



# Standard Test Method for Gross Calorific Value of Coal and Coke by the Adiabatic Bomb Calorimeter<sup>1</sup>

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 ( $\epsilon$ ) indicates an editorial change since the last revision or reapproval.

*This standard has been approved for use by agencies of 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<sup>2</sup>
- D 346 Practice for Collection and Preparation of Coke Samples for Laboratory Analysis<sup>2</sup>
- D 1193 Specification for Reagent Water<sup>3</sup>
- D 2013 Method of Preparing Coal Samples for Analysis<sup>2</sup>
- D 3173 Test Method for Moisture in the Analysis Sample of Coal and Coke<sup>2</sup>
- D 3177 Test Method for Total Sulfur in the Analysis Sample of Coal and Coke<sup>2</sup>
- D 3180 Practice for Calculating Coal and Coke Analyses from As-Determined to Different Bases<sup>2</sup>
- D 4239 Test Method for Sulfur in the Analysis Sample of Coal and Coke Using High Temperature Tube Furnace Combustion Methods<sup>2</sup>
- D 4621 Guide for Quality Management in an Organization that Samples or Tests Coal and Coke<sup>2</sup>
- E 1 Specification for ASTM Thermometers<sup>4</sup>

<sup>1</sup> 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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<sup>2</sup> *Annual Book of ASTM Standards*, Vol 05.06

<sup>3</sup> *Annual Book of ASTM Standards*, Vol 11.01.

<sup>4</sup> *Annual Book of ASTM Standards*, Vol 14.03.

E 144 Practice for Safe Use of Oxygen Combustion Bombs<sup>5</sup>

## 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)  $Q_v(\text{gross})$* —see Terminology D 121.

3.1.3 *net calorific value (net heat of combustion at constant pressure)  $Q_p(\text{net})$* —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 Definitions 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

<sup>5</sup> *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 <sup>A</sup> = 4.1868 J	1.8 Btu/lb = 1.0 cal/g

<sup>A</sup> International tables calorie.

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 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 its 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 as a result of 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.<sup>6</sup> 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<sub>6</sub>H<sub>5</sub>COOH), 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<sub>2</sub>CO<sub>3</sub>), 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<sub>3</sub>) 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 used, extreme caution must be exercised not to exceed the bomb manufacturer's recommendations and 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- $\mu$ m (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

<sup>6</sup> *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<sup>A</sup>**

Standardization Number	Column A	Column B	Column C
	Energy Equivalent (Btu/lb) × (g/°C)	Code to 4400 (Column A – 4400)	(Column B) <sup>2</sup>
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

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

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

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

<sup>A</sup>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.

outliers using 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 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 before 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, and so forth.

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 1-min intervals until the same temperature, within one tenth of the smallest thermometer subdivision, is observed in three successive readings. Record this “initial temperature,”  $t_i$ , 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:

$$t = t_f - t_i + C_e + C_s \quad (1)$$

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