



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

This standard is issued under the fixed designation D 3286; 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.

## 1. Scope

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

1.2 The values stated in SI units are to be regarded as the standard unless otherwise designated. The values given in parentheses are for information only.

1.3 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.* For specific hazard statements, see Section 8.

## 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 Methods 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>
- E 1 Specification for ASTM Thermometers<sup>4</sup>
- 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 test specimen under specific conditions.

3.1.1.1 *Discussion*—It is expressed in this test method in

calories per gram (cal/g) and can also be expressed in British thermal units per pound (Btu/lb) or in the International System of Units (SI), in 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), n*—see Terminology D 121.

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

3.1.4 *calorimeter, n*—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, n*—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.

3.2.1.1 *Discussion*—Temperature is measured in degrees Celsius. Thermometer corrections shall be applied. Temperatures may be recorded in ohms or other arbitrary units as the equivalent of degrees. Consistent units shall be used in standardization and the actual calorific value determination. If arbitrary units other than degrees Celsius are used, the temperature interval over which all tests are made shall not vary so much that an error greater than 0.001°C would result.

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

NOTE 1—Conversion to other units is discussed in Appendix X2. Time is expressed in minutes. Mass is expressed 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 isoperibol 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, and making proper allowances for heat contributed by other processes, and for thermometer and thermochemical corrections.

4.2 Oxidation after sampling of susceptible low-rank coal or lignite may result in a reduction of calorific value.

<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 05.05.

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

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

<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.

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 When mutually agreed upon between the buyer and the seller, the gross calorific value may be used to compute the total calorific content of the quantity of coal represented by the sample for payment purposes.

5.2 The gross calorific value can be used to determine if the coal meets the regulatory requirement for industrial fuels.

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

## 6. Apparatus and Facilities

6.1 *Test Space*—A room or area free from drafts that can be kept at a reasonably uniform temperature for the time required for the determination. The apparatus shall 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 shall be designed so that all liquid combustion products can be completely recovered by washing the inner surfaces. There shall be no gas leakage during a test. The bomb shall 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*—A laboratory balance having the 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*, 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 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*, a double-walled, air, or water-filled jacket. The calorimeter shall be insulated from the jacket by an air space. 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 be capable of maintaining the temperature constant to within  $\pm 0.1^\circ\text{C}$  of room temperature at a calorimeter temperature  $2^\circ\text{C}$  below, and  $2^\circ\text{C}$  or more above room temperature throughout the determination. If a

water-filled jacket is used, it shall have a device for stirring the water at a uniform rate with minimum heat input.

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

6.6.1 *Liquid-in-Glass Thermometers*, conforming to the requirements for ASTM Thermometers 56C, 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 (NIST)). For thermometers 56C, the calibration should be at intervals no larger than  $2.0^\circ\text{C}$  over the entire graduated scale. The maximum difference in correction between any two test points shall be no more than  $0.02^\circ\text{C}$ . For thermometers 116C and 117C, the calibration should be at intervals no larger than  $0.5^\circ\text{C}$  over the entire calibrated range. The maximum difference in correction between any two test points shall not be more than  $0.02^\circ\text{C}$ .

6.6.2 *Beckmann Differential Thermometers*, (glass-enclosed scale, adjustable) having a range of approximately  $6^\circ\text{C}$  in  $0.01^\circ\text{C}$  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 NIST) at intervals no larger than  $1^\circ\text{C}$  over the entire graduated scale. The maximum difference in the correction between any two test points shall not be more than  $0.02^\circ\text{C}$ .

6.6.3 *Other Thermometers*, of precision equal to or better than  $0.001^\circ\text{C}$ , such as platinum resistance or linear thermistor thermometers are satisfactory and may be used if properly calibrated. A Wheatstone bridge and galvanometer capable of measuring resistance to  $0.0001 \Omega$  are necessary for use with  $25 \Omega$  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*—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*—The ignition wire shall be 100 mm of 0.16-mm diameter (No. 34 B & S gage) nickel-chromium alloy, Chromel C alloy, or iron wire. Platinum wire or palladium, 0.10-mm diameter (No. 38 B & S gage) may be used, provided constant ignition energy is supplied. The length or mass of ignition wire shall remain constant for all calibrations and calorific value determinations.

6.10 *Ignition Circuit*, for ignition purposes shall provide a 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 for measuring temperatures before, during, and after combustion of the sample; ignition of the

sample; and calculation of results provided that they meet the minimal functional specifications in Sections 6 and 10.

## 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 specification 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*, 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 NIST certified benzoic acid. The crystals shall be pelletized before use. Commercially prepared pellets may be used provided they are made from NIST certified benzoic acid or made from benzoic acid that has been calibrated against NIST certified benzoic acid. The value of heat of combustion of the benzoic acid for use in the calibration calculations shall be in accordance with the value listed in the NIST 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*, sodium carbonate ( $Na_2CO_3$ ) should be dried for 24 h at 105°C. Dissolve 3.76 g in water and dilute to 1 L. One millilitre of this solution is equivalent to 1.0 cal 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 equipment manufacturer's installation and operating instructions before using the calorimeter.

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

8.3 Inspect the bomb parts carefully after each use and, after 3000 firings, check the bomb for thread wear on any closures. If an inspection reveals any wear, return the parts to the factory for further testing or replacement of the defective parts. It is good practice to return the bomb to the manufacturer for inspection at yearly intervals.

<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.

8.4 The oxygen supply cylinder shall 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 shall not permit any portion of her or his body to extend over the calorimeter.

8.6 When combustion aids are employed, extreme caution shall 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 there is evidence of gas leakage 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 sample should be analyzed simultaneously for moisture content in accordance with Method D 2013 and Test Method D 3173, so that calculations to other bases can be made.

9.3 Sulfur analysis shall be made in accordance with Test Methods D 3177 or D 4239.

## 10. Standardization

10.1 The calorimeter shall be 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 ASTM 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 coals tested in the same laboratory. The usual range of masses is from 0.9 to 1.3 g. Weigh the pellet to the nearest 0.1 mg 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.

TABLE 2 Standard Deviations for Calorimeter Standardization<sup>A</sup>

Standardization Number	Column A	Column B	Column C
	Energy Equivalent (cal/°C)	Code to 2449 (Column A-2449)	(Column B) <sup>2</sup>
1	2450	1	1
2	2448	-1	1
3	2453	4	16
4	2449	0	0
5	2447	-2	4
6	2448	-1	1
7	2446	-3	9
8	2452	3	9
9	2450	1	1
10	2447	-2	4
SUM	241 490	0	46

Average =  $\bar{X} = 2449.24\ 490/10$

Variance =  $s^2 = \frac{\sum \text{Column C} - ((\sum \text{Column B})^2/n)}{n-1} = 5.11$

Standard deviation =  $s = \sqrt{\text{variance}} = \sqrt{5.11} = 2.26$

<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.

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 2.5 to 3 MPa (25 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 and 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 5.0°C below the jacket temperature, but not lower than 20°C. Use the same mass of water in each test weighed to  $\pm 0.5$  g. For 2000-mL calorimeters, the proper quantity can be obtained by use of a volumetric flask calibrated to deliver 1980 to 2020 mL with  $\pm 0.5$  mL repeatability. 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 stirrer(s) and continue to operate it (them) throughout the determination. Examine the thermometers for liquid separation and correct any separation before proceeding. The starting temperature shall be within  $\pm 0.5^\circ\text{C}$  of that used in the analysis of coal or coke samples.

10.3.5.1 The initial temperature adjustment will ensure a final temperature slightly above that of the jacket for 2000-mL calorimeters. Some operators prefer a lower initial temperature so that the final temperature is slightly below that of the jacket. This procedure is also satisfactory. Whichever procedure is used, the same procedure shall be used in all tests, including standardization. A small heater

may be built into the calorimeter so that the desired starting temperature can be easily attained.

NOTE 2—Check all liquid-in-glass thermometers at least daily for any defects, for example, cracked glass, etc.

10.3.6 Allow 5 min for attainment of equilibrium; then record the calorimeter temperature at 1-min intervals for 5 min or until the rate of change has been nearly constant for 5 min. Use a magnifier when using ASTM Bomb Calorimeter Thermometers 56C, and estimate all of the readings (except those during the rapid-rise period) to the nearest 0.002°C. Estimate ASTM Thermometers 115C, 116C, or 117C readings to 0.001°C, and 25  $\Omega$  resistance thermometer readings to the nearest 0.0001  $\Omega$ . Tap mercury thermometers (for instance with a pencil) just before reading to avoid errors caused by mercury sticking to the walls of the capillary. Ignite the charge at the start of the sixth minute and record the time,  $i$ , and the thermometer reading,  $t_i$  (Note 6). Take the next two readings 0.5 min and 1 min after firing because of the rapid rise. Record subsequent readings at 1-min intervals on the minute until the difference between successive readings has been constant for 5 min. If the final temperature is above the bath temperature, the temperature rises to a maximum and then begins to fall. Record the time,  $f$ , and the thermometer reading,  $t_f$ , after the rate of change has become uniform. The calorimeter water temperature shall be at the same temperature ( $\pm 0.05^\circ\text{C}$ ) for every determination, at the time of firing, if the Bureau of Mines method for radiation correction is to be used. See Annex A1.5.

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 any 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 weight 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 Calculation:

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

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

where:

- $t$  = corrected temperature rise, °C,
- $t_i$  = initial temperature reading at time of firing,
- $t_f$  = final temperature reading, °C,
- $C_e$  = thermometer, emergent stem correction, if required (see 10.4.1.1 and Annex A1.4),
- $C_s$  = thermometer setting correction, if required (see 10.4.1.1 and Annex A1.3), and
- $C_r$  = radiation correction (see 10.4.1.1 and Annex A1.5).

10.4.1.1 With all mercury-in-glass thermometers, it is necessary to make corrections if the total calorific value is altered by 2.7 cal/g (5 Btu/lb) or more. This represents a change of 0.001°C in a calorimeter using approximately 2000