



Standard Test Method for Gross Calorific Value of Coal and Coke by Microprocessor Controlled Isoperibol Calorimeters¹

This standard is issued under the fixed designation D 1989; 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.

1. Scope

1.1 This test method covers the determination of the gross calorific value of coal and coke by an isoperibol bomb calorimeter using electronic temperature sensors and automatic calorimeter controllers.

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

NOTE 1—Conversion to other units is discussed in [Appendix X1](#). Time is expressed in minutes. Mass is expressed in grams.

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 Coke²
- D 346 Practice for Collection and Preparation of Coke Samples for Laboratory Analysis²
- D 388 Classification of Coals by Rank²
- D 1193 Specification for Reagent Water³
- D 2013 Method of Preparing Coal Samples for Analysis²
- D 3173 Test Method for Moisture in the Analysis Sample of Coal and Coke²
- D 3177 Test Methods for Total Sulfur in the Analysis Sample of Coal and Coke²
- D 3180 Practice for Calculating Coal and Coke Analyses from As-Determined to Different Bases²
- D 4239 Test Methods for Sulfur in the Analysis Sample of Coal and Coke Using High Temperature Tube Furnace

Combustion Methods²

E 144 Practice for Safe Use of Oxygen Combustion Bombs⁴

E 178 Practice for Dealing with Outlying Observations⁴

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 specified 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 *calorimeter, n*—as used in this test method, not only the bomb and its contents but also includes the bucket, electronic sensing devices, ignition leads, water, and the stirrer when using water.

3.1.3 *calorimeter jacket, n*—the insulating medium surrounding the calorimeter.

3.1.4 *gross calorific value (gross heat of combustion at constant volume), Q_v (gross), n*—see Terminology [D 121](#).

3.1.5 *isoperibol, adj*—a term used in combustion calorimetry meaning constant temperature jacket (environment).

3.1.6 *microprocessor, n*—a central processing chip within the electronic controller section of the apparatus.

3.1.7 *net calorific value (net heat of combustion at constant pressure, Q_p (net), n*—see Terminology [D 121](#).

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 affects as noted in [10.4.1](#).

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, and then adjusted for extraneous heat effects and divided by the mass of the sample, determines the gross calorific value.

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 14.02.

TABLE 1 Calorific Value

1 Btu = 1055.06 J	1 Btu/lb = 2.326 J/g
1 cal ^A = 4.1868 J	1.8 Btu/lb = 1.0 cal/g

^A International tables calorie.

4. Summary of Test Method

4.1 Calorific value is determined in this test method by burning a weighed sample of coal or coke under controlled conditions, in an atmosphere of oxygen, in a calibrated microprocessor controlled isoperibol calorimeter. The calorimeter is calibrated by burning a specified amount of benzoic acid, as defined in 7.3. The calorific value of the test specimen is computed from microprocessor temperature readings made before, during, and after making proper allowances for heat contributions by other processes. The microprocessor may record these temperatures in either of two modes: a full-temperature method and a temperature extrapolation method.

NOTE 2—Oxidation after sampling and before testing a susceptible low-rank coal or lignite can result in a reduction of calorific value. Unnecessary exposure of the sample to air, or unnecessary delay in analysis from the time of sampling, should be avoided to minimize oxidation.

5. Significance and Use

5.1 When mutually agreed upon between the buyer and seller, the gross calorific value can be used to compute the total calorific content of the shipment of coal, represented by the sample, for commercial purposes.

5.2 The gross calorific value can be used to determine whether the coal meets the regulatory specifications and requirements for industrial fuels.

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

5.4 The gross calorific value is required to classify coals according to procedures specified in Classification D 388.

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 sources. Thermostatic control of room temperature and controlled relative humidity are desirable.

6.2 *Combustion Bomb*, constructed of materials that are not affected sufficiently by the combustion process or products to introduce measurable heat input or to alter the 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. 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 accurately weigh the sample to the nearest 0.1 mg. The balance shall be checked periodically to determine its accuracy.

6.4 *Calorimeter Vessel (Bucket)*, made of a suitable metal with a tarnish-resistant coating, with all outer surfaces highly

polished. It shall be of such construction that the environment of the calorimeter's entire outer boundaries are maintained at a uniform temperature.

6.5 *Jacket*—A double-walled, air, or water-filled jacket. The calorimeter shall be insulated from the jacket by an air space or an equally satisfactory isolating medium or both. The sides, top, and bottom of the calorimeter vessels shall be positioned 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°C below, and 2°C or more above room temperature throughout the determination. When a water-filled jacket is used, it shall have a device for stirring the water at a uniform rate.

6.6 *Temperature-Sensing Device*—Thermometers with a precision equal to or better than 0.0001°C . Platinum resistance or other electronic temperature sensors can be used if properly calibrated.

6.7 *Temperature-Measuring Accessories* that measure in degrees Celsius. Equivalent temperatures may be recorded in ohms or other arbitrary units instead of degrees. Consistent units shall be used in standardization as well as in the actual calorific value determination. If arbitrary units other than degrees Celsius are used, the temperature interval shall not vary so as to cause an error greater than 0.001°C .

6.8 *Sample Holder*—An open crucible of platinum, quartz, or base-metal alloy. The base-metal crucibles should be heat-treated for 4 h at 500°C to ensure they are completely oxidized.

6.9 *Ignition Wire*, such as chromium alloy (Chromel C), iron, platinum, or palladium wire that can ignite the sample. It shall be of same length and diameter, or mass, for all calibrations and calorific value determinations.

6.10 *Firing Circuit*, 6- to 24-V ac or dc, required for ignition purposes. A variable transformer connected to an alternating current lighting circuit or batteries can be used.

6.11 *Buret*, having 0.1-mL divisions for the acid titration.

6.12 *Isoperibol Calorimeter, Microprocessor Controlled*—An electronically controlled calorimeter with a central processing unit capable of measuring temperatures, igniting the sample, and calculating the results.

7. Reagents

7.1 *Purity of Reagents*—Reagent grade chemicals conforming to the specification of the Committee on Analytical Reagents of the American Chemical Society shall be used in all tests.⁵

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

⁵ *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 *Anal. Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmaceutical Convention, Inc. (USPC), Rockville, MD.

7.3 *Benzoic Acid, Standard*—(C₆H₅-COOH)—Use pellets made from benzoic acid calibrated against the standard material of the National Institute of Standards and Technology.⁶ The value of heat of combustion of benzoic acid, for use in the calibration calculations, shall conform with the certified value.

7.4 *Methyl Orange, Methyl Red, or Methyl Purple Indicator*—Use the indicator to define the titration limits of the acid formed during combustion. The indicator used shall be the same for both calibration and calorific value determinations. Use as a 0.1 % distilled water solution.

7.5 *Oxygen*—Use oxygen manufactured from liquid air only, free of combustible matter, and guaranteed to be greater than 99.5 % pure. Oxygen made by the electrolytic process can contain a small amount of hydrogen and is unfit for use without purification.

7.6 *Sodium Carbonate, Standard Solution*(Na₂CO₃)—Dissolve 3.76 g of sodium carbonate (that has been dried for 24 h at 105°C) in water and dilute to 1 L. One millilitre of this solution is equivalent to 1.0 cal in the acid titration.

7.7 *Wash Water*—Distilled water containing two drops of indicator per 100 mL.

8. Hazards

8.1 In addition to the safety hazards statement given in 1.3, and the equipment manufacturer’s installation and operating instructions, special precautions are recommended for safe calorimeter operations by consulting with the calorimeter equipment manufacturer or his certified representative prior to and following the installation. Additional precautions are given in Practice E 144.

8.2 The mass of the coal or coke sample and the pressure of the oxygen admitted to the bomb must not exceed the bomb 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 recommendation.

8.4 Equip the oxygen supply cylinder 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 to the bomb. Valves, gages, and gaskets must meet industry safety codes. Suitable reducing valves and adapters for 3- to 4-MPa (300- to 500-psi) discharge pressure are obtainable from commercial sources of compressed gas equipment. Check the pressure gage annually for accuracy or after any accidental overpressures that reach maximum gage pressure.

8.5 During ignition of a sample, the operator’s body shall not be permitted to be directly exposed to the calorimeter.

8.6 Exercise extreme caution not to exceed the bomb manufacturer’s recommendations and avoid damage to the bomb when combustion aids are used. Do not fire loose fluffy

material such as unpeletted 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 gas leakage when the bomb is submerged in the calorimeter water.

9. Sample

9.1 Pulverize the test specimen 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 Analyze separate test specimens 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 Determine sulfur in accordance with Test Methods D 3177 or D 4239.

10. Standardization

10.1 Calibrate the calorimeter (determine the energy equivalent) 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 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 Control the mass of the pellets of benzoic acid in each calibration series to obtain the same temperature rise as obtained with typical coal specimens tested in the same laboratory. The usual range of masses is 0.9 to 1.3g. Weigh the pellet during the same test day and to the nearest 0.0001 g in the sample holder in which it is to be burned and record the mass.

10.3.2 Rinse the bomb with reagent water to lubricate internal seals, dry the exterior surface, and add 1.0 mL of reagent water to the bomb before assembly for a determination.

TABLE 2 Standard Deviations for Calorimeter Standardization—Example^A

Standardization Number	Column A	Column B	Column C
	Energy Equivalent, cal/°C	Code to 2449 (Column A-2449)	(Column B) ²
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		0	46

^A Average = $\bar{X} = 2449 (24490/10)$.

$$\text{Variance} = s^2 = \frac{\text{sum of column C} - [(\text{sum column B})^2/n]}{n - 1} = 5.11.$$

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

⁶ Benzoic acid to be used as a calibration standard is available from the National Institute of Standards and Technology, Gaithersburg, MD 20899.