150 °C. The use of combustion promoters, including tin foil or capsule, shall be utilized as required by the apparatus manufacturer for quantitative recovery of carbon in coke as its corresponding gas (CO_2). 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 vapor or nitrogen. The detection system shall include provisions for evaluating the response in a manner that correlates accurately with the carbon dioxide, water vapor and nitrogen present in the treated combustion gases.

6.2 *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).

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		

6.3 *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.

7. Reagents

7.1 *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.

7.2 *Carrier Gas,* as specified for the instrument by the manufacturer.

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

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

7.5 *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.

7.6 *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) and coke(s) traceable to a certified reference material (CRM) coal(s) and coke(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.

7.7 *Tungsten Oxide (WO_3)*—as specified for the instrument by the manufacturer.

7.8 *Tin (Sn)*—as specified for the instrument by the manufacturer.

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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.

8. Preparation of Analysis Sample

8.1 The sample shall be the analysis sample prepared to a top size of less than 250 µm (No. 60). Coal samples shall be prepared in accordance with Practice D2013. Coke samples shall be prepared in accordance with Practice D346/D346M.

9. Instrument Preparation

9.1 *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.

9.2 *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 (9.4) for each analyte. Re-determine blank analyses whenever the carrier gas or oxygen supplies are changed or any chemicals are renewed.

9.3 *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.

9.4 *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.

9.4.1 *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.

10. Procedure

10.1 *Determination:*

10.1.1 Carry out a determination of the moisture content of each analysis sample or each reference material, 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.

10.1.2 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.

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

10.1.4 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) (7.6). Verify the acceptability of results for the RM 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.

11. Calculation

11.1 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.

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

11.2.1 For the carbon content:

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

11.2.2 For the nitrogen content:

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

11.2.3 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, %.

12. Precision and Bias[5]

12.1 The precision data for Test Method A for the determination of carbon, hydrogen, and nitrogen in coal and carbon in

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

Element	Mass Fraction Range, %	Repeatability Limit	Reproducibility Limit
Carbon in Coal	54.9 to 84.7	0.45	1.00
Hydrogen in Coal	3.25 to 5.10	0.10	0.25
Nitrogen in Coal	0.57 to 1.80	0.05	0.15
Carbon in Coke	86.6 to 97.9	0.85	2.20

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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, RR:D05-1046, and RR:D05-1048.

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

coke 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

12.1.1 *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 %.

12.1.2 *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—Information concerning precision statistics for carbon, hydrogen, and nitrogen in coal appears in Annex A4 and the composition of the coals employed in the interlaboratory study (RR:D05–1034) appears in Annex A5. Information collected during the determination of carbon in coal and coke at 1350 °C interlaboratory study (RR:D05–1046) appears in Annex Annex A6. Information collected during the determination of carbon in coke at 950 °C to 1150 °C interlaboratory study (RR: D05–1048) appears in A4.3.

12.2 *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 (7.5) 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.

12.2.1 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 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.

13. Calculation to Other Bases

13.1 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, six calibration points are required for a linear fit and eight 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.

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

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

NOTE A1.1—The interlaboratory study employed to validate the precision of this test method required laboratories to employ six calibration points for a linear fit and eight 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 (7.5) 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 7.5 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 (9.1), conduct blank analyses (9.2) and condition the instrument (9.3). Calibrate the instrument according to Annex A1 before proceeding with analysis.

A2.5 Since the absolute difference between the verification determination and the certificate of analysis value are within the absolute limit for carbon, hydrogen and nitrogen, the laboratory can continue with analysis of test samples without recalibrating the instrument.

TABLE A2.1 Percent (%) Relative Calibration Acceptance Limits

Carbon	1.20 %
Hydrogen	2.10 %
Nitrogen	1.80 %

TABLE A2.2 Example of Calibration Verification with EDTA

Parameter	Certificate of Analysis %	Relative Limit	Absolute Limit %	Verification Result %	Absolute Difference %
Carbon	41.08	1.20 %	0.49	41.27	0.19
Hydrogen	5.51	2.10 %	0.12	5.59	0.08
Nitrogen	9.60	1.80 %	0.17	9.50	0.11

A3. ACCEPTANCE OF RESULTS FOR REFERENCE MATERIAL COAL(S)

A3.1 Calculate the as determined carbon, hydrogen and nitrogen results to a dry basis (Section 11). Verify the dry basis results for consecutive carbon, hydrogen and nitrogen determinations agree within the repeatability limit (Section 12).

A3.2 For nitrogen verify each dry basis nitrogen result agrees with the assigned value within 0.11 %.

NOTE A3.1—The 0.11 % acceptance limit is derived from the reproducibility limit for nitrogen (Section 12) in accordance with the section on "Comparison with a reference value for one laboratory" of ISO 5725-6.

A3.3 If any of these acceptance criteria fails, reject all determinations back to the last acceptable reference material determinations. Check instrument set-up (9.1), conduct blank analyses (9.2) and condition the instrument (9.3). Calibrate the instrument according to Annex A1 before proceeding with determinations.

NOTE A3.2—For carbon and hydrogen it is recommended a record is kept of the dry basis results. Each dry basis carbon result should agree with the dry basis certificate value within 0.7 %. Each dry basis hydrogen result should agree with the dry basis certificate value within 0.2 %. The certifying agency should be notified when more than seven consecutive dry basis results for carbon or hydrogen, or both, fall outside these limits. The certifying agency should be provided with the purchase date, in service date and expiry date of the reference material coal. The comparison limits for carbon and hydrogen are derived from the reproducibility limit (Section 12) in accordance with the section on "Comparison with a reference value for one laboratory" of ISO 5725-6.

A4. PRECISION STATISTICS

A4.1 The precision of this standard's Method A, characterized by repeatability (s_r, r) and reproducibility (s_R, R) has been determined for the coal materials listed in Tables A4.1-A4.3.

A4.2 The precision of this standard's Method B, characterized by repeatability (s_r, r) and reproducibility (s_R, R), has been determined for the materials listed in Tables A4.4 and A4.5.

A4.3 The precision of this standard's Method A, characterized by repeatability (s_r, r) and reproducibility (s_R, R) has been determined for the coke materials listed in Table A4.6.

TABLE A4.1 Repeatability (s_r, r) and Reproducibility (S_R, R) for Carbon %

Coal Source	Rank	Average Carbon	s_r	r	s_R	R
Australia	hvAb	72.84	0.17	0.48	0.32	0.90
New Zealand	hvAb	84.68	0.20	0.56	0.34	0.96
Canada	Sub	54.86	0.14	0.39	0.40	1.13
United Kingdom	hvAb	65.55	0.14	0.39	0.36	1.02
Australia	lvb	79.88	0.19	0.54	0.28	0.79
Australia	hvAb	74.31	0.13	0.37	0.30	0.85
Australia	hvAb	77.58	0.16	0.45	0.32	0.90
Australia	Brown Coal	67.53	0.13	0.37	0.43	1.21
United States	hvAb	77.22	0.15	0.42	0.27	0.76

TABLE A4.2 Repeatability (S_r, r) and Reproducibility (S_R, R) for Hydrogen %

Coal Source	Rank	Average Hydrogen	S_r	r	S_R	R
Australia	hvAb	4.59	0.022	0.06	0.114	0.32
New Zealand	hvAb	5.08	0.048	0.14	0.096	0.27
Canada	Sub	3.26	0.032	0.09	0.107	0.30
United Kingdom	hvAb	4.19	0.022	0.06	0.06	0.17
Australia	lvb	4.30	0.023	0.06	0.083	0.23
Australia	hvAb	4.47	0.022	0.06	0.07	0.20
Australia	hvAb	4.98	0.017	0.05	0.068	0.19
Australia	Brown Coal	4.53	0.026	0.07	0.08	0.23
United States	hvAb	4.94	0.017	0.05	0.067	0.19

TABLE A4.3 Repeatability (S_r, r) and Reproducibility (S_R, R) for Nitrogen %

Coal Source	Rank	Average Nitrogen	S_r	r	S_R	R
Australia	hvAb	1.58	0.014	0.04	0.036	0.10
New Zealand	hvAb	1.16	0.018	0.05	0.05	0.14
Canada	Sub	0.70	0.011	0.03	0.045	0.13
United Kingdom	hvAb	1.40	0.01	0.03	0.041	0.12
Australia	lvb	1.76	0.021	0.06	0.05	0.14
Australia	hvAb	1.67	0.013	0.04	0.047	0.13
Australia	hvAb	1.75	0.015	0.04	0.058	0.16
Australia	Brown Coal	0.57	0.017	0.05	0.051	0.14
United States	hvAb	1.46	0.012	0.03	0.052	0.15

TABLE A4.4 Repeatability (S_r, r) and Reproducibility (S_R, R) for 1350°C Determination of Carbon in Coke, %

Coke Sample	Coke Type	Average Carbon	S_r	r	S_R	R
Foundry Coke	Met Coke	89.68	0.34	0.61	0.95	1.71
Furnace Coke	Met Coke	89.62	0.26	0.57	0.73	1.60
DOF Coke	Met Coke	87.69	0.26	0.60	0.74	1.68
2017	Calcined Pet Coke	95.42	0.34	0.46	0.96	1.28
3050	Green Pet Coke	88.37	0.27	0.46	0.76	1.27
4070	Calcined Pet Coke	86.27	0.36	0.54	1.02	1.51
5018	Green Pet Coke	86.73	0.21	0.61	0.60	1.70
7009	Met Coke	87.74	0.40	0.99	1.11	2.78
NIST 2718a	Green Pet Coke	89.30	0.29	0.54	0.81	1.51
NIST 2776	Met Coke	89.40	0.32	0.46	0.91	1.28

TABLE A4.5 Repeatability (S_r, r) and Reproducibility (S_R, R) for 1350°C Determination of Carbon in Coal, %

Coal Sample	Coal Rank	Average Carbon	s_r	r	s_R	R
89–2	subB	67.87	0.18	1.17	0.52	3.29
89–4	hvCb	67.05	0.24	0.72	0.68	2.01
89–6	ligA	60.37	0.20	0.99	0.55	2.78
89–7	subA	69.15	0.18	0.78	0.51	2.17
89–8	hvBb	69.05	0.16	0.74	0.43	2.08
89–9	hvAb	69.37	0.18	0.91	0.52	2.54
90–1	ligA	57.74	0.20	0.78	0.57	2.18
91–2	lvb	84.03	0.16	0.53	0.44	1.49
91–5	hvAb	71.45	0.18	0.91	0.49	2.54
NIST 2692c	lvb	82.63	0.26	0.47	0.72	1.31

TABLE A4.6 Repeatability (S_r) and Reproducibility (S_R, *R*) for 950 °C to 1150 °C Determination of Carbon in Coke, %

Coke Sample	Coke Type	Average Carbon	S_r	r	S_R	R
ABC Coke	Met Coke	90.39	0.273	0.76	0.765	2.14
Furnace Coke–2776	Met Coke	89.71	0.440	1.23	0.653	1.83
DOF Coke	Met Coke	88.76	0.251	0.70	0.456	1.28
Foundry Coke–2775	Met Coke	91.44	0.245	0.69	0.689	1.93
SoHo Coke	Met Coke	89.20	0.177	0.50	1.014	2.84
PTP–1410	Green Pet Coke	87.55	0.153	0.43	0.865	2.42
HP40700	Green Pet Coke	86.56	0.226	0.63	0.830	2.32
Pet Coke–2719	Calcined Pet Coke	97.87	0.264	0.74	0.849	2.38
SG–PD Coke	Pet Coke	87.08	0.270	0.76	0.804	2.25
SG–AnodeG	Green Pet Coke	91.85	0.384	1.08	0.624	1.75
SG–AnodeC	Calcined Pet Coke	97.12	0.529	1.48	0.807	2.26
Control B–2718a	Green Pet Coke	89.05	0.196	0.55	0.902	2.53

A5. COMPOSITION OF COALS

A5.1 The composition of the coals employed to establish the precision of this standard's Method A are listed in Table A5.1. This table lists those parameters known to affect the determination of carbon, hydrogen and nitrogen in coal.

TABLE A5.1 Composition of Interlaboratory Study Coals

Country	Rank	Moisture % mm	Ash % Dry Basis	Sulfur % Dry Basis	Chlorine µg/g Dry Basis
Australia	hvAb	3.27	10.71	0.52	225
New Zealand	hvAb	0.96	1.76	1.50	830
Canada	Sub	10.24	24.23	0.25	37
United Kingdom	hvAb	2.97	19.18	1.90	4877
Australia	lvb	1.40	9.81	0.59	530
Australia	hvAb	3.20	11.05	0.56	410
Australia	hvAb	3.10	6.50	0.45	210
Australia	Brown Coal	10.20	1.22	0.31	1220
United States	hvAb	1.61	8.51	0.92	1479

A6. CARBON IN COKE SAMPLES (METHOD B)

A6.1 During the interlaboratory study for the determination of carbon in coke (Method B) the ruggedness testing showed there was a positive bias between the carbon determined in cokes using a 1350 °C furnace and furnaces operated at lower temperatures. The positive bias between the carbon determined in cokes using a 1350 °C furnace and that determined with lower temperatures are shown in Table A6.1 and Table A6.2.

TABLE A6.1 Percentages of Coke Carbon Determined Using Different Furnace Temperatures

Coke Sample	Average of 3[A] Runs at 1350 °C	Average of 3[A] Runs at 1150 °C	Difference
7009	88.17	87.73	0.44
Foundry Coke	89.73	89.44	0.29
Furnace Coke	90.32	89.33	0.99
DOF Coke	88.30	87.67	0.63
3050	88.78	88.26	0.52
5018	87.43	87.08	0.35
2017	94.71	94.95	-0.24
4070	86.35	86.30	0.05
2776	89.78	89.03	0.75
2718a	89.83	89.24	0.59
		Average Difference	0.44

[A] Average of 3 runs performed on the same day.

TABLE A6.2 Percentages of Coke Carbon Determined Using Different Furnace Temperatures

Coke Sample	Average of 4[A] Runs at 1350 °C	Average of 4[A] Runs at 950 °C	Difference
7009	88.36	87.58	0.78
Foundry Coke	89.70	88.78	0.92
Furnace Coke	89.98	88.49	1.49
DOF Coke	87.74	87.23	0.51
3050	88.76	88.29	0.47
5018	87.27	86.47	0.80
2017	95.06	93.89	1.17
4070	86.53	85.68	0.85
2776	89.64	88.34	1.30
2718a	89.74	88.44	1.30
		Average Difference	0.96

[A] Average of duplicate runs on two different days.

APPENDIXES

(Nonmandatory Information)

X1. PURE SUBSTANCE MASSES FOR CALIBRATION AND CALIBRATION VERIFICATION

X1.1 This appendix describes a procedure that can be used to calculate the range of calibrant masses from the expected range of carbon, % and hydrogen, % in the analysis sample (7.1).

NOTE X1.1—The hydrogen, % determined on a test portion of the analysis sample includes the hydrogen in the residual moisture of the test portion.

NOTE X1.2—The amount of hydrogen in majority of coal employed for power production purposes is in the range of 4.5 % to 6.1 % when the hydrogen in the coal moisture is taken into account. This information is provided to assist in the selection of calibration and calibration verification materials.

NOTE X1.3—The amount of nitrogen in majority of coal employed for power production purposes is in the range of 0.5 % to 1.8 %. None of the calibration materials (7.5) yield percent nitrogen values within the ranges expected for coal.

X1.2 A laboratory intends to calibrate an instrument to cover carbon in the range of 55 % to 85 % and hydrogen in the range 4.5 % to 5.3 %. The laboratory uses a test portion mass of 75 ± 5 mg.

X1.3 Calculate to the nearest milligram the mass of calibrant required for the lower and upper limits of carbon % as well as the lower and upper limits of hydrogen % using the following equation.

$$Mc = (Mt \times Av)/C_{AC} \qquad (X1.1)$$

where:

Mc = mass of test portion in milligrams,
C_{AC} = mid range mass of the calibration material,
Mt = as determined heating value of the analysis sample, and
Av = heating value of the calibration material.

X1.4 The mass of EDTA in milligrams with a certificate of analysis value of 41.02 % carbon required to produce the same mass of carbon as a 75 mg test portion containing 55 % carbon is given by:

$$Mc = (75 \times 55)/ 41.02 = 101 \text{ mg to the nearest mg}$$

X1.5 The mass of EDTA with a certificate of analysis value of 41.02 % carbon required to produce the same mass of carbon as a 75 mg test portion containing 85 % carbon is given by:

$$Mc = (75 \times 85)/ 41.02 = 155 \text{ mg to the nearest mg}$$

X1.6 The mass of EDTA with a certificate of analysis value of 5.56 % hydrogen required to produce the same mass of hydrogen as a 75 mg test portion containing 4.5 % hydrogen is given by:

$$Mc = (75 \times 4.5)/ 5.56 = 60 \text{ mg to the nearest mg}$$

X1.7 The mass of EDTA with a certificate of analysis value of 5.56 % hydrogen required to produce the same mass of hydrogen as a 75 mg test portion containing 5.3 % hydrogen is given by:

$$Mc = (75 \times 5.3)/ 5.56 = 71 \text{ mg to the nearest mg}$$

X1.8 Pick the smallest calculated calibration mass. In this case it is 60 mg.

X1.9 Pick the largest calculated calibration mass. In this case it is 155 mg.

X1.10 Calculate the difference. In this case it is 95 mg.

X1.11 The mid range calibration mass of EDTA is (60+155)/2 = 108 mg to the nearest mg.

X1.12 The calibrant mass interval for a linear fit using 6 points is given by 95/5 or 19 mg the nearest mg.

X1.13 The calibrant mass interval for a non linear fit using 8 points is given by 95/7 mg or 14 mg to the nearest mg.

X1.14 Table X1.1 summarizes the masses EDTA for the range of 55 % to 85 % carbon and 4.5 % to 5.3 % hydrogen for a test portion of 75 ± 5 mg.

TABLE X1.5 Masses of EDTA in mg for Calibration

Linear	60	79	98	117	136	155		
Non Linear	60	74	88	102	116	130	144	158

X1.15 Calculate the mass of the material used for calibration verification that will yield the same mass of carbon as a mass of the material within the range of the calibration using the following equation.

$$Mv = (Mc \times C_{AC})/C_{AV} \qquad (X1.2)$$

where:

Mv = mass of verification material in milligrams,
Mc = mass of calibrant in milligrams,
C_{AC} = value for carbon or hydrogen from the certificate of analysis of the calibrant, %, and
C_{AV} = value for carbon or hydrogen from the certificate of analysis of the verification material, %.

X1.16 The laboratory uses phenylalanine as the calibration verification material.

X1.17 The mass of phenylalanine with a certificate of analysis of 65.38 % carbon that will yield the same mass of carbon as the mid range mass of EDTA is given by:

$$(108 \times 41.02)/\ 65.38 = 68 \text{ mg to the nearest mg}$$

X1.18 The mass of phenylalanine with a certificate of analysis of 65.38 % carbon that will yield the same mass of carbon as the smallest calculated calibration mass of EDTA is given by:

$$(60 \times 41.02)/\ 65.38 = 38 \text{ mg to the nearest mg}$$

X1.19 The mass of phenylalanine with a certificate of analysis of 65.38 % carbon that will yield the same mass of carbon as the largest calculated calibration mass of EDTA is given by:

$$(155 \times 41.02)/\ 65.38 = 98 \text{ mg to the nearest mg}$$

X2. OPTIMUM TEST SAMPLE MASS FOR THE DETERMINATION OF TOTAL CARBON

X2.1 This appendix describes a procedure that can improve the reliability of carbon results. This can be important in cases where carbon results are employed for carbon accounting purposes.

X2.2 The minimum error of a result derived from a regression occurs near the mid range of the calibration. The mass of the test portion that produces a mass of carbon similar to the mid range mass of the calibration material can be estimated from the as determined heating value (HV) of the analysis sample, determined according to Test Method D5865 and the heating value of the calibration material.

X2.3 The test portion mass equivalent to the mid range mass of calibration material is given by:

$$Mt = M_{CM} \times (H_{VC}/H_{VS}) \qquad (X2.1)$$

where:

Mt = mass of test portion in milligrams,
M_{CM} = mid range mass of the calibration material,
H_{VS} = as determined heating value of the analysis sample, and
H_{VC} = heating value of the calibration material.

TABLE X2.1 Heating Value (HV) of Calibrants

Calibrant	MJ/kg	Cal/gm	Btu/lb
EDTA	16.91	4038	7268
Phenylalanine	26.96	6439	11590
Acetanilide	31.34	7485	13473
BBOT	29.84	7127	12828

X2.4 A laboratory employs EDTA to calibrate an instrument.

X2.5 The test portion mass is 75 ± 5 mg.

X2.6 The mid range calibration mass is 108 mg.

X2.7 Two analysis samples are to be tested for carbon, hydrogen and nitrogen.

X2.8 The as determined heating value of analysis sample A is 23.88 MJ/kg.

X2.9 The test portion mass for analysis sample A that would yield a mass of carbon similar to the mid range mass of calibration material is given by:

$$M_t = 108 \times (16.91/23.88) = 76 \text{ mg to the nearest mg}$$

X2.10 The as determined heating value of analysis sample B is 34.03 MJ/kg.

X2.11 The test portion mass for analysis sample B that would yield a mass of carbon similar to the mid range mass of calibration material is given by:

$$M_t = 108 \times (16.91/34.03) = 54 \text{ mg to the nearest mg}$$

X3. CHECKING TEST RESULTS AND DETERMINING THE FINAL QUOTED RESULT

X3.1 The procedures described in this appendix are taken from the section on "Methods for checking the acceptability of test results and determining the final quoted result," of ISO 5725-6.

X3.2 *Checking the Acceptability of Results Obtained Under Repeatability Conditions*:

X3.2.1 For analysis samples that do not meet the repeatability limit (Section 12) of this standard conduct analysis of two additional consecutive test portions on the same day as the initial runs. Calculate the as determined carbon, hydrogen and nitrogen results to a dry basis (Section 11). Calculate the range of all four carbon, hydrogen and nitrogen values.

X3.2.2 If the range is less than or equal to 1.3 times the repeatability limit report the mean of the four determinations. Indicate the value reported is a mean value. If the range is greater than 1.3r, where r is the repeatability limit (Section 12) of this standard, report the median of the four determinations. Indicate the value reported is a median value.

X3.3 *Checking the Acceptability of Results Obtained Under Reproducibility Conditions*:

X3.3.1 The cause for discrepancy between the final quoted results from two different laboratories that exceeds the reproducibility limit (Section 12) of this standard can be resolved by exchanging analysis samples and/or reference materials (7.6) as well as calibrant(s) (7.5). Where such an exchange is not practical each laboratory should obtain test results on a common sample preferably of known composition. Where use of a common material of known composition is not possible agreement should be reached between the two laboratories to refer to a third laboratory.