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Standard Test Methods for Carbon and Hydrogen in the Analysis Sample of Coal and Coke¹

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1. Scope

1.1 These test methods cover the determination of total carbon and hydrogen in samples of coal or coke. Both the carbon and hydrogen are determined in one operation. These test methods yield the total percentages of carbon and hydrogen in the coal as analyzed and the results include not only the carbon and hydrogen in the organic matter, but also the carbon present in mineral carbonates and the hydrogen present in the free moisture accompanying the sample as well as hydrogen present as water of hydration of silicates.

NOTE 1—It is recognized that certain technical applications of the data derived from this test procedure may justify additional corrections. These corrections could involve compensation for the carbon present as carbonates, the hydrogen of free moisture accompanying the sample, and the calculated hydrogen present as water of hydration of silicates.

1.2 When data are converted and reported on the “dry” basis, the hydrogen value is corrected for the hydrogen present in the free moisture accompanying the sample.

1.3 *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.*

1.4 The values stated in SI units are to be regarded as the standard.

2. Referenced Documents

2.1 ASTM Standards:

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

D 1193 Specification for Reagent Water³

D 2013 Practice for Preparing Coal Samples for Analysis²

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

D 3176 Practice for Ultimate Analysis of Coal and Coke²

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 *Annual Book of ASTM Standards*, Vol 05.06.

³ *Annual Book of ASTM Standards*, Vol 11.01.

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

TOTAL CARBON AND TOTAL HYDROGEN

3. Summary of Test Methods

3.1 The determination of carbon and hydrogen is made by burning a weighed quantity of sample in a closed system and fixing the products of combustion in an absorption train after complete oxidation and purification from interfering substances. These test methods give the total percentages of carbon and hydrogen in the coal as analyzed, and include the carbon in carbonates and the hydrogen in the moisture and in the water of hydration of silicates.

4. Significance and Use

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

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

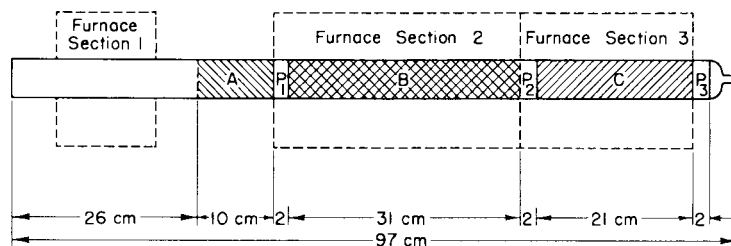
5. Sample

5.1 The sample shall be the material pulverized to pass No. 60 (250- μ m) sieve and well mixed according to Method D 346 or Method D 2013. It may be beneficial to grind the ash, pit ash, calcined coke and high mineral content materials to pass a No. 100 (150- μ m) sieve.

5.2 The test sample shall be weighed just prior to commencing the analysis to minimize chance for moisture change. A change in moisture content would introduce error in the hydrogen analysis. In order to provide the data necessary to correct for the hydrogen present in the moisture and ensuing final calculations of both the hydrogen and carbon, a separate sample shall be weighed out at the same time for a moisture analysis, and analyzed in accordance with Test Method D 3173.

6. Apparatus

6.1 *Oxygen Purifying Train*, consisting of the following units arranged as listed in the order of passage of oxygen:



A—Clear fused quartz section (optional) when a translucent quartz tube is used.
B—Cupric oxide filling.
C—Lead chromate or silver filling.
P₁, P₂, or P₃—oxidized copper gauze plugs.

NOTE 1—All dimensions are given in centimetres. When furnace sections longer than those specified in 6.3 are to be used, changes in the above dimensions shall be in accordance with the provisions of Note 5.

FIG. 1 Arrangement of Tube Fillings for Combustion Tube

6.1.1 *First Water Absorber*—A container for the solid dehydrating reagent. It shall be so constructed that the oxygen must pass through a column of reagent adequate to secure water equilibrium equal to that secured in the prescribed absorption train. A container of large volume and long path of oxygen travel through the reagent will be found to be advantageous where many carbon and hydrogen determinations are made.

6.1.2 *Carbon Dioxide Absorber*—A container for solid carbon dioxide absorbing agent. It shall be constructed as described in 6.1.1 and shall provide for a column of reagent adequate to remove carbon dioxide completely.

6.1.3 *Second Water Absorber*, same as specified in 6.1.1

6.2 *Flowmeter*, used to permit volumetric measurement of the rate of flow of oxygen during the determination. It shall be suitable for measuring flow rates within the range from 50 to 100 mL/min (standard temperature and pressure). The use of a double-stage pressure-reducing regulator with gage and needle valve preceding the first water absorber is recommended to permit easy and accurate adjustment of the rate of flow.

6.3 *Combustion Unit*—The combustion unit shall consist of three electrically heated furnace sections, individually controlled, which may be mounted on rails for easy movement; the upper part of each furnace may be hinged so that it can be opened for inspection of the combustion tube. The three furnace sections shall be as follows:

6.3.1 *Furnace Section 1*, nearest the oxygen inlet end of the combustion tube, approximately 130-mm long and used to heat the inlet end of the combustion tube and the sample. It shall be capable of rapidly attaining an operating temperature of 850 to 900°C. Combustion tube temperature shall be measured by means of a thermocouple placed immediately adjacent to the tube near the center of the tube section.

6.3.2 *Furnace Section 2*, approximately 330 mm in length and used to heat that portion of the tube filled with cupric oxide. The operating temperature shall be $850 \pm 20^\circ\text{C}$. Combustion tube temperature shall be measured by means of a thermocouple placed immediately adjacent to the tube near the center of the tube section.

6.3.3 *Furnace Section 3*, approximately 230 mm-long, and used to heat that portion of the tube filled with lead chromate or silver. The operating temperature shall be $500 \pm 50^\circ\text{C}$. Combustion tube temperature shall be measured by means of a

thermocouple placed immediately adjacent to the tube near the center of the tube section.

6.3.4 *Combustion Tube*—The combustion tube shall be made of fused quartz or high-silica glass⁴ and shall have a nominal inside diameter which may vary within the limits of 19 to 22 mm and a minimum total length of 970 mm. The exit end shall be tapered down to provide a tubulated section for connection to the absorption train. The tubulated section shall have a length of 20 to 25 mm, an internal diameter of not less than 3 mm, and an external diameter of approximately 7 mm. The total length of the reduced end shall not exceed 60 mm. If a translucent fused quartz tube is used, a transparent section 190-mm long, located 250 mm from the oxygen inlet end of the tube, will be found convenient (see Fig. 1).

6.3.5 *Combustion Boat*—This shall be either glazed porcelain, fused silica, or platinum. Boats with internal dimensions of approximately 70 by 8 by 8 mm have been found convenient.

6.4 *Absorption Train*—The absorption train shall consist of the following units arranged as listed in the order of passage of oxygen:

6.4.1 *Water Absorber*, having a capacity for 45 cm³ of solid reagent and a minimum length of gas travel through the reagent of 80 mm.⁵

6.4.2 *Carbon Dioxide Absorber*—If solid reagents are used for carbon dioxide absorption the container shall be as described in 6.4.1. If a solution is used, the container shall be a Vanier bulb.

6.4.3 *Guard Tube*—A container as described in 6.4.1.

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,

⁴ Vycor has been found satisfactory for this purpose.

⁵ Glass-stoppered containers such as the Nesbitt, Schwartz U-tube and the Stetser-Norton bulbs have been found satisfactory.

where such specifications are available.⁶ 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 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean Type IV reagent water, conforming to Specification D 1193.

7.3 *Oxygen, 99.5 % purity or better* (Note 5).

7.4 *Combustion Tube Reagents:*

7.4.1 *Cupric Oxide (CuO)*, wire form, dust-free.

7.4.2 *Fused Lead Chromate, (PbCrO₄)* approximately 2.38 to 0.84 mm size.

7.4.3 *Silver Gauze, 99.9 % silver minimum purity, 0.84 mm*, made from approximately No. 27 B&S gage wire.

7.4.4 *Copper Gauze, 99.0 % copper minimum purity, 0.84 mm* made from approximately No. 26 B&S gage wire.

7.5 *Purification and Absorption Train Reagents:*

7.5.1 *Water Absorbent*—Anhydrous magnesium perchlorate (Mg(ClO₄)₂) of approximately 2.38 to 0.35 mm size.

NOTE 2—Trade names of the reagents are Anhydrone and Dehydrite.

7.5.2 *Carbon Dioxide Absorbent*—If a solid reagent is used, it shall be sodium or potassium hydroxide (NaOH or KOH) impregnated in an inert carrier of approximately 2.38 to 0.84 mm size. Use of soda lime in place of the above or in admixture with them is permissible (Note 3). If a solution is used, it shall be 30 weight % potassium hydroxide (KOH).

NOTE 3—Trade names of the sodium and potassium hydroxide permissible solid carbon dioxide absorbing reagents are: Ascarite II, Caroxite, and Mikohbite. If soda lime is used in admixture with any of the foregoing, it should not exceed 30 weight % of the total reagent. In using Ascarite it may be necessary to add a few drops of water to this reagent to assure complete absorption of carbon dioxide.

8. Preparation of Apparatus

8.1 *Combustion Tube Packing*—To ensure complete oxidation of combustion products and complete removal of interfering substances such as oxides of sulfur, the combustion tube shall be packed with cupric oxide and lead chromate or silver. The arrangement and lengths of the tube fillings and separating plugs shall be as shown in Fig. 1. It is recommended that the tube be placed in a vertical position (constricted end downward) for packing. When filling the tube with lead chromate, any residual reagent adhering to the walls of the empty portion of the tube must be removed. When silver is used as a tube filling, the required length of filling may be prepared conveniently from three or four strips of silver gauze 150 to 200-mm long, by rolling each strip into a cylindrical plug and inserting the strips end-to-end in the tube.

NOTE 4—Longer furnaces with appropriate lengths of tube packing will be satisfactory.

8.2 *Absorption Train:*

8.2.1 *Water Absorber*—A container that is filled with a permissible solid desiccant by adding the required amount in small portions and settling each portion by gentle tapping between additions. Place a glass wool plug between the reagent and the absorber outlet to prevent loss of reagent dust.

8.2.2 *Carbon Dioxide Absorber*—If a solid reagent is used for the retention of carbon dioxide, fill the absorber as described in 8.2.1. Place in the outlet section of the container a layer or cap of desiccant that is the same as that used in the water absorber. This layer shall have a bulk volume not less than one fourth nor more than one third of the combined volume of both reagents. If a liquid absorbent is used, fill the inner tube of the Vanier bulb with the same desiccant used in the water absorber. Place a glass wool plug in the outlet section of the container to prevent loss of reagent dust.

8.2.3 *Guard Tube*, packed with equal volumes of the water absorbent and a solid carbon dioxide absorbent.

8.2.4 *Connections*—To ensure a closed system from the supply tank of oxygen to the guard tube at the end of the absorption train, it is recommended that all connections by glass-to-glass or glass-to-quartz butt joints be sealed with short lengths of flexible tubing. The connection between the purification train and the combustion tube may be made by means of a rubber stopper or other suitable device. All connections shall be gas tight. No lubricant shall be used for making tubing connections in the absorption train.

8.3 *Conditioning of Apparatus:*

8.3.1 *Newly Packed Combustion Tube*—Burn a sample of coal or coke as described in 9.4 except that the products of combustion need not be fixed in a weighed absorption train.

8.3.2 *Used Combustion Tube*—After any extended shut down, one day or more, test the combustion train under procedure conditions, but without burning a sample, for 40 min with weighed absorption bulbs connected. A variation of not more than 0.5 mg of either bulb shall be considered satisfactory.

NOTE 5—If the blank tests for flow indicate interfering impurities in the oxygen supply by consistent weight-gain in the absorption bulbs, eliminate these impurities by using a preheater furnace and tube, filled with cupric oxide. Operate this preheater furnace at $850 \pm 20^\circ\text{C}$ and insert in series between the supply tank of oxygen and the purification train.

8.3.3 *Absorption Train*—Condition freshly packed absorber and guard tubes by burning a sample of coal or coke as described in 9.4 except that tube weights need not be determined.

8.3.4 *Standard Checks* shall be made frequently, particularly when intermittent use of the combustion train is common or when any changes have been made in the system. A standard substance of certified analysis, such as benzoic acid or sucrose as furnished by the National Bureau of Standards shall be burned as described in Section 9. A variation from the theoretical of not more than 0.07 % for hydrogen nor more than 0.30 % for carbon shall be considered satisfactory.

9. Procedure

9.1 After the combustion tube and absorbers have been conditioned as prescribed in Section 8, conduct the test as follows:

9.2 *Absorption Train*—Bring the absorption tubes to room

⁶ *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.



temperature near the balance for 15 to 20 min, vent momentarily to the atmosphere, wipe with a chamois or lint-free cloth in the areas where handled, and weigh to the nearest 0.1 mg.

9.3 *Sample*—Weigh approximately 0.2 g (weighed to the nearest 0.1 mg) of air-dry sample ground to pass a No. 60 (250- μ m) sieve into a combustion boat.

9.4 *Sample Analysis*—With furnace (6.3.2 and 6.3.3) at specified temperatures and positioned as shown in Fig. 1, perform the following operations in rapid succession in the order listed:

9.4.1 If a conventional type of sample heating furnace is used for heating (6.3.1), place it so that its left-hand edge is about 100 mm from the oxygen inlet end of the combustion tube.

9.4.2 Attach the weighed absorption train to the tube:

9.4.3 Push the sample boat into the tube to a point within approximately 20 mm from plug P_1 ;

9.4.4 Close the tube and adjust the oxygen flow to a rate of 50 to 100 mL/min (standard temperature and pressure) being the same as used in blanking (see 8.3.2).

9.4.5 Apply full heat to heating section No. 1 to bring it to an operating temperature of 850 to 900°C as rapidly as possible. Move the heater slowly toward the boat so that it completely covers the boat and is brought into contact with heating (6.3.2) in a period of 10 to 20 min (Note 6). Allow it to remain in this position for an additional 5 to 10 min and then shut off the heat and return the sample heater to its original position. Continue to the flow of oxygen through the tube for 10 min (Note 7), close the absorbers under a positive pressure of oxygen, and detach them from the train. Remove the absorbers to the vicinity of the balance, allow them to cool to room temperature for 15 to 20 min, vent momentarily to atmosphere, wipe them with a chamois or lint-free cloth in the areas handled, and finally weigh them to the nearest 0.1 mg. While the absorbers are cooling, it is recommended that the ash remaining in the combustion boat be examined for traces of unburned carbon which, if present, will nullify the determination.

NOTE 6—Some variation in operating technique and heater manipulation may be permitted here at the discretion of the analyst, provided that it is conducive to a gradual and controlled release of volatile matter. Conditions that lead to visible burning (flame combustion) of the sample shall be avoided.

NOTE 7—Since water may condense in the cooler outlet end of the combustion tube or in the inlet arm of the water absorber, the use of an external or internal heat conducting device (a metal heat bridge) is recommended to prevent such condensation or promote reevaporation during this flushing period.

10. Calculation

10.1 Calculate the percentage of carbon (Note 8) in the analysis sample as follows:

$$\text{Carbon, \%} = (A \times 27.289)/B \quad (1)$$

where:

A = increase in weight of CO₂ absorption bulb, g, and

B = grams of sample used.

NOTE 8—It is recognized that formation of oxides of nitrogen during the combustion procedure may lead to slightly high results for carbon. However, extensive study of this effect by five laboratories led to the conclusion that error so incurred would not be significant in commercial application. In certain research applications, where accuracy of a higher order is required, means of removing oxides of nitrogen prior to water and carbon dioxide absorption should be included.

10.2 *Hydrogen*—Calculate the percentage of hydrogen in the analysis sample (Note 9) as follows:

$$\text{Hydrogen, \%} = (C \times 11.19)/B \quad (2)$$

where:

B = grams of sample used, and

C = increase of weight of water absorption bulb, g.

NOTE 9—The water absorbed in the water absorption tube includes not only water formed as a product of combustion, but also free water (moisture) in the sample and water of hydration of any clay minerals present.

11. Report

11.1 The results of the carbon and hydrogen analysis may be reported on any of a number of bases, differing from each other in the manner by which moisture is treated.

11.2 A separate portion of the analysis sample shall be analyzed for moisture content in accordance with Test Method D 3173, in order to allow calculation of the as-analyzed data to other bases.

11.3 Procedures for converting the values obtained on the analysis sample to other bases are described in Methods D 3176 and D 3180.

12. Precision and Bias

12.1 The permissible differences between two or more determinations shall not exceed the following values:

	Repeatability, %	Reproducibility, %
Carbon	0.3	...
Hydrogen	0.07	...

12.2 The bias of this test method cannot be determined at this time.

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