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Standard Test Method for Gross Calorific and Ash Value of Waste Materials¹

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1. Scope

1.1 This test method covers the determination of the gross calorific value of waste materials by either an isoperibol, aneroid, air-jacketed isoperibol, or adiabatic bomb calorimeter using electronic temperature sensors, automatic calorimeter controllers, and subsequent analysis of the residue for ash. After calorific analysis, the bomb washings may be collected for subsequent elemental analysis.

1.2 The values stated in SI units are regarded as the standard.

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.* Specific hazard statements are given in Section 8.

2. Referenced Documents

2.1 *ASTM Standards:*²

D 121 Terminology of Coal and Coke

D 240 Test Method for Heat of Combustion of Liquid Hydrocarbon Fuels by Bomb Calorimeter

D 1018 Test Method for Hydrogen in Petroleum Fractions

D 1193 Specification for Reagent Water

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

D 4239 Test Method for Sulfur in the Analysis Sample of Coal and Coke Using High Temperature Tube Furnace Combustion Methods

E 144 Practice for Safe Use of Oxygen Combustion Bombs

3. Terminology

3.1 *Definitions:*

3.1.1 *calorific value*—the heat produced by combustion of a unit quantity of a specimen under specified conditions. It is expressed in this test method in joules per kilogram (J/kg). Calorific value may also be expressed in calories per gram (cal/g) or in the British thermal units per pound (Btu/lb), when required. The unit equivalents are given in Table 1.

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

3.1.2.1 *adiabatic calorimeter*—a calorimeter that has a jacket temperature adjusted to follow the calorimeter temperature as closely as possible so as to maintain zero thermal head.

3.1.2.2 *calorimeter jacket*—the insulating medium surrounding the calorimeter.

3.1.2.3 *isoperibol calorimeter*—the calorimeter has a jacket of uniform and constant temperature.

3.1.3 *gross calorific value (gross heat of combustion), Q_v (gross)*—the heat produced by combustion of unit quantity of a solid or liquid fuel when burned at constant volume in an oxygen bomb calorimeter under specified conditions with the resulting water condensed to a liquid.

3.1.4 *heat capacity*—the quantity of heat required to raise a system one degree in temperature either at constant volume or constant pressure.

3.1.5 *heat of formation*—the increase in heat content resulting from the formation of 1 mole of a substance from its elements at constant pressure.

3.1.6 *net calorific value (net heat of combustion at constant pressure), Q_p* —the heat produced by combustion of unit quantity of a solid or liquid fuel when burned at a constant pressure of 0.1 MPa (1 atm), under conditions such that all the water in the products remain in the form of vapor.

3.1.7 *static calorimeter*—a calorimeter without a thermostated jacket.

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *corrected temperature rise*—the temperature of the calorimeter caused by the process that occurs inside the bomb, which is, the observed temperature change corrected for various effects.

3.2.2 *heat capacity, energy equivalent, or water equivalent*—the energy required to raise the temperature of the calorimeter one arbitrary unit. This is the quantity that, when

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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.

TABLE 1 Calorific Value

1 Btu = 1055.06 J	1 J/g = 0.430 Btu/lb
1 cal ^A = 4.1868 J	1 J/g = 0.239 cal/g

^A International tables calorie.

multiplied by the corrected temperature, rises, then when adjusted for extraneous heat effects and divided by the mass of the sample, gives the gross calorific value.

4. Summary of Test Method

4.1 Calorific value is determined in this test method by burning a weighed sample under controlled conditions, in oxygen, in a calibrated calorimeter. The calorimeter is standardized by burning a specified amount of benzoic acid. The calorific value of the test specimen is computed from temperature observations made before, during, and after combustion and making proper allowances for heat contribution by other processes.

4.2 After disassembly of the bomb, estimate the ash content by one of two of the following procedures:

4.2.1 Dry the fuel capsule at 200°C for 5 to 10 min and weigh to provide an estimation of the ash content of the waste material.

4.2.2 Wipe any moisture from the exterior surface of the capsule and weigh to provide an estimation of the ash content of the waste material.

5. Significance and Use

5.1 This test method is used to compute the calorific value and estimated ash content of the waste material represented by the sample for incineration purposes or as fuel for cement kilns.

5.2 The gross calorific and ash value may be used for evaluating the effectiveness of any beneficiation process.

6. Apparatus and Facilities

6.1 *Test Room*—A room or area free from drafts and that can be kept at a constant temperature equal to $\pm 3^\circ\text{C}$, for all calorimetric tests. 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 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. 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 shall be checked for accuracy at the beginning of each week that the calorimeter tests will be made.

6.4 *Calorimeter Vessel (Bucket)*—Made of metal with a tarnish-resistant coating, with all outer surfaces highly polished. For calorimeters having a bucket it may be a separate

component or integral component of the bomb. It shall be of such construction that the environment of the calorimeter's entire outer boundaries is maintained at a uniform temperature.

6.5 *Jacket*—An insulated container that keeps the inner perimeter of the jacket at constant temperature (isoperibol), or at the same temperature as the calorimeter (adiabatic), or is monitored continuously for temperature changes (aneroid).

6.6 *Temperature Sensing Device*—Thermometers such as platinum resistance, thermistors, or mercurial thermometers are satisfactory and may be used if properly calibrated.

NOTE 1—Temperature is measured in either degrees Celsius, degrees Fahrenheit, ohms, or other arbitrary units instead of degrees. Consistent units must be used in standardization and the actual calorific value determination.

6.7 *Sample Holder*—An open crucible of platinum, quartz, or acceptable base-metal alloy. The base metal crucibles should be heat-treated for 24 h at 500°C to ensure the capsules are completely oxidized.

6.8 *Ignition Fuse*—The ignition fuse shall be 100 mm of 0.16-mm diameter or smaller (No. 34 B & S gage), nickel-chromium alloy (Chromel C) alloy, platinum, cotton thread, or iron wire. The same length or mass of ignition fuse shall be used for all calibrations and calorific value determinations.

6.9 *Firing Circuit*—A 6 to 24-V alternating or direct current is required for ignition purposes. A step-down transformer connected to an alternating current lighting circuit, capacitors, or batteries may be used.

6.10 *Buret*—Used for the acid titration and shall have 0.1 mL divisions.

6.11 *Gelatin Capsules or Cellulose Tape*—Used to minimize vaporization of volatile samples. These items should be halogen free.

6.12 *pH Titrators or mV Meters*—May be used for pH titration of wash solution.

7. Reagents

7.1 *Reagent Water*—Conforming to conductivity requirements for Type II of Specification **D 1193**, it shall be used for preparation of reagents and washing of the bomb interior.

7.2 *Purity or Reagents*—Reagent-grade chemicals conforming to the specifications of the Committee on Analytical Reagents of the American Chemical Society shall be used in all tests.³

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

7.4 *Methyl Orange, Methyl Red, or Methyl Purple Indicator*—May be used to titrate the acid formed during

³ *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. Pharmaceutical Convention, Inc. (USPC), Rockville, MD.

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, shall be used. Oxygen made by the electrolytic process may contain a small amount of hydrogen, rendering it unfit without purification by passage over copper oxide at 500°C.

7.6 *Standard Solution*—Sodium carbonate (Na₂CO₃) or other suitable standard solution. 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 4.2 J (1.0 cal) in the acid titration when the entire rinse solution is used as the analytical sample. Alternatively, the titrant volume is to be corrected by the volume fraction of the rinse that is used as the analytical sample. (See 10.4.2.)

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 waste 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. When halogenated organic compounds are being tested, replace all O-rings and valve seats after 100 firings. If no halogenated organic compounds are being tested, replace all O-rings and valve seats after 500 firings. At least every 3000 firings, check the bomb for thread wear on any closures or return to the manufacturer for these tests. These are recommendations for worst case situations. For more details, contact the manufacturer.

8.4 Equip 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 feed 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 over pressures that reach maximum gage pressure.

8.5 During ignition of a sample, the operator must not permit any portion of the operator’s body to extend over the calorimeter.

8.6 Exercise extreme caution not to exceed the bomb manufacturer’s recommendations and to avoid damage to the bomb when combustion aids are employed. Do not fire loose fluffy material, such as unpelleted benzoic acid, unless thoroughly mixed with the 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.

8.8 When volatile materials are present, explosive firings can result and the procedure in 12.2 should be followed.

9. Sampling

9.1 The sample shall be representative of the material of interest (see Appendix X3).

10. Standardization

10.1 The calorimeter is standardized by combustion of benzoic acid.

10.2 Determine heat capacity as the average of a minimum of 6 individual runs made over a period of not less than 3 days nor more than 5 days. To be acceptable for highprecision work, the relative standard deviation of the series shall be 0.15 % or less. See Table 2. For users of static-type calorimeters, an acceptable relative standard deviation would be 0.40 % or less. For this purpose, any individual test may be discarded only if there is evidence of incomplete combustion. If this limit is not met, the entire series shall be repeated until a series is obtained with a relative standard deviation below the acceptable limit.

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 the waste specimen tested in the same laboratory. 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 weight.

10.3.2 Rinse the bomb with water to lubricate internal seals and dry surfaces. Add approximately 1 mL of water or desired amount of other appropriate solution (see Note 2) to the bomb prior to assembly for a test.

NOTE 2—If the washing will be used for elemental analysis, then add 5 mL of a 10 % sodium carbonate solution or other solution of desired amount rather than 1 mL of water to the bomb prior to assembly for both standardization and analysis procedures.

10.3.3 Connect a measured fuse to the ignition terminals, in accordance with the manufacturer’s guidelines. (See 6.8.)

10.3.4 Assemble the bomb and charge it with oxygen to a consistent pressure of 3 MPa (30 atm). Lower charging pressures may be used if they will not result in incomplete combustion as evident by visual inspection for carbon residues

TABLE 2 Standard Deviations for Calorimeter Standardization

NOTE 1—Average = X = 10253.5.

NOTE 2—Variance =

$$s^2 = \frac{\text{Sum Column C} - [(\text{Sum Column B})^2/n]}{n - 1} = 26.34$$

NOTE 3—Standard Deviation = s = √variance = √26.34 = 5.14.

Standardization Number	Column A	Column B	Column C
	Energy Equivalent, J/°C	Difference from Average	(Column B) ²
1	10257.7	4.2	17.6
2	10249.3	4.2	17.6
3	10270.2	16.7	278.9
4	10253.5	0	0
5	10245.1	8.4	70.6
6	10249.3	4.2	17.6
7	10240.9	12.6	158.8
8	10266.0	12.5	156.3
9	10257.7	4.2	17.6
10	10245.1	8.4	70.6
SUM		75.4	805.6

or the formation of carbon monoxide rather than carbon dioxide. 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, detach the filling connection and exhaust the bomb in the usual manner, then discard the sample and bucket of water. Transfer the bucket, bomb, and calorimeter water to the jacket. Finish assembly of the apparatus and start the calorimeter. The calorimeter initial water temperature shall be at the same temperature $\pm 0.5^\circ\text{C}$ for every determination. The calorimeter monitors and determines whether the calorimeter has been constant over a period of 30 s. For adiabatic calorimeters with microprocessor control this stability requirement is 10^{-3}°C , and it is 10^{-3}°C/s or better for the isoperibol calorimeter with microprocessor control.

NOTE 3—The initial temperature adjustment will ensure a final temperature slightly below that of the jacket for isoperibol calorimeters.

10.3.5 Temperature Observations:

10.3.5.1 *Observations (Extrapolation Method)*—The controller will fire the charge, record the temperature rise, and correct the temperature rise for any appropriate heat leak corrections as recommended or defined, or both, by the instrument manufacturer. The controller may terminate the test when the observed thermal curve matches the manufacturer's thermal curve, which allows extrapolation to a final temperature. The extrapolated temperature rise should have a maximum uncertainty of $\pm 0.002^\circ\text{C}$.

10.3.5.2 *Observations (Full Development Method)*—The controller will fire the bomb and record the temperature rise until the temperature has stabilized for a period of 30 s.

10.3.5.3 *Manual Full Development Method*—Fire the charge at time a and record this temperature as t_a . For adiabatic calorimeters record subsequent readings at intervals no greater than 1 min until the difference between 3 or more pairs of successive readings are the same. For isoperibol calorimeters record the subsequent readings until the difference between 3 or more pairs of successive readings are the same within 1 millidegree per min. Record the time of stabilization as c and the final temperature as t_c , the first reading after the rate of change has become uniform.

10.3.6 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. Unburned samples or sooty deposits are indications of incomplete combustion possibly due to high-ash content or high-moisture content, or both. The results are suspect and generally require combustion aid such as ethylene glycol for water-based compounds or mineral oil for high-ash content compounds. When combustion aids are used, be sure heat liberation for any test meets the calorimeter manufacturer's guidelines. Discard the test if unburned sample or sooty deposits are found. Use the manufacturer's recommended constant value for acid correction or wash the interior of the bomb with distilled water containing the titration indicator until the washings are free of acid. Rinse only the exterior of the fuel capsule, taking care not to disturb the ash residue in the

fuel capsule. Titrate the washings with standard solution as defined under reagents, or titrate with pH meter.

10.3.7 Use the manufacturer's recommended constant value or remove and measure, or weigh, the combined pieces of unburned ignition (firing) wire and subtract from the original length or weigh 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. When cotton thread fuse is used, use the manufacturer's recommended calorific correction.

10.4 Calculations:

10.4.1 *Temperature Rise*—Where applicable use data obtained as prescribed in 10.3.5; compute the corrected temperature rise, t , as follows:

$$t = t_c - t_a + C_r \quad (1)$$

where:

- t = corrected temperature rise, $^\circ\text{C}$ ($^\circ\text{F}$),
- t_a = initial temperature reading at time of firing,
- t_c = final temperature reading, and
- C_r = radiation correction (see A1.1.3).

10.4.2 *Thermochemical Corrections (see Appendix X1)*—Compute the following for each test:

e_1 = correction for the heat of formation of HNO_3 , in joules. Each millilitre of standard Na_2CO_3 is equivalent to 4.2 J (1.0 cal) and may be considered to be a constant value as recommended by the calorimeter manufacturer.

e_2 = correction for heat of combustion of firing fuse, in joules, or may be considered to be a constant value as recommended by the calorimeter manufacturer.

$e_2 = 0.96 \text{ J/mm}$ (0.23 cal/mm) or 5.9 J/mg (1.4 cal/mg) for No. 34 B&S gage Chromel C.

$e_2 = 1.13 \text{ J/mm}$ (0.27 cal/mm) or 7.5 J/mg (1.8 cal/mg) for No. 34 B&S gage iron wire.

10.4.3 Compute the calorimeter heat capacity by substituting in the following:

$$E = [(H_c m) + e_1 + e_2]/t \quad (2)$$

where:

- E = calorimeter heat capacity,
- H_c = heat of combustion of benzoic acid, as stated in the NIST Certificate, J/kg in air,
- m = mass (weight in air) of benzoic acid, g,
- e_1 = titration correction (10.4.2),
- e_2 = fuse correction (10.4.2), and
- t = corrected temperature rise (10.4.1).

For sample calculations, see Appendix X4.

10.5 Repeat the procedure for a total of ten standardizations or a minimum of six standardizations. Compute the standard deviation as illustrated in Table 2. (The percent relative standard deviation is the standard deviation times 100 and divided by the average value.)

11. Restandardization

11.1 Make checks on the heat capacity value, after changing any part of the bomb or calorimeter, at a minimum of at least once a month.