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Document Name: ASTM E711: Standard Test Method for Gross Calorific Value of Refuse-Derived Fuel by the Bomb Calorimeter

CFR Section(s): 40 CFR 63, Subpart DDDDD, Table 6

Standards Body: American Society for Testing and Materials

APPROVED

Official Incorporator:

THE EXECUTIVE DIRECTOR
OFFICE OF THE FEDERAL REGISTER
WASHINGTON, D.C.

Designation: E 711 – 87 (Reapproved 1992)

Standard Test Method for Gross Calorific Value of Refuse-Derived Fuel by the Bomb Calorimeter[1]

This standard is issued under the fixed designation E 711; 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 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 problems, 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 Water[2]

D 3177 Test Method for Total Sulfur in the Analysis Sample of Coal and Coke[3]

E 1 Specification for ASTM Thermometers[4]

E 180 Practice for Determining the Precision of ASTM Methods for Analysis and Testing of Industrial Chemicals[5]

E 775 Test Methods for Total Sulfur in the Analysis Sample of Refuse-Derived Fuel[6]

E 790 Test Method for Residual Moisture in a Refuse-Derived Fuel Analysis Sample[6]

E 829 Practice for Preparing Refuse-Derived Fuels (RDF) Laboratory Samples for Analysis[6]

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 *Descriptions of Terms Specific to This Method*:

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.

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.

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[1] This test method is under the jurisdiction of ASTM Committee D-34 on Waste Management and is the direct responsibility of Subcommittee D34.08 on Thermal Treatment.

Current edition approved Aug. 28, 1987. Published October 1987.

[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.

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

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 1. Other thermometers 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 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 ±0.003°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 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 1193.

7.3 *Benzoic Acid, Standard (C_6H_5COOH)*—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.

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[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 "Analar Standards for Laboratory U.K. Chemicals," BDH Ltd., Poole, Dorset, and the "United States Pharmacopeia."

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 (HNO_3) titration. Dissolve 18.02 g of anhydrous sodium carbonate (Na_2CO_3) in water and dilute to 1 L. The Na_2CO_3 should be previously dried for 24 h at 105°C. The buret used for the HNO_3 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. Sampling[9]

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 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). 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 HNO_3 and firing wire as described in 12.2 and substitute into the following equation:

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

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.

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 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.

[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.

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 ±0.01°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 ±0.01°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 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:

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

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

$$T = T_f - T_a$$

where:

T = corrected temperature rise, °C or °F,
T_a = initial temperature when charge was fired, corrected for thermometer error (Note 8), and
T_f = final temperature corrected for thermometer error.

NOTE 8—With all mercury-in-glass thermometers, it is necessary to make the following corrections if the total heat value is altered by 12 J/g or more. This represents a change of 0.001°C (0.002°F) in a calorimeter using approximately 2000 g of water. The corrections include the calibration correction as stated on the calibration certificate, the setting correction for Beckman thermometers according to the directions furnished by the calibration authority, and the correction for emergent stem. Directions for these corrections are given in Appendix X2.

12.3 *Thermochemical Corrections* (Appendix X3)—Compute the following for each test:

e_1 = correction for the heat of formation of HNO_3, J. Each millilitre of standard alkali is equivalent to 20.0 J.
e_2 = correction for heat of formation of H_2SO_4, J
= 55.2 × percent of sulfur in sample × weight of sample, g.
e_3 = correction for heat of combustion of firing wire, J (Note 10)
= 9.6 J/cm or 5980 J/g for No. 34 B & S gage Chromel C
= 11.3 J/cm or 7330 J/g for No. 34 B & S iron wire.
e_4 = correction for ignition energy of platinum or palladium if measured and corrected for.

NOTE 9—There is no correction for platinum or palladium wire, provided the ignition energy is constant.

12.4 *Calorific Value*:

12.4.1 Calculate the gross calorific value (gross heat of combustion) as follows:

$$H_s = [(T)(E) - e_1 - e_2 - e_3 - e_4]/g$$

where:

H_s = gross calorific value, J/g,
T = corrected temperature rise as calculated in 12.1 or 12.2, °C or °F, consistent with the water equivalent value,
E = energy equivalent (see Section 10),
e_1, e_2, e_3, e_4 = corrections as prescribed in 12.3, and
g = weight of sample, g.

12.4.2 Calculate the net calorific value (net heat of combustion) as follows:

$$H_i = H_s - 23.96\ (H \times 9)$$

where:

H_i = net calorific value (net heat of combustion), J/g,
H_s = gross calorific value (gross heat of combustion), J/g, and
H = total hydrogen, %.

13. Precision and Bias[10]

13.1 *Precision*—The standard deviations of individual determinations, in Btu/lb, are:

Average	Within-laboratory	Between-laboratories
HHV-1:		
6400	27.1	135.5
5200	48.8	239.6
HHV-2:		
7900	32.3	118.0
7400	38.1	227.8
HHV-3:		
9700	111.3	290.4
9500	99.2	249.2
9300	40.3	67.6

13.2 These precision estimates are based on an interlaboratory study conducted in accordance with Practice E 180.

[10] Supporting data are available on loan from ASTM Headquarters. Request RR:E38-1000.

APPENDIXES

(Nonmandatory Information)

X1. CALCULATION OF STANDARD DEVIATIONS FOR CALORIMETER STANDARDIZATION

X1.1 The example given in Table X1.1 illustrates the method of calculating standard deviations for calorimeter standardizations.

TABLE X1.1 Standard Deviations for Calorimeter Standardization[A]

Standardization Number	Column A Water Equivalent, (Btu/lb) × (g/°C)	Column B Code to 4400 (Column A-4400)	Column C (Column B)²
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

Average = $\bar{x}^2$ = x/10 = (92/10) + 4400 = 4409
Variance = s^2 = Column C − (Column B)²/n/n − 1 = 940 − (92)²/10/9 = 10.4
Standard deviation, s = Variance = 10.4 = 3.22

[A] In this example the values of water equivalent are typical for a calorimeter calibrated such that the water equivalent multiplied by the temperature rise in °C/g of sample will give the calorific value of the sample in Btu/lb.

X2. THERMOMETER CORRECTIONS

X2.1 It is necessary to make the following corrections in the event they result in an equivalent change of 0.001°C or more.

X2.1.1 *Calibration Correction* shall be made in accordance with the calibration certificate furnished by the calibration authority.

X2.1.2 *Setting Correction* is necessary for the Beckmann thermometer. It shall be made in accordance with the directions furnished by the calibration authority.

X2.1.3 *Differential Emergent Stem Correction*—The calculation depends upon the way the thermometer was calibrated and how it is used. The following two conditions are possible:

(*a*) *Thermometers Calibrated in Total Immersion and Used in Partial Immersion*—This emergent stem correction is made as follows:

$$\text{Correction} = K(t_c - t_a)(t_c + t_a - L - T)$$

where:

K = 0.00016 for thermometers calibrated in °C,
0.00009 for thermometers calibrated in °F,
L = scale reading to which the thermometer was immersed,
T = mean temperature of emergent stem,
t_a = initial temperature reading, and
t_c = final temperature reading.

NOTE X2.1: *Example*—Suppose the point L, to which the thermometer was immersed was 16°C; its initial reading, t_a, was 24.127°C, its final reading, t_c, was 27.876°C, the mean temperature of the emergent stem, T, was 26°C,

then:

Differential stem correction

$$= +0.00016\ (28 - 24)\ (28 + 24 - 16 - 26)$$
$$= + 0.006°\text{C}$$

(*b*) *Thermometers Calibrated and Used in Partial Immersion but at a Different Temperature than the Calibration Temperature*—This emergent stem correction is made as follows:

$$\text{Correction} = K(t_c - t_a)(t_1 - t^{\circ})$$

where:

K = 0.00016 for thermometers calibrated in °C,
0.00009 for thermometers calibrated in °F,
t_a = initial temperature reading,
t_c = final temperature reading,
t_1 = observed stem temperature, and
t° = stem temperature at which the thermometer was calibrated.

NOTE X2.2: *Example*—Suppose the initial reading, t_a, was 80°F, the final reading, t_c, was 86°F, and that the observed stem temperature, t_1, was 82°F, and the calibration temperature, t°, was 72°F; then:

Differential stem correction

$$= 0.00009\ (86 - 90)(82 - 72)$$
$$= 0.005°\text{F}$$

X3. THERMOCHEMICAL CORRECTIONS

X3.1 *Heat of Formation of Nitric Acid*—A correction (e^1, in 12.3) of 20 J is applied for each 1 mL of standard Na_2CO_3 solution used in the acid titration. The standard solution (0.34 *N*) contains 18.02 g of Na_2CO_3/L. This correction is based on assumption that all the acid titrated is HNO_3 formed by the following reaction: ½ N_2 (g + 5⁄4 O_2 (g) + ½ H_2O (l) = HNO_3 (in 500 mol H_2O), and (*2*) the energy of formation of 1 mol of HNO_3 is approximately 500 mol of water under bomb conditions is 14.1 kcal/mol.[6] When H_2SO_4 is also present part of the correction for H_2SO_4 is contained in the e_1 correction and the remainder in the e_2 correction.

X3.2 *Heat of Formation of Sulfuric Acid*—By definition the gross calorific value is obtained when the product of the combustion of sulfur in the sample is SO_2 (g). However, in actual bomb combustion processes, the sulfur is found as H_2SO_4 in the bomb washings. A correction (e_2 in 12.4.1) of 55.2 J is applied for each percent of sulfur in the 1-g sample, that is converted to H_2SO_4. This correction is based upon the energy of formation of H_2SO_4 in solutions such as will be present in the bomb at the end of a combustion. This energy is taken as −70.5 kcal/mol.[11] A correction, of 2 × 14.1 kcal/mol of sulfur was applied in the e_1 correction, so the additional correction necessary is 70.5 − (2 × 14.1) = 42.3 kcal/mol or 5520 J of sulfur in the sample (55.2 J × weight of sample in grams × % sulfur in sample).

X3.2.1 The value of 5520 J/g of sulfur is based on a coal containing about 5 % sulfur and about 5 % hydrogen. The assumption is also made that the H_2SO_4 is dissolved entirely in water condensed during combustion of the sample.[12] If a 1-g sample of such a fuel is burned, the resulting H_2SO_4 condensed with water formed on the walls of the bomb will have a ratio of about 15 mol of water to 1 mol of H_2SO_4. For this concentration the energy of the reaction.

$$SO_2\ (g) + ½O_2\ (g) + H_2O\ (l) = H_2SO_4\ (\text{in 15 mol } H_2O)$$

under the conditions of the bomb process is −70.5 kcal/mol.

X3.2.2 Basing the calculation upon a sample of comparatively large sulfur content reduces the overall possible errors, because for smaller percentages of sulfur the correction is smaller.

X3.3 *Fuse Wire*—Calculate the heat in SI units contributed by burning the fuse wire in accordance with the directions furnished by the supplier of the wire. For example, the heat of combustion of No. 34 B & S gage Chromel C wire

[11] Calculated from data in National Bureau of Standards Circular 500.

[12] Mott, R. A., and Parker, C., "Studies in Bomb Calorimetry IX-Formation of Sulfuric Acid," *Fuel*, Vol 37, 1958, p. 371.

is equivalent to 9.6 J/cm or 5980 J/g and that of No. 34 B & S gage iron wire is equivalent to 11.3 J/cm or 7330 J/g. There is no correction for platinum or palladium wire provided the ignition energy is constant.

X4. REPORTING RESULTS IN OTHER UNITS

X4.1 *Reporting Results in British Thermal Units (Btu) per Pound*—The gross calorific value can be expressed in British thermal units by using the thermochemical correction factors in Table X4.1 and the water equivalent expressed in (Btu/lb) × (g/°C).

TABLE X4.1 Thermochemical Correction Factors (Units in BTU)

Correction	Multiplication Factor	Multiply by
e_1 (HNO_3)	10.0	mL of 0.394 *N* Na_2CO_3 solution
e_2 (H_2SO_4)	23.7	% of sulfur in sample times weight of sample in grams
e_3 (fuse wire)	4.1 or	cm of No. 34 B & S gage Chromel C wire
	2570	weight (g) of Chromel C wire
e_3 (fuse wire)	4.9 or	cm of No. 34 B & S gage iron wire
	3150	weight (g) of iron wire

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