



Designation: D5865/D5865M – 19

Standard Test Method for Gross Calorific Value of Coal and Coke¹

This standard is issued under the fixed designation D5865/D5865M; 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 pertains to the determination of the gross calorific value of coal and coke by either an isoperibol or adiabatic combustion calorimeter.

1.2 The values stated in either SI units or inch-pound units are to be regarded separately as standard. The values stated in each system are not necessarily exact equivalents; therefore, to ensure conformance with the standard, each system shall be used independently of the other, and values from the two systems shall not be combined.

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, health, and environmental practices and determine the applicability of regulatory limitations prior to use.* Specific hazard statements are given in Section 8.

1.4 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

2. Referenced Documents

2.1 *ASTM Standards:*²

- D121 Terminology of Coal and Coke
- D346 Practice for Collection and Preparation of Coke Samples for Laboratory Analysis
- D388 Classification of Coals by Rank
- D1193 Specification for Reagent Water
- D2013 Practice for Preparing Coal Samples for Analysis
- D3173 Test Method for Moisture in the Analysis Sample of Coal and Coke

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

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² For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

- D3177 Test Methods for Total Sulfur in the Analysis Sample of Coal and Coke (Withdrawn 2012)³
- D3180 Practice for Calculating Coal and Coke Analyses from As-Determined to Different Bases
- D4239 Test Method for Sulfur in the Analysis Sample of Coal and Coke Using High-Temperature Tube Furnace Combustion
- D7582 Test Methods for Proximate Analysis of Coal and Coke by Macro Thermogravimetric Analysis
- E144 Practice for Safe Use of Oxygen Combustion Vessels
- E178 Practice for Dealing With Outlying Observations
- E691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method
- E882 Guide for Accountability and Quality Control in the Chemical Analysis Laboratory
- E2251 Specification for Liquid-in-Glass ASTM Thermometers with Low-Hazard Precision Liquids

3. Terminology

3.1 For additional definitions of terms used in this test method, refer to Terminology D121.

3.2 *Definitions:*

3.2.1 *adiabatic calorimeter, n*—a calorimeter that operates in the adiabatic mode and may or may not use a microprocessor; the initial temperature before initiating the combustion and the final temperatures are recorded by the operator or the microprocessor.

3.2.2 *automated calorimeter, n*—a calorimeter which has a microprocessor that takes the thermometric readings and calculates the Calibration Value and the Heat of Combustion Values.

3.2.3 *British thermal unit [Btu], n*—the amount of heat required to raise the temperature of one pound - mass [lbm] of liquid water at one atmosphere pressure one degree Fahrenheit at a stated temperature.

3.2.3.1 *Discussion*—The results of combustion calorimetric tests of fuels for steam power plants may be expressed in terms of the 1956 International Steam Table calorie (I.T. cal) which is defined by the relation, 1 I.T. cal = 4.1868 J. The Btu used in

³ The last approved version of this historical standard is referenced on www.astm.org.

*A Summary of Changes section appears at the end of this standard

modern steam tables is defined by the means of the relation, 1 I.T. cal/g = 1.8 I.T. Btu/lb. Thus, 1 I.T. Btu/lb = 2.326 J/g.

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

3.2.5 *calorimeter, n*—a device for measuring calorific value consisting of a combustion vessel, its contents, a vessel for holding the combustion vessel, temperature measuring devices, ignition leads, water, stirrer, and a jacket maintained at specified temperature conditions.

3.2.6 *gross calorific value (gross heat of combustion at constant volume), Q_v (gross), n*—the heat produced by complete combustion of a substance at constant volume with all water formed condensed to a liquid.

3.2.7 *heat of formation, n*—the change in heat content resulting from the formation of 1 mole of a substance from its elements at constant pressure.

3.2.8 *isoperibol calorimeter, n*—a calorimeter that operates in the isoperibol mode and uses a microprocessor to record the initial and final temperatures and make the appropriate heat leak corrections during the temperature rise; it determines when the calorimeter is in equilibrium and ignites the sample and determines when the calorimeter has reached equilibrium after ignition.

3.2.9 *net calorific value (net heat of combustion at constant pressure), Q_p (net), n*—the heat produced by combustion of a substance at a constant pressure of 0.1 MPa [1 atm], with any water formed remaining as vapor.

3.3 Definitions of Terms Specific to This Standard:

3.3.1 *corrected temperature rise, n*—the calorimeter temperature change caused by the process that occurs inside the combustion vessel corrected for various effects.

3.3.2 *heat capacity, n*—the energy required to raise the temperature of the calorimeter one arbitrary unit.

3.3.2.1 *Discussion*—The heat capacity can also be referred to as the energy equivalent or water equivalent of the calorimeter.

4. Summary of Test Method

4.1 The heat capacity of the calorimeter is determined by burning a specified mass of benzoic acid in oxygen. A comparable amount of the analysis sample is burned under the same conditions in the calorimeter. The calorific value of the analysis sample is computed by multiplying the corrected temperature rise, adjusted for extraneous heat effects, by the heat capacity and dividing by the mass of the sample.

4.2 Oxidation of coal after sampling can result in a reduction of calorific value. In particular, lignite and sub-bituminous rank coal samples may experience greater oxidation effects than samples of higher rank coals. Unnecessary exposure of the samples to the air for the time of sampling or delay in analysis shall be avoided. (See X2.1.)

5. Significance and Use

5.1 The gross calorific value can be used to compute the total calorific content of the quantity of coal or coke represented by the sample for payment purposes.

5.2 The gross calorific value can be used for computing the calorific value versus sulfur content to determine whether the coal meets regulatory requirements for industrial fuels.

5.3 The gross calorific value can be used to evaluate the effectiveness of beneficiation processes.

5.4 The gross calorific value can be required to classify coals according to Classification D388.

6. Apparatus and Facilities

6.1 *Test Area*—An area free from drafts, shielded from direct sunlight and other radiation sources. Thermostatic control of room temperature and controlled relative humidity are desirable.

6.2 *Combustion Vessel*—Constructed of materials that are not affected by the combustion process or the products formed to introduce measurable heat input or alteration of end products. The combustion vessel 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 combustion vessel shall be capable of withstanding a hydrostatic pressure test to 20 MPa [3000 psig] at room temperature without stressing any part beyond its specified elastic limit.

6.3 *Balance*—A laboratory balance capable of weighing the analysis sample to the nearest 0.0001 g. The balance shall be checked weekly, at a minimum, for accuracy.

6.4 *Calorimeter Vessel*—Made of metal with a tarnish-resistant coating, with all outer surfaces highly polished. Its size shall be such that the combustion vessel is completely immersed in water during a determination. A stirrer shall be provided for uniform mixing of the water. The immersed portion of the stirrer shall be accessible to the outside through a coupler of low thermal conductivity. The stirrer speed shall remain constant to minimize any temperature variations due to stirring. Continuous stirring for 10 min shall not raise the calorimeter temperature more than 0.01 °C when starting with identical temperatures in the calorimeter, test area, and jacket. For calorimeters having a bucket it can be a separate component or integral component of the combustion vessel. The vessel shall be of such construction that the environment of the calorimeter's entire outer boundaries can be maintained at a uniform temperature.

6.5 *Jacket*—A container with the inner perimeter maintained at constant temperature ± 0.1 °C (isoperibol) or at the same temperature ± 0.1 °C as the calorimeter vessel (adiabatic) during the test. To minimize convection, the sides, top, and bottom of the calorimeter vessel shall not be more than 10 mm from the inner surface of the jacket. Mechanical supports for the calorimeter vessel shall be of low thermal conductivity.

6.6 Thermometers:

6.6.1 *Platinum Resistance or Thermistor Thermometers* shall be capable of measuring to the nearest 0.0001 °C. These types of thermometers consist of two major subsystems. The first and most obvious is the temperature sensing probe itself. The second and equally important aspect is the measurement subsystem. For both subsystems, the relationship between the

thermometer resistance and temperature shall be well characterized. The absolute temperature shall be known to ± 0.1 °C at the temperature of the calorimetric measurement.

6.6.2 Assessing the valid working range of the calorimeter, as outlined in 10.9, is sufficient to demonstrate that all important aspects of the calorimeter functionality, including the thermometry, are in good working order. The traceability of the heat of combustion measurement is governed by the traceability of the heat of combustion of the benzoic acid calibrant in addition to meeting the aforementioned criteria.

6.6.3 *Liquid-in-Glass Thermometers*—Conforming to the requirements for thermometers S56C, S116C, or S117C as prescribed in Specification E2251.

6.6.3.1 *Thermometer Accessories*—A magnifier is required for reading liquid-in-glass thermometers to one tenth of the smallest scale division. The magnifier shall have a lens and holder designed so as to minimize errors as a result of parallax.

6.7 *Sample Holder*—An open crucible of platinum, quartz, or base metal alloy. Before use in the calorimeter, heat treat base metal crucibles for a minimum of 4 h at 500 °C to ensure the crucible surface is completely oxidized. Base metal alloy crucibles are acceptable, if after three preliminary firings, the mass does not change by more than 0.0001 g.

6.8 *Ignition Fuse*—Ignition fuse of 100 mm length and 0.16 mm [No. 34 B&S gauge] diameter or smaller. Nickel-chromium alloy (Chromel C) alloy, cotton thread, or iron wire are acceptable. Platinum or palladium wire, 0.10 mm diameter [No. 38 B&S gauge], can be used provided constant ignition energy is supplied. Use the same type and length (or mass) of ignition fuse for calorific value determinations as used for standardization.

6.9 *Ignition Circuit*—A 6 V to 30 V alternating or direct current is required for ignition purposes. A step-down transformer connected to an alternating current circuit, capacitors, or batteries can be used. 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. An ammeter or pilot light can be used in the circuit to indicate when current is flowing.

6.10 *Controller*—For automated calorimeters, capable of charging the combustion vessel; filling the calorimeter vessel; firing the ignition circuit; recording calorimeter temperatures before, during, and after the test; recording the balance weights; and carrying out all necessary corrections and calculations.

6.11 *Crucible Liner*—Quartz fiber or alundum for lining the crucible to promote complete combustion of samples that do not burn completely during the determination of the calorific value.⁴

7. Reagents

7.1 *Reagent Water*—Conforming to conductivity requirements for Type II of Specification D1193 for preparation of reagents and washing of the combustion vessel interior.

⁴ Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D05-1025. Contact ASTM Customer Service at service@astm.org.

7.2 *Purity of Reagents*—Use reagent grade chemicals conforming to the specification of the Committee on Analytical Reagents of the American Chemical Society in all tests.⁵

7.3 *Benzoic Acid—Standard (C₆H₅COOH)*—Pellets made from benzoic acid available from the National Institute of Standards and Technology (NIST) or benzoic acid calibrated against NIST standard material. The calorific value of benzoic acid, for use in the calibration calculations, shall be traceable to a recognized certificate value.

7.4 *Oxygen*—Manufactured from liquid air, guaranteed to be greater than 99.5 % pure, and free of combustible matter. Oxygen made by the electrolytic process contains small amounts of hydrogen rendering it unfit unless purified by passage over copper oxide at 500 °C.

7.5 *Titration Indicator*—Methyl orange, methyl red, or methyl purple for indicating the end point when titrating the acid formed during combustion. The same indicator shall be used for both calibration and calorific value determinations.

7.6 *Standard Solution*—Sodium carbonate (Na₂CO₃) or other suitable standard solution. A convenient standard solution may be prepared as follows. Dissolve 3.706 g of sodium carbonate, dried for 24 h at 105 °C, in water and dilute to 1 L. The resulting concentration (0.0699 *N*) assumes the energy of formation of HNO₃ under combustion vessel conditions is -59.7 kJ/mol [-14.3 kcal/mole] (see X1.1). One milliliter of this solution is equivalent to 4.2 J [1.0 cal] in the acid titration. Alternatively, 1.0 mL of a 0.1000 *N* base solution is equivalent to 6.0 J [1.4 cal] in the acid titration. In general, 1 mL of an arbitrary standard titrant solution is equivalent to its concentration (equivalents/liter or normality [*N*]) times 59.7 J [14.3 cal].

8. Hazards

8.1 The following precautions are recommended for safe calorimeter operation. Additional precautions are noted in Practice E144. Also consult the calorimeter equipment manufacturer's installation and operating instructions before using the calorimeter.

8.1.1 The mass of sample and any combustion aid as well as the pressure of the oxygen admitted to the combustion vessel shall not exceed the combustion vessel manufacturer's specifications.

8.1.2 Inspect the combustion vessel parts carefully after each use. Replace cracked or significantly worn parts. Replace O-rings and valve seats in accordance with manufacturer's instruction. For more details, consult the manufacturer.

8.1.3 Equip the oxygen supply cylinder with an approved type of safety device, such as a relief valve, in addition to the needle valve and pressure gauge used in regulating the oxygen feed to the combustion vessel. Valves, gauges, and gaskets shall meet industry safety codes. Suitable reducing valves and

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 *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.