



Designation: **D 6316 – 9900**

Standard Test Method for Determination of Total, Combustible and Carbonate Carbon in Solid Residues from Coal and Coke¹

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1. Scope

1.1 This test method covers the determination of total, combustible, and carbonate carbon remaining in the solid byproducts of combustion from boiler furnaces and similar reactors, including ash, flyash, char, slag, and similar materials.

1.2 This test method is intended for the use of industry to determine the performance of boiler furnaces and similar combustion reactors and aid in determining the quality of the solid residue from combustion.

1.3 This test method comprises the use of any of several methods to determine total carbon content combined with any of several methods to determine carbonate carbon, and the calculation, by difference, of the combustible carbon remaining in a sample.

1.4 Alternatively, this test method applies to the determination of total carbon remaining in a material after acidification with strong acid to evolve carbonate carbon. In this case, the combustible carbon is the total carbon measured in the sample after acidification.

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

1.6 *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 to determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 ASTM Standards:

D 121 Terminology of Coal and Coke^{2,3}

¹ This test method is under the jurisdiction of ASTM Committee D-5 on Coal and Coke and is the direct responsibility of Subcommittee D05.29 on Major Elements in Ash and Trace Elements of Coal.

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D 513 Test Methods for Total and Dissolved Carbon Dioxide in Water⁴

D 1756 Test Method for Determination as Carbon Dioxide of Carbonate Carbon in Coal³

D 3178 Test Methods for Carbon and Hydrogen in the Analysis Sample of Coal and Coke³

D 5373 Test Methods for Instrumental Determination of Carbon, Hydrogen, and Nitrogen in Laboratory Samples of Coal and Coke³

E 691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method⁵

3. Terminology

3.1 Definitions:

3.1.1 *carbonate carbon, n* —the carbon content present in the solid products derived from the combustion or reaction of coal, coal byproducts, or coke as carbonates and which is non-combustible in standard industry practice.

3.1.2 *combustible carbon, n* —carbon content remaining in the solid products derived from the combustion or reaction of coal, coal byproducts, or coke, exclusive of carbonate in any form.

3.1.3 *total carbon, n* —carbon content remaining in the solid products derived from the combustion or reaction of coal, coal byproducts, or coke, inclusive of carbonate in any form.

4. Summary of Test Method

4.1 *Total Carbon*—The determination of total carbon is made by the oxidative thermal decomposition of a weighed quantity of sample in a closed system and, after complete oxidation and purification of the resulting gaseous products, measurement of the carbon dioxide produced by one of several methods.

4.1.1 *Absorptive Determination of Total Carbon*—The evolved carbon dioxide is fixed on an absorption train and is measured quantitatively by weighing the absorbent (see Test Methods D 3178).

4.1.2 *Instrumental Determination of Total Carbon*—The carbon dioxide is measured quantitatively by an electronic detection system calibrated against an appropriate reference standard (see Test Methods D 5373).

4.2 *Carbonate Carbon*—The determination of carbonate carbon is made by decomposing a weighed quantity of the sample with a dilute mineral acid, and after the purification of the evolved gases, measuring quantitatively the evolved carbon dioxide.

4.2.1 *Absorptive Determination of Carbonate Carbon*—The carbon dioxide is liberated by acidification and heating. The evolved gases are passed through a purification train and the CO₂ is fixed as Na₂CO₃ on a preweighed absorption unit and is measured gravimetrically (see Test Method D 1756).

4.2.2 *Coulometric Determination of Carbonate Carbon*—The carbon dioxide is liberated by acidification and heating. The evolved gas is swept through a scrubber and into an absorption cell where it is coulometrically titrated (see Part B of Test Methods D 513).

4.2.3 *Instrumental Determination of Carbonate Carbon*—The carbon dioxide is liberated by acidification and heating. The evolved gases are purified and measured quantitatively by an electronic detection system against an appropriate reference stream. This test method resembles that for the instrumental determination of total carbon, with the provision for sample combustion replaced by a provision for acidification. In practice, this test method uses an adaptation to instruments designed to measure total carbon content.

4.3 *Combustible Carbon by Prior Acidification*—The determination of combustible carbon is made directly by first acidifying and heating to dryness a weighed sample. All carbonate carbon present is evolved as carbon dioxide. The dried sample is then analyzed for total carbon content as above. No determination of carbonate carbon is made and the carbon content measured as total carbon is the combustible carbon.

5. Significance and Use

5.1 The combustible carbon content of solid residues is used to calculate efficiency of fuel combustion in boiler furnaces and similar combustors.

5.2 Combustible carbon values are also used to determine the residual fuel value of incompletely combusted coal and coke in fluidized bed furnaces and other reactors which consume carbonaceous fuels.

5.3 The combustible carbon content of flyash is an important parameter in the use of flyash as a cement additive.

6. Interferences

6.1 The interferences for the determination of total carbon content are those specified in the referenced standard methods, Test Methods D 3178 and Test Methods D 5373, with the following added stipulation.

² Other related standards include ANSI/ASME Standard, PTC 38-1980 Determining the Concentration of Particulate Matter in A Gas Stream and US EPA Standard CFR 60 Appendix A, Method 17, p. 120:1235.

³ *Annual Book of ASTM Standards*, Vol 05.056.

⁴ *Annual Book of ASTM Standards*, Vol 11.01.

⁵ *Annual Book of ASTM Standards*, Vol 14.02.

6.1.1 The temperature and conditions of combustion that ensure complete conversion of a residue sample's total carbon content to carbon dioxide may be different than those required for conversion in coal samples. It is absolutely imperative that the instrumental conditions used will ensure complete conversion of mineral carbonate in any amount or form.

6.2 The interferences for the determination of carbonate carbon are those specified in the referenced methods, Test Method D 1756 and Part B of Test Methods D 513 with the following stipulation

6.2.1 Some coal combustion residues contain significant amounts of reactive elements such as CaO which will absorb carbon dioxide on exposure to open air and form mineral carbonates. This will influence the calculated amount of combustible carbon in the sample only if there was carbon dioxide chemisorption from the air between the time of the carbonate determination and the total carbon determination. Therefore, it is necessary that the sample be protected from air exposure.

6.3 The mineral acid and temperature required for prior acidification of the analytical sample shall not interfere with the amount of combustible carbon present in the sample or the analytical determination of carbon. The use of oxidizing acids such as concentrated nitric acid may oxidize a portion of the combustible carbon. Other acids such as hydrochloric acid may be incompatible with the reagents used to purify the gas stream in the instrumental determination of carbon. Sulfuric acid has a relatively high boiling point and is difficult to remove from the sample by drying. A solution of 10 % nitric acid is suggested for use in this procedure.

7. Apparatus

7.1 The apparatus used is specified in the respective referenced method.

7.2 *Total Carbon Content:*

7.2.1 *Absorptive Determination of Total Carbon*—The apparatus consists of an oxygen-purifying train, combustion unit, and absorption train of the type and configuration specified in Test Methods D 3178.

7.2.2 *Instrumental Determination of Total Carbon*—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. However, the apparatus shall be capable of completely converting the carbon content to carbon dioxide, and the detection system shall determine the carbon dioxide individually and without interference.

7.3 *Carbonate Carbon Content:*

7.3.1 *Absorptive Determination of Carbonate Carbon*—The apparatus shall consist of an air purifying train, reaction unit, and absorption unit of the type and configuration specified in Test Method D 1756.

7.3.2 *Coulometric Determination of Carbonate Carbon*—The apparatus shall consist of an evolution unit, a carbon dioxide coulometer, scrubber, and pH meter of the type and configuration specified in Part B of Test Methods D 513.

7.3.3 *Instrumental Determination of Carbonate Carbon*—The apparatus shall consist of a heated acidification unit that is installed by bypassing the combustion system in a device designed for the determination of total carbon content. The gas-purifying system of such instrument shall be capable of completely removing the water content and acid gases produced as byproducts of the carbon dioxide evolution. The detection system shall measure the evolved carbon dioxide as an individual species and without interference.

7.4 *Combustible Carbon by Prior Acidification*—The crucibles used for this method must be free of carbonate, inert to the mineral acid used, and compatible with the instrument used for measuring total carbon. The acidified sample is heated to dryness using a laboratory hotplate capable of maintaining the fine temperature control required to dry the sample without material loss of sample as a result of spattering or boilover. The instrument used shall meet the requirements of Test Methods D 5373 and be capable of removing the additional acid gases that result from the mineral acid used for evolving the carbon dioxide before determining carbon content.

8. Reagents

8.1 *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.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.

9. Standards

9.1 There are currently no standard reference materials of coal or coke residues that are certified for combustible carbon or carbonate carbon content. However, other types of standard materials can be used for both method validation and instrument calibration. These include:

9.1.1 *Buffalo River Sediment* (NIST 2704)—Total carbon = 3.348 ± 0.016 %.

9.1.2 *Carbonate Primary Standard Grade*—For example, CaCO₃ total carbonate carbon = 12.00 %.

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., Pool, Dorset, U.K., and the *United States Pharmacopoeia and National Formulary*, U.S. Pharmacopoeial Convention, Inc. (USPC), Rockville, MD.

9.1.3 *Coal*—Bituminous (NIST 1632b) total carbon = 76.86 ± 0.26 %.

9.1.4 *EDTA Primary Standard Grade* —Total carbon = 41.07 %.

10. Sample Preparation

10.1 If moist or wet, the combustion residue sample⁷ will be predried at $107 \pm 3^\circ\text{C}$. Drying time should be the minimum required to ensure complete dryness of the sample to minimize absorption of carbon dioxide from the air (see 6.2.1).

10.2 The method of sample preparation used is specified in the respective referenced method.

10.3 Samples in excess of 50 g should be divided by riffing to ensure a representative analysis sample. Samples of 50 g or less should be prepared in their entirety.

10.4 The analysis sample shall initially be prepared to pass through a 250- μm (# 60 U.S. standard) sieve. If required by the characteristics of the instrument system or analytical precision of the resulting data or both, the analysis sample should be ground to pass through a 75- μm (# 200 U.S. standard) sieve.⁸

11. Instrument Preparation and Verification

11.1 The preparation of equipment and instruments is specified in the respective referenced methods and the manufacturer's instructions.

11.2 The proper functioning of the equipment and the operational parameters should be verified by analyzing blanks and standard materials that contain carbonate carbon and combustible carbon.

11.2.1 The proper combustion temperature and conditions necessary to convert the carbonate carbon to carbon dioxide may be determined by measuring the carbon content of a carbonate standard. Measured carbon values of less than the certified value indicate incomplete conversion of carbonates.

11.2.2 Combustion accelerants such as magnesium powder, thermite (aluminum powder and iron oxide), and tin powder can be used to ensure the total conversion of carbonates to carbon dioxide by significantly raising the reaction temperature during combustion.

12. Procedure

12.1 Calibrate the instruments using the methods described in the referenced methods.

12.1.1 The calibration range for these measurements should be in the range of expected carbon values for the analytical samples.

12.2 Determine the total carbon content of the sample material by any of the referenced methods.

12.3 Determine the carbonate carbon content of the sample material by any of the referenced methods, or

12.4 *Combustible Carbon by Prior Acidification*—Tare a crucible appropriate to the carbon analyzer used⁹ to the nearest 0.1 mg. Weigh a 100- to 500-mg portion of the analysis sample to the nearest 0.1 mg. Add a sufficient amount of 10 % HNO_3 dropwise to wet the sample. Allow the sample to stand for several minutes. Dry the sample completely on a hotplate with low heat ($<150^\circ\text{C}$), taking care that the sample does not spatter. Allow the sample and crucible to cool. Proceed to analyze the sample for total carbon with the method prescribed in the appropriate standard method.

13. Calculation

13.1 For samples in which the total carbon and carbonate carbon have been determined, calculate the combustible carbon as follows:

$$\text{combustible carbon} = \text{total carbon} - \text{carbonate carbon}$$

13.2 For combustible carbon by prior acidification, report the combustible carbon content measured as the total carbon content.

13.3 For samples in which the total carbon and combustible carbon have been determined, calculate the carbonate carbon as follows:

$$\text{carbonate carbon} = \text{total carbon} - \text{combustible carbon}$$

14. Precision and Bias¹⁰

14.1 *Precision*—The precision of this test method; for the determination of carbon forms in solid residues from coal and coke are shown in Table 1. The precision characterized by the repeatability (S_r, r) and reproductibility (S_R, R, R) has been determined for the following materials to be:

⁷ *Sample Collection*—Analysis samples are intended to originate by collection according to appropriate standard industry practice suitable for the intended purpose. In the case of combustion boilers, it may be necessary to collect bottom ash, fly ash, and slag samples for analysis. The type and location of sample collection therefore depends on the ultimate use of the data and the current industry practice. In the special case of calculating combustor efficiency, the standard industry sampling practice is prescribed in ANSI ASME PTC 38-1980 or EPA CRF 60 Appendix A, Method 17, or both.

⁸ Thorough mixing of the sample must be maintained throughout the preparation stages to prevent separation between the high and low carbon fractions.

⁹ Because of the necessity of acidifying and drying the sample in the same container used for carbon determination, this method may be unsuitable for some carbon-measuring instruments.

¹⁰ An interlaboratory study, designed consistent with ASTM Practice E 691, was conducted in 1997–1998. Eight laboratories participated. The details of the study and supporting data are given in ASTM Research Report RR: D05–1023 filed at ASTM Headquarters.

TABLE 1 Concentration Ranges and Limits for Repeatability and Reproducibility for Carbon Forms in Solid Residues from Coal and Coke

Parameter	Range	Repeatability Limit (<i>r</i>)	Reproducibility Limit (<i>R</i>)
Total carbon	0.34–15.12 %	$0.14 + 0.04 \bar{x}^A$	$0.07 + 0.12 \bar{x}^A$
Combustible carbon	0.14–14.00 %	$0.25 + 0.06 \bar{x}^A$	$0.82 + 0.14 \bar{x}^A$
Carbonate carbon	0.01–2.75	$0.01 + 0.08 \bar{x}^A$	$0.04 + 0.13 \bar{x}^A$

^AWhere \bar{x} is the average of two single test results.

Total Carbon

Material	Average	S_r	S_R	<i>r</i>	<i>R</i>
SHPS	-0.34	0.023 11	0.036 32	0.0647	0.1017
WAL-4	-0.37	0.064 00	0.083 11	0.1792	0.2327
Canspecs-5	-1.59	0.091 71	0.120 96	0.2568	0.3387
BRS	-3.36	0.074 46	0.132 50	0.2085	0.3710
Canspecs-4	-4.97	0.124 50	0.181 54	0.3486	0.5083
Canspecs-3	-7.66	0.156 46	0.284 68	0.4381	0.7971
Canspecs-2	-9.46	0.301 75	0.461 04	0.8449	1.2909
FBC-9	14.10	0.172 39	0.897 43	0.4827	2.5128
Canspecs-1	15.12	0.293 82	0.436 89	0.8227	1.2233

Combustible Carbon

Material	Average	S_r	S_R	<i>r</i>	<i>R</i>
SHPS	-0.13	0.014 75	0.032 75	0.0413	0.0917
WAL-4	-0.42	0.054 79	0.102 04	0.1534	0.2857
Canspecs-5	-1.48	0.121 75	0.261 68	0.3409	0.7327
BRS	-2.27	0.147 07	0.229 29	0.4118	0.6420
Canspecs-4	-4.35	0.241 46	0.881 46	0.6761	0.4681
Canspecs-3	-6.85	0.293 71	1.364 18	0.8224	3.8197
Canspecs-2	-8.27	0.341 86	2.037 46	0.9572	5.7049
WAL-1	-8.42	0.950 18	1.761 07	2.6605	4.9310
FBC-9	11.16	0.457 75	1.110 96	1.2817	3.1107
Canspecs-1	14.51	0.257 21	0.375 82	0.7202	1.0523

Carbonate Carbon

Material	Average	S_r	S_R	<i>r</i>	<i>R</i>
WAL-4	0.008	0.003 34	0.003 49	0.009 34	0.009 78
Canspecs-5	0.025	0.003 44	0.016 61	0.009 64	0.046 51
Canspecs-4	0.038	0.005 49	0.007 03	0.015 37	0.019 67
WAL-1	0.049	0.006 39	0.015 32	0.017 88	0.042 90
Canspecs-2	0.056	0.008 89	0.018 81	0.024 90	0.052 68
Canspecs-3	0.057	0.005 92	0.014 35	0.016 59	0.040 19
Canspecs-1	0.097	0.007 51	0.014 03	0.021 03	0.039 27
SHPS	0.27	0.015 89	0.024 15	0.044 50	0.067 61
BRS	0.82	0.023 62	0.093 20	0.066 14	0.260 96
FBC-9	2.75	0.087 27	0.130 83	0.244 35	0.366 31

is described in Table A1.1.

14.1.1 *Repeatability Limit (r)*—The value below which the difference in absolute value difference between two test results 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 %.

The repeatability limits for this method are (see footnote 10):

— Total carbon	$0.14 + 0.04 \bar{x}$
— Combustible carbon	$0.25 + 0.06 \bar{x}$
— Carbonate carbon	$0.01 + 0.08 \bar{x}$

where \bar{x} is the average of two single test results.

14.1.2 *Reproducibility Limit (R)*—The value below which the difference in absolute value difference between replicate determinations, two test results, carried out in different laboratories using representative samples prepared from the same gross sample, samples, taken at random from a single sample prepared from the same bulk sample after the last stage quantity of reduction, material that is as nearly homogeneous as possible, may be expected to occur with a probability of approximately 95 %.

The reproducibility limits for this method are (see footnote 10):

— Total carbon	$0.07 + 0.12 \bar{x}$
— Combustible carbon	$0.82 + 0.14 \bar{x}$
— Carbonate carbon	$0.04 + 0.13 \bar{x}$

where \bar{x} is the average of two single between-laboratory results.

14.2 *Bias*—Certified standard reference materials are not available for the determination of bias by this test method.

14.3 An interlaboratory study, consistent with Practice E 691, was conducted in 1997–98. Eight labs participated.¹¹

15. Keywords

15.1 ash; carbon; carbon dioxide; carbonate; char; coal; coke; coulometric; combustible; fly ash; slag; solid residues

¹¹ This test method is under the jurisdiction of ASTM Committee D-5 on Coal and Coke and is the direct responsibility of Subcommittee D05.29 on Major Elements in Ash and Trace Elements of Coal.

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ANNEX

(Mandatory Information)

A1. PRECISION STATISTICS

A1.1 The precision of this test method, characterized by repeatability (S_r , r) and reproducibility (S_R , R) has been determined for the following materials as listed in Table A1.1.

A1.2 *Repeatability Standard Deviation (S_r)*—The standard deviation of test results obtained under repeatability conditions.

A1.3 *Reproducibility Standard Deviation (S_R)*—The standard deviation of test results obtained under reproducibility conditions.

**TABLE A1.1 Repeatability (S_r , r) and Reproducibility (S_R , R)
Parameters Used for Calculation of Precision Statement**

Material	Average	Total Carbon		r	R
		S_r	S_R		
SHPS	0.34	0.023 11	0.036 32	0.0647	0.1017
WAL 4	0.37	0.064 00	0.083 11	0.1792	0.2327
Sample 5	1.59	0.091 71	0.120 96	0.2568	0.3387
BRS	3.36	0.074 46	0.132 50	0.2085	0.3710
Sample 4	4.97	0.124 50	0.181 54	0.3486	0.5083
Sample 3	7.66	0.156 46	0.284 68	0.4381	0.7971
Sample 2	9.46	0.301 75	0.461 04	0.8449	1.2909
Sample 9	14.10	0.172 39	0.897 43	0.4827	2.5128
Sample 1	15.12	0.293 82	0.436 89	0.8227	1.2233
Material	Average	Combustible Carbon		r	R
		S_r	S_R		
SHPS	0.13	0.014 75	0.032 75	0.0413	0.0917
WAL 4	0.42	0.054 79	0.102 04	0.1534	0.2857
Sample 5	1.48	0.121 75	0.261 68	0.3409	0.7327
BRS	2.27	0.147 07	0.229 29	0.4118	0.6420
Sample 4	4.35	0.241 46	0.881 46	0.6761	2.4681
Sample 3	6.85	0.293 71	1.364 18	0.8224	3.8197
Sample 2	8.27	0.341 86	2.037 46	0.9572	5.7049
WAL 1	8.42	0.950 18	1.761 07	2.6605	4.9310
Sample 9	11.16	0.457 75	1.110 96	1.2817	3.1107
Sample 1	14.51	0.257 21	0.375 82	0.7202	1.0523
Material	Average	Carbonate Carbon		r	R
		S_r	S_R		
WAL 4	0.008	0.003 34	0.003 49	0.009 34	0.009 78
Sample 5	0.025	0.003 44	0.016 61	0.009 64	0.046 51
Sample 4	0.038	0.005 49	0.007 03	0.015 37	0.019 67
WAL 1	0.049	0.006 39	0.015 32	0.017 88	0.042 90
Sample 2	0.056	0.008 89	0.018 81	0.024 90	0.052 68
Sample 3	0.057	0.059 25	0.014 35	0.165 90	0.040 19
Sample 1	0.097	0.007 51	0.014 03	0.021 03	0.039 27
SHPS	0.27	0.015 89	0.024 15	0.044 50	0.067 61
BRS	0.82	0.023 62	0.093 20	0.066 14	0.260 96
Sample 9	2.75	0.087 27	0.130 83	0.244 35	0.366 31

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