



Designation: E 711 – 87 (Reapproved 1996)

Standard Test Method for Gross Calorific Value of Refuse-Derived Fuel by the Bomb Calorimeter¹

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1. Scope

1.1 This test method covers the determination of the gross calorific value of a prepared analysis sample of solid forms of refuse-derived fuel (RDF) by the bomb calorimeter method.

1.2 *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 cautionary and precautionary statements see 6.10 and Section 8.

2. Referenced Documents

2.1 *ASTM Standards:*

D 1193 Specification for Reagent Water²

D 3177 Test Method for Total Sulfur in the Analysis Sample of Coal and Coke³

E 1 Specification for ASTM Thermometers⁴

E 180 Practice for Determining the Precision of ASTM Methods for Analysis and Testing of Industrial Chemicals⁵

E 775 Test Methods for Total Sulfur in the Analysis Sample of Refuse-Derived Fuel⁶

E 790 Test Method for Residual Moisture in a Refuse-Derived Fuel Analysis Sample⁶

E 829 Practice for Preparing Refuse-Derived Fuels (RDF) Laboratory Samples for Analysis⁶

3. Terminology

3.1 *Definitions:*

3.1.1 *calorific value*—the heat of combustion of a unit quantity of a substance. It may be expressed in joules per gram (J/g), British thermal units per pound (Btu/lb), or calories per gram (cal/g) when required.

NOTE 1—The unit equivalents are as follows:

1 Btu (International Table) = 1055.06 absolute joules

1 Calorie (International Table) = 4.1868 absolute joules

1 Btu/lb = 2.326 J/g

1.8 Btu/lb = 1.0 cal/g

3.1.2 *gross calorific value*—the heat produced by combustion of a unit quantity of solid fuel, at constant volume, in an oxygen bomb calorimeter under specified conditions such that all water in the products remains in liquid form.

3.1.3 *net calorific value*—a lower value calculated from the gross calorific value. It is equivalent to the heat produced by combustion of a unit quantity of solid fuel at a constant pressure of one atmosphere, under the assumption that all water in the products remains in the form of vapor.

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *calorimeter*—describes the bomb, the vessel with stirrer, and the water in which the bomb is immersed.

3.2.2 *energy equivalent*—the energy required to raise the temperature (Note 2) of the calorimeter system 1°C (or 1°F) per gram of sample. This is the number that is multiplied by the corrected temperature rise in degrees and divided by the sample weight in grams to give the gross calorific value after thermochemical corrections have been applied.

NOTE 2—Temperature change is measured in thermal units. Temperature changes may also be recorded in electromotive force, ohms, or other units when other types of temperature sensors are used. Consistent units must be used in both the standardization and actual calorific determination. Time is expressed in minutes. Weights are measured in grams.

3.2.3 *refuse-derived fuels*—solid forms of refuse-derived fuels from which appropriate analytical samples may be prepared are defined as follows in ASTM STP 832:⁷

RDF-1—Wastes used as a fuel in as-discarded form with only bulky wastes removed.

RDF-2—Wastes processed to coarse particle size with or without ferrous metal separation.

RDF-3—Combustible waste fraction processed to particle sizes, 95 % passing 2-in. square screening.

RDF-4—Combustible waste fraction processed into powder form, 95 % passing 10-mesh screening.

RDF-5—Combustible waste fraction densified (compressed) into the form of pellets, slugs, cubettes, or briquettes.

⁷ *Thesaurus on Resource Recovery Terminology*, ASTM STP 832, ASTM, 1983, p. 72.

¹ This test method is under the jurisdiction of ASTM Committee D34 on Waste Management and is the direct responsibility of Subcommittee D34.06 on Recovery and Reuse.

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² *Annual Book of ASTM Standards*, Vol 11.01.

³ *Annual Book of ASTM Standards*, Vol 05.05.

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

⁵ *Annual Book of ASTM Standards*, Vol 15.05.

⁶ *Annual Book of ASTM Standards*, Vol 11.04.

4. Summary of Test Method

4.1 Calorific value is determined in this method by burning a weighed analysis sample in an oxygen bomb calorimeter under controlled conditions. The calorific value is computed from temperature observations made before and after combustion, taking proper allowance for thermometer and thermochemical corrections. Either isothermal or adiabatic calorimeter jackets may be used.

5. Significance and Use

5.1 The calorific value, or heat of combustion, is a measure of the energy available from a fuel. Knowledge of this value is essential in assessing the commercial worth of the fuel and to provide the basis of contract between producer and user.

6. Apparatus

6.1 *Test Room*—The apparatus should be operated in a room or area free of drafts that can be kept at a reasonably uniform temperature and humidity for the time required for the determination. The apparatus should be shielded from direct sunlight and radiation from other sources. Controlled room temperature and humidity are desirable.

6.2 *Oxygen Bomb*, constructed of materials that are not affected by the combustion process or products sufficiently to introduce measurable heat input or alteration of end products. If the bomb is lined with platinum or gold, all openings shall be sealed to prevent combustion products from reaching the base metal. 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 to 21 MPa (3000 psig) at room temperature without stressing any part beyond its elastic limit.

6.3 *Calorimeter*, made of metal (preferably copper or brass) 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.

6.4 *Jacket*—The calorimeter shall be completely enclosed within a stirred water jacket and supported so that its sides, top, and bottom are approximately 10 mm from the jacket walls. The jacket may be arranged so as to remain at constant temperature or with provisions for rapidly adjusting the jacket temperature to equal that of the calorimeter for adiabatic operation. It shall be constructed so that any water evaporating from the jacket will not condense on the calorimeter.

6.5 *Thermometers*—Temperatures in the calorimeter and jacket shall be measured with the following thermometers or combinations thereof:

6.5.1 *Mercury-in-Glass Thermometers*, conforming to the requirements for Thermometers 116°C or 117°C (56°F or 57°F) as prescribed in Specification E 1E 1. Other thermom-

eters of equal or better accuracy are satisfactory. These thermometers shall be tested for accuracy against a known standard (preferably by the National Bureau of Standards) at intervals no greater than 2.0°C (3.6°F) over the entire graduated scale. The maximum difference in correction between any two test points shall not be more than 0.02°C (0.04°F).

6.5.2 *Beckmann Differential Thermometer*, having a range of approximately 6°C in 0.01°C subdivisions reading upward and conforming to the requirements for Thermometer 115°C, as prescribed in Specification E 1E 1. Each of these thermometers shall be tested for accuracy against a known standard at intervals no larger than 1°C over the entire graduated scale. The maximum difference between any two test points shall not be more than 0.02°C.

6.5.3 *Calorimetric-Type Platinum Resistance Thermometer*, 25-, tested for accuracy against a known standard.

6.5.4 *Other Thermometers*—A high precision electronic thermometer employing balanced thermistors or a quartz thermometer may be used, provided the temperature rise indication is accurate within $\pm 0.003^\circ\text{C}$ per 1°C rise.

6.6 *Thermometer Accessories*—A magnifier is required for reading mercury-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. A Wheatstone bridge and galvanometer capable of measuring resistance to 0.0001 Ω are necessary for use with resistance thermometers.

6.7 *Sample Holder*—Samples shall be burned in 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 tasks.

6.8 *Firing Wire* shall be 100 mm of No. 34 B & S nickel-chromium alloy wire or 100 mm of No. 34 B & S iron wire. Equivalent platinum or palladium wire may be used provided constant ignition energy is supplied, or measured, and appropriate corrections made.

6.9 *Firing Circuit*—A 6 to 16-V alternating or direct current is required for ignition purposes with an ammeter or pilot light in the circuit to indicate when current is flowing. A stepdown transformer connected to an alternating current lighting circuit or batteries may be used.

6.10 **CAUTION:** The ignition circuit switch shall be of momentary double-contact type, normally open, except when held closed by the operator. The switch should be depressed only long enough to fire the bomb.

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.⁸ Other grades may be used, provided it is first ascertained that the reagent is of

⁸ "Reagent Chemicals, American Chemical Society Specifications," Am. Chemical Soc., Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see "Analytical Standards for Laboratory U.K. Chemicals," BDH Ltd., Poole, Dorset, and the "United States Pharmacopeia."

sufficiently high purity to permit its use without lessening the accuracy of the determination.

7.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean reagent water, Type III, conforming to Specification D 1193D 1193.

7.3 *Benzoic Acid, Standard (C₆H₅COOH)*—Use National Bureau of Standards SRM (Standard Reference Material) benzoic acid. The crystals shall be pelletized before use. Commercially prepared pellets may be used provided they are made from National Bureau of Standards 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 Bureau of Standards certificate issued with the standard.

7.4 *Methyl Orange, Methyl Red, or Methyl Purple Indicator*—may be used to titrate the acid formed in the combustion. The indicator selected shall be used consistently in both calibrations and calorific determinations.

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

7.6 *Sodium Carbonate, Standard Solution (0.34 N)*—One millilitre of this solution should be equivalent to 20.0 J in the nitric acid (HNO₃) titration. Dissolve 18.02 g of anhydrous sodium carbonate (Na₂CO₃) in water and dilute to 1 L. The Na₂CO₃ should be previously dried for 24 h at 105°C. The buret used for the HNO₃ titration shall be of such accuracy that estimations to 0.1 mL can be made. A more dilute standard solution may be used for higher sensitivity.

8. Precautions

8.1 Due to the origins of RDF in municipal waste, common sense dictates that some precautions should be observed when conducting tests on the samples. Recommended hygienic practices include use of gloves when handling RDF and washing hands before eating or smoking.

8.2 The following precautions are recommended for safe calorimeter operation:

8.2.1 The weight of solid fuel sample and the pressure of the oxygen admitted to the bomb must not exceed the bomb manufacturer's recommendations.

8.2.2 Bomb parts should be inspected carefully after each use. Threads on the main closure should be checked frequently for wear. The bomb should be returned to the manufacturer occasionally for inspection and possibly proof of firing.

8.2.3 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 codes. Suitable reducing valves and adaptors for 2 to 3.5-MPa (300 to 500-psig) discharge pressure are obtainable from commercial sources of compressed gas equipment. The pressure gage shall be checked periodically for accuracy.

8.2.4 During ignition of a sample, the operator shall not permit any portion of his body to extend over the calorimeter.

9. Sampling⁹

9.1 RDF products are frequently nonhomogeneous. For this reason significant care should be exercised to obtain a representative laboratory sample for the RDF lot to be characterized.

9.2 The sampling method for this procedure should be based on agreement between the involved parties.

9.3 The laboratory sample must be air-dried and particle size reduced to pass a 0.5-mm screen as described in Practice E 829E 829.

10. Standardization

10.1 Determine the energy equivalent of the calorimeter as the average of a series of ten individual runs, made over a period of not less than 3 days or more than 5 days. To be acceptable, the standard deviation of the series shall be 6.9 kJ/°C (6.5 Btu/°C) or less (see Appendix X1, Table X1.1). For this purpose, any individual run may be discarded only if there is evidence indicating incomplete combustion. If this limit is not met, repeat the entire series until a series is obtained with a standard deviation below the acceptable limit.

10.2 The weights of the pellets of benzoic acid in each series should be regulated to yield the same temperature rise as that obtained with the various samples tested in the individual laboratories. The usual range of weight is 0.9 to 1.3 g. Make each determination in accordance with the procedure described in Section 11, and compute the corrected temperature rise, T , as described in 12.1. Determine the corrections for HNO₃ and firing wire as described in 12.2 and substitute into the following equation:

$$E = [(H)(g) + e_1 + e_3 + e_4] \times t \quad (1)$$

where:

E = energy equivalent, J/°C,

H = heat of combustion of benzoic acid, as stated in the National Bureau of Standards certificate, J/g,

g = weight of benzoic acid, g,

t = corrected temperature rise, °C,

e_1 = titration correction, J,

e_3 = fuse wire correction, J, and

e_4 = correction for ignition energy if measured and corrected for, J.

10.3 Standardization tests should be repeated after changing any part of the calorimeter and occasionally as a check on both calorimeter and operating technique.

11. Procedure

11.1 *Weight of Sample*—Thoroughly mix the analysis sample of solid fuel in the sample bottle, taking care that the heavies and lights (fluff) are distributed in the sample (Note 3). Carefully weigh approximately 1 g of the sample directly into the crucible in which it is to be burned or into a tared weighing scoop from which the sample is transferred to the crucible. Weigh the sample to the nearest 0.1 mg. Some form of compaction may be necessary to ensure satisfactory ignition and complete combustion.

⁹ ASTM Subcommittee E38.01 is currently in the process of developing procedures for sampling RDF-3 and the preparation of an analysis sample. The chairman of E38.01 should be contacted for details.

NOTE 3—In the event segregation of the heavies and lights cannot be avoided, attempt to remove sample from the bottle in such a way that a representative sample is transferred.

NOTE 4—Perform the residual moisture determination of the sample simultaneously using Test Method E 790E 790.

11.2 *Water in Bomb*—Add 1.0 mL of water to the bomb by a pipet. Before adding this water, rinse the bomb, and drain the excess water, and leave undried.

11.3 *Firing Wire*—Connect a measured length of firing wire to the ignition terminals with enough slack to allow the firing wire to maintain contact with the sample.

11.4 *Oxygen*—Charge the bomb with oxygen to a consistent pressure between 20 and 30 atm (2.03 and 3.04 MPa). This pressure must remain the same for each calibration and for each calorific determination. If, by accident, the oxygen introduced into the bomb should exceed the specified pressure, do not proceed with the combustion. Detach the filling connection and exhaust the bomb in the usual manner. Discard this sample.

11.5 *Calorimeter Water*—It is recommended that calorimeter water temperature be adjusted before weighing as follows:

11.5.1 *Isothermal Jacket Method*, 1.6 to 2.0°C (3.0 to 3.5°F) below jacket temperature (Note 4).

11.5.2 *Adiabatic Jacket Method*, 1.0 to 1.4°C (2.0 to 2.5°F) below room temperature.

NOTE 5—This initial adjustment will ensure a final temperature slightly above that of the jacket for calorimeters having an energy equivalent of approximately 10 200 J/K (2450 cal/°C). Some operators prefer a lower initial temperature so that the final temperature is slightly below that of the jacket. This procedure is acceptable, provided it is used in all tests, including standardization. Use the same amount (± 0.5 g) of water in the calorimeter vessel for each test and for calibration. The amount of water (2000 g is usual) can be most satisfactorily determined by weighing the calorimeter vessel and water together on a balance. The water may be measured volumetrically if it is always measured at the same temperature. Tap water may be satisfactory for use in calorimeter bucket.

11.6 *Observations, Isothermal Jacket Method*—Assemble the calorimeter in the jacket and start the stirrer. Allow 5 min for attainment of equilibrium; then record the calorimeter temperatures (Note 6) at 1-min intervals for 5 min. Fire the charge at the start of the sixth minute and record the time and temperature, T^a . Add to this temperature 60 % of the expected temperature rise, and record the time at which the 60 % point is reached (Note 5). After the rapid-rise period (about 4 to 5 min), record temperatures at 1-min intervals on the minute until the difference between successive readings has been constant for 5 min.

NOTE 6—Use a magnifier and estimate all readings (except those during the rapid rise period) to the nearest 0.002°C (0.005°F) when using ASTM Bomb Calorimeter Thermometer 56C (56F). Estimate Beckmann thermometer readings to the nearest 0.001°C. Tap mercurial thermometers with a pencil just before reading to avoid errors caused by mercury sticking to the walls of the capillary.

NOTE 7—When the approximate expected rise is unknown, the time at which the temperature reaches 60 % of the total can be determined by recording temperatures at 45, 60, 75, 90, and 105 s after firing and interpolating.

11.7 *Observations, Adiabatic Jacket Method*—Assemble the calorimeter in the jacket and start the stirrer. Adjust the jacket temperature to be equal to or slightly lower than the

calorimeter, and run for 5 min to obtain equilibrium. Adjust the jacket temperature to match the calorimeter with $\pm 0.01^\circ\text{C}$ (0.02°F) and hold for 3 min. Record the initial temperature (Note 6) and fire the charge. Adjust the jacket temperature to match that of the calorimeter during the period of rise, keeping the two temperatures as nearly equal as possible during the rapid rise, and adjusting to within $\pm 0.01^\circ\text{C}$ (0.02°F) when approaching the final equilibrium temperature. Take calorimeter readings at 1-min intervals until the same temperature is observed in three successive readings. Record this as the final temperature. Do not record time intervals since they are not critical in the adiabatic method.

11.8 *Analysis of Bomb Contents*—Remove the bomb and release the pressure at a uniform rate, in such a way that the operation will require not less than 1 min. Examine the bomb interior and discard the test if unburned sample or sooty deposits are found. Carefully wash the interior of the bomb including the capsule with distilled or deionized water containing the titration indicator until the washings are free of acid. Collect the washings in a beaker and titrate the washings with standard carbonate solution. Remove and measure or weigh the combined pieces of unburned firing wire, and subtract from the original length or weight to determine the wire consumed in firing. Determine the sulfur content of the sample by any of the procedures described in Test Methods E 775E 775.

12. Calculation

12.1 *Temperature Rise in Isothermal Jacket Calorimeter*—Using data obtained as prescribed in 11.6, compute the temperature rise, T , in an isothermal jacket calorimeter as follows:

$$T = T_c - T_a - r_1(b - a) - r_2(c - b) \quad (2)$$

where:

- T = corrected temperature rise,
- a = time of firing,
- b = time (to nearest 0.1 min) when the temperature rise reaches 60 % of total,
- c = time at beginning of period in which the rate of temperature change with time has become constant (after combustion),
- T_a = temperature at time of firing, corrected for thermometer error (Note 7),
- T_c = temperature at time c , corrected for thermometer error (Note 7),
- r_1 = rate (temperature units per minute) at which temperature was rising during 5-min period before firing, and
- r_2 = rate (temperature units per minute) at which temperature was rising during the 5-min period after time c . If the temperature is falling, r_2 is negative and the quantity $r_2(c - b)$ is positive.

12.2 *Temperature Rise in Adiabatic Jacket Calorimeter*—Using data obtained as prescribed in 11.7 compute the corrected temperature rise, T , as follows:

$$T = T_f - T_a \quad (3)$$

where:

- T = corrected temperature rise, °C or °F,