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Standard Test Method for Gross Calorific Value of Coal and Coke by the Adiabatic Bomb Calorimeter[1]

This standard is issued under the fixed designation D 2015; 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.

This standard has been approved for use by agencies of the Department of Defense. Consult the DoD Index of Specifications and Standards for the specific year of issue which has been adopted by the Department of Defense.

1. Scope

1.1 This test method covers the determination of the gross calorific value of coal and coke by the adiabatic bomb calorimeter.

1.2 The values stated in SI units and British thermal units are to be regarded as the standard. The values given in parentheses are for information only.

1.3 *This standard does not purport to address 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.* For specific hazard statements see Section 8.

1.4 All accountability and quality control aspects of Guide D 4621 apply to this standard.

2. Referenced Documents

2.1 *ASTM Standards:*

D 121 Terminology of Coal and Coke[2]

D 346 Practice for Collection and Preparation of Coke Samples for Laboratory Analysis[2]

D 1193 Specification for Reagent Water[3]

D 2013 Method of Preparing Coal Samples for Analysis[2]

D 3173 Test Method for Moisture in the Analysis Sample of Coal and Coke[2]

D 3177 Test Methods for Total Sulfur in the Analysis Sample of Coal and Coke[2]

D 3180 Practice for Calculating Coal and Coke Analyses from As-Determined to Different Bases[2]

D 4239 Test Method for Sulfur in the Analysis Sample of Coal and Coke Using High Temperature Tube Furnace Combustion Methods[2]

D 4621 Guide for Accountability and Quality Control in the Coal Analysis Laboratory[2]

E 1 Specification for ASTM Thermometers[4]

E 144 Practice for Safe Use of Oxygen Combustion Bombs[5]

3. Terminology

3.1 *Definitions:*

3.1.1 *calorific value, n*—the heat produced by combustion of a unit quantity of a substance under specified conditions.

3.1.1.1 *Discussion*—It is expressed in this test method in British thermal units per pound (Btu/lb). Calorific value may also be expressed in calories per gram (cal/g) or in the International System of Units (SI), joules per gram (J/g), when required. The unit equivalents are given in Table 1.

3.1.2 *gross calorific value (gross heat of combustion at constant volume) Q_v (gross)*—see Terminology D 121.

3.1.3 *net calorific value (net heat of combustion at constant pressure) Q_p (net)*—see Terminology D 121.

3.1.4 *calorimeter—as used in this test method,* consists of the bomb and its contents, the calorimeter vessel (bucket) with stirrer, the water in which the bomb is immersed, and the portions of the thermometer and the ignition leads within the calorimeter vessel.

3.2 *Descriptions of Terms Specific to This Standard:*

3.2.1 *corrected temperature rise*—the temperature change of the calorimeter caused by the process that occurs inside the bomb, that is, the observed temperature change corrected for various effects as noted in 10.4.1.

NOTE 1—Temperature is measured in either degrees Celsius or degrees Fahrenheit. Thermometer corrections should be applied. Temperatures may be recorded in ohms or other arbitrary units instead of degrees. Consistent units must be used in standardization and the actual calorific value determination. If arbitrary units other than degrees Celsius or Fahrenheit are used, the temperature interval over which all tests are made, must not vary so much that an error greater than 0.001°C would be caused.

3.2.2 *energy equivalent, heat capacity, or water equivalent*—the energy required to raise the temperature of the calorimeter one arbitrary unit. This is the quantity that, when multiplied by the corrected temperature rise, then adjusted for extraneous heat effects, and divided by the mass of the sample, gives the gross calorific value.

NOTE 2—Energy units for quantities listed throughout this test method are such that the number of energy units per gram of sample corresponds exactly to the number of British thermal units per pound of sample. For brevity these are referred to as British thermal units. The actual energies are smaller than those stated by the ratio of the number of pounds per gram (1/453.59). The energy equivalent of the calorimeter has the units (British thermal units per pound) times (grams per degree). Conversion to other units is discussed in Appendix X1.2. Time is expressed in minutes. Mass is expressed in grams.

4. Summary of Test Method

4.1 Calorific value is determined in this test method by

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[1] This test method is under the jurisdiction of ASTM Committee D-5 on Coal and Coke and is the direct responsibility of Subcommittee D05.21 on Methods of Analysis.

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[2] *Annual Book of ASTM Standards,* Vol 05.05.

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

[4] *Annual Book of ASTM Standards,* Vol 14.03.

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

TABLE 1 Calorific Value

1 Btu = 1055.06 J	1 Btu/lb = 2.326 J/g
1 Calorie[A] = 4.1868 J	1.8 Btu/lb = 1.0 cal/g

[A] International tables calorie.

burning a weighed sample, in oxygen, in a calibrated adiabatic bomb calorimeter under controlled conditions. The calorimeter is standardized by burning benzoic acid. The calorific value of the sample is computed from temperature observations made before, during and after combustion, making proper allowances for heat contributed by other processes, and for thermometer and thermochemical corrections.

NOTE 3—Oxidation after sampling of susceptible low-rank coal or lignite may result in a reduction of calorific value. Unnecessary exposure of the sample to air from the time of sampling or delay in analysis shall be avoided.

5. Significance and Use

5.1 The gross calorific value is used to compute the total calorific content of the quantity of coal represented by the sample for payment purposes, provided the buyer and the seller mutually agree upon this.

5.2 The gross calorific value is used in computing the calorific value versus sulfur content to determine if the coal meets regulatory requirements for industrial fuels.

5.3 The gross calorific value may be used for evaluating the effectiveness of beneficiation processes, or for research purposes.

6. Apparatus and Facilities

6.1 *Test Space,* shall be a room or area free from drafts and that can be kept at a reasonably uniform temperature for the time required for the determination. The apparatus should be shielded from direct sunlight and radiation from other heat sources. Thermostatic control of room temperature and controlled relative humidity are desirable.

6.2 *Combustion Bomb,* shall be constructed of materials that are not affected by the combustion process or products sufficiently to introduce measurable heat input or alteration of end products. The bomb must be designed so that all liquid combustion products can be completely recovered by washing the inner surfaces. There must be no gas leakage during a test. The bomb must be capable of withstanding a hydrostatic pressure test of 20 MPa (3000 psig) at room temperature without stressing any part beyond its elastic limit.

6.3 *Balance,* shall be a laboratory balance having capability to weigh the sample to the nearest 0.0001 g. The balance should be checked periodically to determine is accuracy.

6.4 *Calorimeter Vessel,* shall be made of metal with a tarnish-resistant coating, and with all outer surfaces highly polished. Its size shall be such that the bomb will be completely immersed in water when the calorimeter is assembled. It shall have a device for stirring the water thoroughly and at a uniform rate, but with minimum heat input. Continuous stirring for 10 min shall not raise the calorimeter temperature more than 0.01°C (0.02°F) starting with identical temperatures in the calorimeter, room, and jacket. The immersed portion of the stirrer shall be coupled to the outside through a material of low-heat conductivity.

6.5 *Jacket,* shall be a double-walled, water-filled jacket fully enclosing the calorimeter. The sides, top, and bottom of the calorimeter vessel shall be approximately 10 mm from the inner wall of the jacket to minimize convection currents. Mechanical supports for the calorimeter vessel shall provide as little thermal conduction as possible. The jacket shall have a device for stirring the water thoroughly and at a uniform rate with minimum heat input.

6.6 *Thermometers,* used to measure temperature in the calorimeter and jacket shall be any of the following types or combinations thereof:

6.6.1 *Liquid-in-Glass Thermometers,* conforming to the requirements for ASTM Thermometers 56C, 56F, 116C, or 117C as prescribed in Specification E 1. The thermometers shall be tested for accuracy against a known standard (preferably by the National Institute of Standards and Technology). For Thermometers 56C and 56F the calibration should be at intervals no larger than 2.0°C or 2.5°F over the entire graduated scale. The maximum difference in correction between any two test points shall be no more than 0.02°C or 0.05°F. For Thermometers 116C and 117C, the calibration should be at intervals no larger than 0.5°C over the entire calibrated range. The maximum difference in correction between any two test points shall not be more than 0.02°C.

6.6.2 *Beckman Differential Thermometer,* (glass enclosed scale, adjustable), having a range of approximately 6°C in 0.01°C subdivisions reading upward and conforming to the requirements for Thermometer 115C, as prescribed in Specification E 1, may be used. Each of these thermometers shall be tested for accuracy against a known standard (preferably by the National Institute of Standards and Technology) at intervals no larger than 1°C over the entire graduated scale. The maximum difference in the correction between any two test points shall not be more than 0.02°C.

6.6.3 *Other Thermometers,* of an accuracy equal to or better than 0.001°C, such as platinum resistance or linear thermistors are preferred if properly calibrated. A Wheatstone bridge and galvanometer capable of measuring resistance to 0.0001 Ω are necessary for use with 25-Ω platinum resistance thermometers.

6.7 *Thermometer Accessories*—A magnifier is required for reading liquid-in-glass thermometers to one tenth of the smallest scale division. This shall have a lens and holder designed so as to introduce no significant errors due to parallax.

6.8 *Sample Holder,* shall be an open crucible of platinum, quartz, or acceptable base-metal alloy. Base-metal alloy crucibles are acceptable, if after a few preliminary firings, the weight does not change significantly between tests.

6.9 *Ignition Wire,* shall be 100 mm of 0.16 mm diameter (No. 34 B & S gage) nickel-chromium (Chromel C) alloy or iron wire. Platinum or palladium wire, 0.10 mm diameter (No. 38 B & S gage), may be used, provided constant ignition energy is supplied. The length, or mass, of the ignition wire shall remain constant for all calibrations and calorific value determinations.

6.10 *Ignition Circuit,* for ignition purposes shall provide 6 to 16 V alternating or direct current to the ignition wire. An ammeter or pilot light is required in the circuit to indicate when current is flowing. A step-down transformer, connected to an alternating current lighting circuit or batteries, may be used.

6.11 *Buret,* used for the acid titration shall have 0.1-mL divisions.

6.12 *Automated Controller and Temperature Measuring Accessories,* may be used.

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.[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 *Reagent Water*—Reagent water conforming to Type II of Specification D 1193, shall be used for preparation of reagents and washing of the bomb interior.

7.3 *Benzoic Acid,* (C_6H_5COOH), shall be the National Institute of Standards and Technology benzoic acid. The crystals shall be pelleted before use. Commercially prepared pellets may be used provided they are made from National Institute of Standards and Technology benzoic acid. The value of heat of combustion of benzoic acid for use in the calibration calculations shall be in accordance with the value listed in the National Institute of Standards and Technology certificate issued with the standard.

7.4 *Methyl Orange, Methyl Red, or Methyl Purple Indicator,* may be used to titrate the acid formed during combustion. The indicator used shall be the same for both calibration and calorific value determinations.

7.5 *Oxygen,* shall be free of combustible matter. Only oxygen manufactured from liquid air, guaranteed to be greater than 99.5 % pure, should be used. Oxygen made by the electrolytic process may contain a small amount of hydrogen rendering it unfit without purification.

7.6 *Sodium Carbonate Standard Solution,* (Na_2CO_3), should be dried for 24 h at 105°C. Dissolve 20.9 g in water and dilute to 1 L. One millilitre of this solution is equivalent to 10.0 Btu in the nitric acid (HNO_3) titration.

8. Hazards

8.1 The following precautions are recommended for safe calorimeter operation. Additional precautions are given in Practice E 144. Also consult the calorimeter manufacturer's installation and operating manuals before using the calorimeter.

8.2 The mass of coal or coke sample and the pressure of the oxygen admitted to the bomb must not exceed the manufacturer's recommendations.

8.3 Inspect the bomb parts carefully after each use. Check the bomb for thread wear on any closures; if an inspection reveals any wear, replace the worn parts or return the bomb to the factory for testing or replacement of the defective parts. It is good practice to replace the o-rings and seals, inspect screw cap threads, and hydrostatically test the bomb as per the manufacturer's recommendations.

8.4 The oxygen supply cylinder should be equipped with an approved type of safety device, such as a reducing valve, in addition to the needle valve and pressure gage used in regulating the oxygen feed to the bomb. Valves, gages, and gaskets must meet industry safety code. Suitable reducing valves and adaptors for 3 to 4-MPa (300 to 500-psi) discharge pressure are obtainable from commercial sources of compressed gas equipment. The pressure gage shall be checked periodically for accuracy.

8.5 During ignition of a sample, the operator must not permit any portion of her or his body to extend over the calorimeter.

8.6 When combustion aids are employed, extreme caution must be exercised not to exceed the bomb manufacturer's recommendations and to avoid damage to the bomb. Do not fire loose fluffy material such as unpelleted benzoic acid, unless thoroughly mixed with the coal sample.

8.7 Do not fire the bomb if the bomb has been dropped or turned over after loading, or if there is evidence of a gas leak when the bomb is submerged in the calorimeter water.

8.8 For manually operated calorimeters, the ignition circuit switch shall be of the momentary double-contact type, normally open, except when held closed by the operator. The switch should be depressed only long enough to fire the charge.

9. Sample

9.1 The sample shall be the material pulverized to pass a 250-µm (No. 60) sieve, prepared in accordance with either Practice D 346 for coke, or Method D 2013 for coal.

9.2 A separate portion of the analysis sample should be analyzed simultaneously for moisture content in accordance with Method D 2013 and Test Method D 3173, so that calculation to other bases can be made.

9.3 Sulfur analysis shall be made in accordance with Test Methods D 3177.

10. Standardization

10.1 The calorimeter is standardized by combustion of benzoic acid.

10.2 Determine the energy equivalent as the average of a series of ten individual test runs. To be acceptable the relative standard deviation of the series shall be 0.15 % or less of the average energy equivalent (see Table 2). For this purpose, any individual test may be discarded if there is evidence of incomplete combustion. If, after considering the possibility of outliers utilizing criterion established in Practice E 178, this limit is not met, one should review operation of the calorimeter for any assignable cause which should be corrected before repeating the series.

10.3 *Procedure:*

10.3.1 Regulate the weights of the pellets of benzoic acid in each series to yield approximately the same temperature rise as that obtained with the coal tested in the same laboratory. The usual range of masses is 0.9 to 1.3 g. Weigh

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[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. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

TABLE 2 Standard Deviations for Calorimeter Standardization[A]

Standardization Number	Column A	Column B	Column C
	Energy Equivalent (Btu/lb) × (g/°C)	Code to 4400 (Column A − 4400)	(Column B)^2
1	4412	12	144
2	4407	7	49
3	4415	15	225
4	4408	8	64
5	4404	4	16
6	4406	6	36
7	4409	9	81
8	4410	10	100
9	4412	12	144
10	4409	9	81
SUM		92	940

Average = $\bar{X} = \Sigma X/10 = (92/10) + 4400 = 4409$

$$\text{Variance} = s^2 = \frac{\Sigma\text{ Column C} - [(\Sigma\text{ Column B})^2/n]}{n-1} = \frac{940 - [(92)^2/10]}{9} = 10.4$$

Standard deviation = $s = \sqrt{\text{variance}} = \sqrt{10.4} = 3.22$

[A] In this example the values of energy equivalent are typical for a calorimeter calibrated so that, if the energy equivalent is multiplied by the temperature rise in degrees Celsius per gram of sample, the calorific value of the sample will be obtained in British Thermal units per pound.

the pellet to the nearest 0.0001 g in the sample holder in which it is to be burned, and record the weight as the mass.

10.3.2 Rinse the bomb, invert to drain, and leave undried. Add 1.0 mL of water to the bomb prior to assembly for a determination.

10.3.3 Connect a measured length of ignition wire to the ignition terminals, with enough slack to allow the ignition wire to maintain contact with the sample.

10.3.4 Assemble the bomb and charge it with oxygen to a consistent pressure between 2 to 3 MPa (20 to 30 atm). This pressure must remain the same for each calibration and each calorific-value determination. Admit the oxygen slowly into the bomb so as not to blow powdered material from the sample holder. If the pressure exceeds the specified pressure, do not proceed with the combustion. Instead, detach the filling connection, exhaust the bomb in the usual manner, and discard the sample.

10.3.5 Fill the calorimeter vessel (bucket) with the measured (or weighed) quantity of water adjusted from 1.0 to 2.0°C (2.0 to 4.0°F) below room temperature, but not lower than 20°C (68°F). Use the same mass of water in each test weighed to +0.5 g. For 2000-mL calorimeters, the proper quantity can be obtained by use of a volumetric flask calibrated to deliver 2000 ± 0.5 mL. As the density of water varies with temperature, make suitable corrections if the water temperature varies from the temperature at which the flask was calibrated. Place the assembled bomb in the calorimeter vessel. Check that no oxygen bubbles are leaking from the bomb. Place the calorimeter vessel in the jacket; connect the electrodes; place the stirrers, thermometers, and cover in position. Start the stirrers and continue to operate them throughout the determination. Examine the thermometers for liquid separation and correct any separation before proceeding. The starting temperature should be within ±0.5°C (0.9°F) of that used in analysis of coal or coke samples.

Note 4—Check all liquid-in-glass thermometers at least daily for defects, for example, cracked glass, etc.

10.3.6 Allow 5 min for attainment of equilibrium. Adjust the jacket temperature to match the calorimeter temperature within 0.01°C (0.02°F) and maintain for 3 min. Use a magnifier when using ASTM Bomb Calorimeter Thermometers 56C or 56F, and estimate all readings (except those during the rapid-rise period) to the nearest 0.002°C or 0.005°F. Estimate ASTM Thermometers 115C, 116C, or 117C readings to 0.001°C, and 25 Ω resistance thermometer readings to the nearest 0.0001 Ω. Tap mercury thermometers (for instance, with a pencil) just before reading to avoid errors caused by mercury sticking to the walls of the capillary. Take calorimeter temperature readings at one-minute intervals until the same temperature, within one-tenth of the smallest thermometer subdivision, is observed in three successive readings. Record this "initial temperature", t_1, 20°C (68°F) or higher, to within one-tenth of the smallest thermometer subdivision and ignite the charge. Adjust the jacket temperature to match the calorimeter temperature during the period of rise; keep the two temperatures as nearly equal as possible during the rapid rise and adjust to within 0.01°C (0.02°F) when approaching the final equilibrium temperature. Take calorimeter temperature readings at 1-min intervals until the same temperature, within one-tenth of the smallest thermometer subdivision, is observed in three successive readings. Record this as the "final temperature", t_f.

10.3.7 Open the cover and remove the bomb. Release the pressure at a uniform rate, such that the operation will require not less than 1 min. Open the bomb and examine the bomb interior. Discard the test if unburned sample or sooty deposits are found. Wash the interior of the bomb with distilled water containing the titration indicator, until the washings are free of acid, and titrate the washings with standard sodium carbonate solution.

10.3.8 Remove and measure, or weigh, the combined pieces of unburned ignition (firing) wire and subtract from the original length, or weigh to determine the wire consumed in firing. If the wire is weighed, remove the ball of oxidized metal from the end of each piece of wire before weighing.

10.4 *Calculations:*

10.4.1 *Temperature Rise*—Using data obtained as prescribed in 10.3.6, compute the corrected temperature rise, t, as follows:

$$t = t_f - t_i + C_e + C_s \tag{1}$$

where:

t = corrected temperature rise, °C or °F,
t_i = initial temperature reading at time of firing, °C or °F,
t_f = final temperature reading, °C or °F,
C_e = thermometer emergent stem correction, if required (see Note 5 and Annex A1.1.4), and
C_s = thermometer setting correction, if required (see Note 5 and Annex A1.1.3).

Note 5—With all mercury-in-glass thermometers, it is necessary to make corrections if the total calorific value is altered by 5.0 Btu or more. This represents a change of 0.001°C or 0.002°F in a calorimeter using approximately 2000 g of water. Beckmann thermometers also require a setting correction and an emergent stem correction (see Annex A1.1.3 and A1.1.4). Solid-stem ASTM Thermometers 56C and 56F do not require emergent stem corrections if all tests, including standardization, are performed within the same 5.5°C (10°F) interval. If operating temperatures range beyond this limit, a differential emergent stem correction (see Annex A1.1.4) must be applied to the corrected temperature rise, t, in all tests including standardization.

10.4.2 *Thermochemical Corrections* (see Appendix X1.1, X1.2, and X1.3)—Compute the following for each test:

e_1 = correction for the heat of formation of HNO_3, Btu. Each millilitre of standard Na_2CO_3 is equivalent to 10.0 Btu, and
e_2 = correction for heat of combustion of firing wire, Btu (Note 6).
= 0.41 Btu/mm or 2.6 Btu/mg for No. 34 B & S gage Chromel C wire.
= 0.49 Btu/mm or 3.2 Btu/mg for No. 34 B & S gage iron wire.

NOTE 6—There is no correction for platinum wire provided the ignition energy is constant.

10.4.3 Compute the calorimeter energy equivalent, *E*, by substituting in the following:

$$E = [(Hg) + e_1 + e_2]/t \qquad (2)$$

where:

E = calorimeter energy equivalent (Note 7),
H = heat of combustion of benzoic acid, as stated in the National Institute of Standards and Technology Certificate, Btu/lb in air,
g = mass (weight in air) of benzoic acid, g,
e_1 = titration correction (10.4.2),
e_2 = fuse wire correction (10.4.2), and
t = corrected temperature rise.

NOTE 7—Using the units and corrections as given in 10.4.1 and 10.4.2, the energy equivalent of the calorimeter is such that the calorific value of the coal sample will be obtained directly in British thermal units per pound when the mass of sample is taken in grams. The units of the energy equivalent are therefore: (British thermal units per pound) times (grams per degree).

10.5 Repeat the procedure for a total of ten determinations. Compute the standard deviation as illustrated in Table 2.

11. Restandardization

11.1 Make checks on the energy equivalent value after changing the oxygen supply, after changing any part of the calorimeter, and at least once a month otherwise.

11.1.1 If a single new determination differs from the old value by 6 Btu/°C (4 Btu/°F), the old standard is suspect, thereby requiring a second test.

11.1.2 The difference between the two new determinations must not exceed 8 Btu/°C (5 Btu/°F), and the average of the two new determinations must not differ from the old standard by more than 4 Btu/°C (3 Btu/°F). If these requirements are met, do not change the calorimeter standard.

11.1.3 If the requirements given in 11.1.2 are not met, two more determinations must be run. The range of the four values must not exceed 14 Btu/°C (8 Btu/°F), and the average of the four new determinations must not differ from the old standard value by more than 3 Btu/°C (2 Btu/°F). If these requirements are met, do not change the calorimeter standard.

11.1.4 If the requirements given in 11.1.3 are not met, a fifth and sixth determination must be run. The range of the six new values must not exceed 17 Btu/°C (10 Btu/°F), and the average of the six new values must not differ from the old standard value by more than 2 Btu/°C (2 Btu/°F). If these requirements are met, do not change the calorimeter standard.

TABLE 3 Summary of Numerical Requirements

NOTE—Test values exceeding table limits require additional runs.[A]

Number of Runs	Maximum Range of Results		Maximum Difference between $\bar{X}_1$ and $\bar{X}_2$[B]	
	Btu/°C	Btu/°F	Btu/°C	Btu/°F
1	. . .	. . .	±6	±4
2	8	5	±4	±3
4	14	8	±3	±2
6	17	10	±2	±2
10	20	12	±1	±1

[A] Values in this table have been rounded off after statistical calculation, and are therefore not precisely in a ratio from 1.8 to 1.0.

[B] $\bar{X}_1$ = average of original standard. $\bar{X}_2$ = average of check runs.

11.1.5 If the requirements given in 11.1.4 are not met, four more determinations must be run to complete a series of ten runs. The range of these ten results must not exceed 20 Btu/°C (12 Btu/°F), and the average of the ten new standards must not differ from the old standard by more than 1 Btu/°C (1 Btu/°F). If these requirements are met, do not change the calorimeter standard.

11.1.6 If the requirements given in 11.1.5 are not met, the average value from the ten new values must be used for the new standard energy equivalent, provided that the standard deviation of the series does not exceed 6.5 Btu/°C (3.6 Btu/°F).

11.2 The summary of the numerical requirements at each stage of restandardization is given in Table 3.

12. Procedure for Coal and Coke Samples (Note 8)

12.1 Thoroughly mix the analysis sample of coal or coke in the sample bottle and carefully weigh approximately 1 g of it into the sample holder. Weigh the sample to the nearest 0.0001 g. Make each determination in accordance with the procedure described in 10.3.2 through 10.3.8.

NOTE 8—For anthracite, coke, and coal of high ash content, that do not readily burn completely, one of the following procedures are recommended: (*1*) The inside of the sample holder is lined completely with ignited asbestos in a thin layer pressed well down in the angles, and the sample is then sprinkled evenly over the surface of the asbestos. (*2*) The mass of the sample may be varied to obtain good ignition. If the mass is varied, it will be necessary to recalibrate the calorimeter so that the water equivalent will be based on the same temperature rise as that obtained with the sample weight. (*3*) A known amount of benzoic acid may be mixed with the sample. Proper allowance must be made for the heat of combustion of benzoic acid when determining the calorific value of the sample.

NOTE 9—For the calorific value of coke, it is necessary to use 3-MPa (30-atm) pressure for both standardization and analysis.

12.2 Determine the sulfur content of the sample by any of the procedures described in Test Methods D 3177.

13. Calculation (Note 2)

13.1 Compute the corrected temperature rise, *t*, as shown in 10.4.1.

13.2 *Thermochemical Corrections* (Appendix X1)—Compute the following for each test:

e_1 = correction for the heat of formation of HNO_3, Btu. Each millilitre of standard sodium carbonate is equivalent to 10.0 Btu,
e_2 = correction for heat of combustion of ignition wire, Btu,
= 0.41 Btu/mm or 2.6 Btu/mg for No. 34 B & S gage Chromel C wire,

= 0.49 Btu/mm or 3.2 Btu/mg for No. 34 B & S gage iron wire, and

e_3 = correction for difference between heat of formation of H_2SO_4 from the heat of formation of HNO_3, Btu,

= 23.7 times percent of sulfur in sample times mass of sample, g.

14. Calorific Value (Note 10)

14.1 *Gross Calorific Value*—Calculate the gross calorific value (gross heat of combustion at constant volume), Q_v (gross), as follows:

$$Q_v \text{ (gross)} = [(tE) - e_1 - e_2 - e_3]/g \qquad (3)$$

where:

Q_v (gross) = gross calorific value, Btu/lb,

t = corrected temperature rise calculated in 13.1, °C or °F,

E = energy equivalent calculated in 10.4.3,

e_1, e_2, e_3 = corrections as prescribed in 13.2, and

g = mass of sample, g.

NOTE 10—This calculation gives calorific value in British thermal units per pound. To obtain calorific value in joules per gram, see Appendix X2.

14.2 *Net Calorific Value*—Calculate the net calorific value (net heat of combustion at a constant pressure), Q_p (net), as follows:

$$Q_p \text{ (net)}_{ar} = Q_v \text{ (gross)}_{ar} - 5.72\ (H_{ar} \times 9) \qquad (4)$$

where:

Q_p (net)$_{ar}$ = net calorific value at constant pressure, cal/g

Q_v (gross)$_{ar}$ = gross calorific value at constant volume, as-received basis, cal/g, and

H_{ar} = total hydrogen as-received basis, where hydrogen includes the hydrogen in sample moisture, %.

NOTE 11—Example for converting from the as-determined (air-dried) sample basis to the as-received net calorific value basis:[7]

Calories, as determined (gram/Cal$_{ad}$) = 7506

Calories, as received (gram/Cal$_{ar}$) = 7056

Moisture, as determined (M_{ad}) = 2.13

Moisture, as received (M_{ar}) = 8.00

Hydrogen, as determined (H_{ad}) = 5.00

To convert H_{ad} to H_{ar}:

$$H_{ar} = \left[(H_{ad} - 0.1119\ M_{ad}) \times \frac{100 - M_{ar}}{100 - M_{ad}}\right] + 0.1119\ M_{ar}$$

$$= \left[(5.00 - 0.1119 \times 2.13) \times \left(\frac{100 - 8.00}{100 - 2.13}\right)\right] + 0.1119 \times 8.00$$

$$H_{ar} = 5.37$$

$$\begin{aligned} Q_p \text{ (net)}_{ar} &= 7056 - 5.72\ (5.37 \times 9) \\ &= 7056 - 276 \\ &= 6780 \text{ cal/g (International Table Calories)} \\ &= 12204 \text{ Btu/lb} \\ &= 28390 \text{ J/g} \\ &= 28.39 \text{ MJ/kg} \end{aligned}$$

15. Report

15.1 The results of the calorific value may be reported on any of a number of bases, differing from each other in the manner that moisture is treated.

15.2 Use the percent moisture in the sample passing a 250-µm (No. 60) sieve (Test Method D 3173) to calculate the results of the analysis sample to a dry basis.

15.3 Procedures for converting the value obtained on the analysis sample to other bases are described in Practice D 3180.

16. Precision and Bias

16.1 *Precision*—The relative precision of this test method for the determination of gross calorific value (Btu) covers the range from 7,112 to 8,120 cal/g (12,700 to 14,500 Btu/lb) for bituminous coals and from 4,922 to 7,140 cal/g (8,790 to 12,750 Btu/lb) for subbituminous and lignite coals.

16.1.1 *Repeatability*—The difference in absolute value between two consecutive test results, carried out on the same sample of 250-µm (No. 60) pulp, in the same laboratory, by the same operator, using the same apparatus, should not exceed the repeatability interval for more than 5 % of such paired values (95 % confidence level). When such a difference is found to exceed the repeatability interval, there is reason to question one, or both, of the test results. The repeatability interval for this test method is 28 cal/g (50 Btu/lb) on a dry basis.

16.1.2 *Repeatability*—The difference in absolute value between test results, obtained in the same laboratory, by the same operator, using the same riffle, determined on a single test specimen of two separate 2.36-mm (No. 8) test units of coal reduced entirely to 250-µm (No. 60) and prepared from the same bulk sample should not exceed the repeatability limit for more than 5 % of such paired values (95 % confidence level). When such a difference is found to exceed the repeatability limit, there is reason to question one, or both, of the test results. The repeatability limit for this test method on a dry basis is:

Bituminous coals	39 cal/g (69 Btu/lb)
Subbituminous and lignite coals	33 cal/g (59 Btu/lb)

16.1.3 *Reproducibility*—The difference in absolute value of replicate determinations, carried out in different laboratories on representative 250-µm (No. 60) samples, prepared from the same bulk sample after the last stage of reduction, should not exceed the reproducibility interval for more than 5 % of such paired values (95 % confidence level). When such a difference is found to exceed the reproducibility interval, there is reason to question one, or both, of the test results. The reproducibility interval for this test method is 56 cal/g (100 Btu/lb) on a dry basis.

16.1.4 *Reproducibility*—The difference in absolute value between test results obtained in different laboratories calculated as the average of determinations on single test specimens of two separate 2.36-mm (No. 8) test units of coal reduced entirely to 250-µm (No. 60) and prepared from the same bulk sample, should not exceed the reproducibility limit for more than 5 % of such paired values (95 % confidence level). When such a difference is found to exceed the reproducibility limit, there is reason to question one, or both, of the test results. The reproducibility limit for this test method on a dry basis is:

Bituminous coals	60 cal/g (107 Btu/lb)
Subbituminous and lignite coals	78 cal/g (140 Btu/lb)

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[7] For a comprehensive theoretical derivation of calculations for converting gross calorific value at constant volume to net calorific value at constant pressure, request Research Report RR: D05-1014.

NOTE 7—Supporting data for 2.36-mm (No. 8) coal has been filed at ASTM Headquarters and may be obtained by requesting RR:DO5-1015.

NOTE 8—The precision for 250-µm (No. 60) coal is currently being evaluated.

16.2 *Bias*—The equipment used in this test method for measuring gross calorific value has no bias because it is standardized with a compound having a known heat of combustion. This procedure may involve tests that produce varying levels of heat formation not accounted for in standardization. If the thermochemical corrections for heat of formation are not done correctly, a bias may be present in the determination.

ANNEX

(Mandatory Information)

A1. THERMOMETRIC CORRECTIONS

A1.1 Thermometer Corrections

A1.1.1 It is necessary to make the following individual corrections, if not making the correction would result in an equivalent change of 5.0 Btu or more.

A1.1.2 *Calibration Correction* shall be made in accordance with the calibration certificate furnished by the calibration authority.

A1.1.3 *Setting Correction* is necessary for the Beckmann thermometer. It shall be made in accordance with the directions furnished by the calibration authority.

A1.1.4 *Differential Emergent Stem Correction*—The calculation of differential stem correction depends upon the way the thermometer was calibrated and how it was used. Two conditions are possible:

A1.1.4.1 *Thermometers Calibrated in Total Immersion and Used in Partial Immersion*—This emergent stem correction is made as follows:

$$\text{Correction} = C_e = K\,(t_f - t_i)\,(t_f + t_i - L - T) \qquad \text{(A1.1)}$$

where:

C_e = emergent stem correction,
K = 0.00016 for thermometers calibrated in °C,
= 0.0009 for thermometers calibrated in °F,
L = scale reading to which the thermometer was immersed,
T = mean temperature of emergent stem, °C or °F,
t_i = initial temperature reading, °C or °F, and,
t_f = final temperature reading, °C or °F.

NOTE A1.1—*Example:* Assume the point L, to which the thermometer was immersed was 16°C; its initial reading, t_i, was 24.127°C, its final reading, t_f, was 27.876, the mean temperature of the emergent stem, T was 26°C; then:

$$\begin{aligned}\text{Differential stem correction, } C_e &\\ &= 0.00016\,(28 - 24)\,(28 + 24 - 16 - 26)\\ &= +\,0.0064°\text{C.}\end{aligned}$$

A1.1.4.2 *Thermometers Calibrated and Used in Partial Immersion, but at a Different Temperature than the Calibration Temperature*—This emergent stem correction is made as follows:

$$\text{Correction} = C_e = K\,(t_f - t_i)\,(t_c - t_o) \qquad \text{(A1.2)}$$

where:

C_e = emergent stem correction,
K = 0.00016 for thermometers calibrated in °C,
= 0.00009 for thermometers calibrated in °F,
t_i = initial temperature reading, °C or °F,
t_f = final temperature reading, °C or °F,
t_o = observed stem temperature, °C or °F, and
t_c = stem temperature at which the thermometer was calibrated, °C or °F.

NOTE A1.2—*Example:* Assume the initial reading, t_i, was 80°F, the final reading, t_f, was 86°F, and that the observed stem temperature, t_o, was 82°F, and calibration temperature, t_c, was 72°F then:

$$\begin{aligned}\text{Differential stem correction} &\\ &= 0.00009\,(86 - 80)\,(82 - 72)\\ &= 0.005°\text{F}\end{aligned}$$

APPENDIXES

(Nonmandatory Information)

X1. THERMOCHEMICAL CORRECTIONS

X1.1 *Energy of Formation of Nitric Acid*—A correction, e_1, (10.4.2 and 13.2), is applied for the acid titration. This correction is based on the assumptions (*1*) that all the acid titrated is HNO_3 formed by the following reaction: 1/2 N_2 (gas) + 5/4 O_2 (gas) + 1/2 H_2O (liquid) = HNO_3 (in 500 mol H_2O), and (*2*) that the energy of formation of HNO_3 in approximately 500 mol of water under bomb conditions is −59.0 kJ/mol.[8]

X1.1.1 A convenient concentration of Na_2CO_3 is 0.394 *N* (20.9 g Na_2CO_3/1000 mL) which gives e_1 = 10 times *V*, where *V* is the volume of Na_2CO_3 in millilitres. The factor 10.0 (0.394 × 59.0 = 2.326) is to be used for calculating calorific value in British thermal units per pound. For other units see Table X2.1. When H_2SO_4 is also present, a part of the correction for H_2SO_4 is contained in the e_1 correction and remainder in the e_3 correction.

X1.2 *Energy of Formation of Sulfuric Acid*—By definition (see Terminology D 121) the gross calorific value is obtained when the product of the combustion of sulfur in the sample is SO_4 (in grams). However, in actual bomb combustion process, all the sulfur is found as H_2SO_4 in the bomb washings. A correction, e_3 (see 13.2) is applied for the sulfur that is converted to H_2SO_4. This correction is based upon the energy of formation of H_2SO_4 in solutions, such as will be present in the bomb at the end of a combustion. This energy is taken as −295.0 kJ/mol.[9] A correction of 2 times 59.0 kJ/mol of sulfur was applied in the e_1 correction, so the additional correction necessary is 295.0 − (2 times 59.0) = 177 kJ/mol, or 5.52 kJ/per gram of sulfur in the sample (55.2 J times weight of sample in grams times percent sulfur in sample). This causes e_2 to be 23.7 times weight of sample in grams times percent sulfur in sample. The factor 23.7 (equals 55.2/2.326), for e_3 (see 13.2) is to be used for calculating calorific value in British thermal units per pound. For other units, see Appendix X2. The values above are based on a coal containing about 5 % sulfur and about 5 % hydrogen. The assumption is also made that the H_2SO_4 is dissolved entirely in the water condensed during combustion of the sample.

X1.2.1 If a 1-g sample of such a fuel is burned, the resulting H_2SO_4 condensed with water formed on the walls of the bomb, will have a ratio of about 15 mol of water to 1 mol of H_2SO_4. For this concentration, the energy of the reaction SO_2 (gas) + ½ O_2 + H_2O (liquid) = H_2SO_4 (in 15 moles of H_2O) under the conditions of the bomb process is −295.0 kJ/mol.[10] Basing the calculation upon a sample of comparatively large sulfur content reduces the possible overall errors, because, for small percent of sulfur, the correction is smaller.

X1.3 *Fuse (Ignition) Wire*—Calculate the energy contributed by burning the fuse wire in accordance with the directions furnished by the supplier of the wire. For example, the energy of the combustion of No. 34 B & S gage Chromel C wire is 6.0 J/mg or approximately 0.95 J/mm. For calculating e_2 for use in Eqs 2 and 3, these give e_2 = 0.41 times length (mm) of wire or e_2 = 2.6 times weight (mg) of wire. The energy required to melt a platinum wire is constant for each experiment if the same amount of platinum wire is used. As the energy is small, its effect is essentially cancelled out in the relationship between the standardization experiments and the calorific value determinations, and it can be neglected. The factors listed above for e_2 (10.4.2 and 13.2) are suitable for calculating calorific value in British thermal units per pound. For other units, see Appendix X2.

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[8] Calculated from data in National Bureau of Standards Technical Note 270-3.

[9] Calculated from data in National Bureau of Standards Circular 500.

[10] Mott, R. A. and Parker, C., "Studies in Bomb Calorimetry IX—Formation of Sulfuric Acid," *Fuel*, Vol 37, 1958, p. 371.

X2. REPORTING RESULTS IN OTHER UNITS

X2.1 *Reporting Results in Joules per Gram:*

X2.1.1 The gross calorific value can be expressed in joules per gram, calories per gram, or British thermal units per pound. The relationships between these units are given in Table 1.

X2.1.2 Because the energy of combustion of the reference material is measured and certified by the National Institute of Standards and Technology (NIST) in joules per gram, the most straightforward usage of the reference material would lead to the calorific value of the fuel in joules per gram. To carry out this procedure, make the changes outlined in X2.1.3 through X2.1.5.

X2.1.3 For calculating energy equivalent, substitute Eq X2.1 for Eq 2:

$$E = [(H'g) + e_1']/t \qquad \text{(X2.1)}$$

where the meanings of the symbols in Eq X2.1 are the same as in Eq 2 except that:

E' = energy equivalent in units of joules per temperature unit,

H' = the heat of combustion of reference material in units of joules per gram weight in air (J/g from the certificate for the NIST benzoic acid), and

e_1' and e_3' = corrections in units of joules, (see Table X2.1).

X2.1.4 For calculating gross calorific value, substitute Eq X2.2 for Eq 3:

$$Q_v\,(\text{gross}) = [(t_E') - e_1' - e_2']/g \qquad \text{(X2.2)}$$

where the meanings of the symbols in Eq X2.2 are the same as in Eq 3 except that:

Q_v (gross) = gross calorific value with units of joules per gram (weight in air),

E' = energy equivalent units, of joules per temperature unit, and

e_1', e_2', and e_3' = corrections in units of joules (see Table X2.1).

X2.1.5 *Precision:*

X2.1.5.1 *Repeatability*—Duplicate results by the same laboratory, using the same operator and equipment, should not be considered suspect unless they differ by more than 120 J/g.

X2.1.5.2 *Reproducibility*—The results submitted by two or more laboratories (different equipment, operators, date of test, and different portions of the same sample) should not be considered suspect unless the results differ by more than 240 J/g.

TABLE X2.1 Alternative Thermochemical Correction Factors (Units in Joules)[A]

Correction	Multiplication Factor	Multiply By
e_1' (HNO_3)	20 J/mL	mL of 0.34 *N* Na_2CO_3
e_3' (H_2SO_4)	55.2 J/cgS	percent of sulfur in sample times mass of sample in grams
e_2' (fuse wire) or	0.95 J/mm	length (mm) of No. 34 B & S gage Chromel C wire
e_2' (fuse wire)	1.14 J/mm	length (mm) of No. 34 B & S gage iron wire
e_2' (fuse wire) or	6.0 J/mg	mass (mg) of Chromel C wire
e_2' (fuse wire)	7.4 J/mg	mass (mg) of iron wire

[A] To be used in Eqs X2.1 and X2.2 only.