



Designation: D 5865 – 03

## Standard Test Method for Gross Calorific Value of Coal and Coke<sup>1</sup>

This standard is issued under the fixed designation D 5865; 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 approval. A superscript epsilon ( $\epsilon$ ) 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 bomb calorimeter.

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:

- D 121 Terminology of Coal and Coke<sup>2</sup>
- D 346 Practice for Collection and Preparation of Coke Samples for Laboratory Analysis<sup>2</sup>
- D 388 Classification of Coals by Rank<sup>2</sup>
- D 1193 Specification for Reagent Water<sup>3</sup>
- D 2013 Practice for Preparing Coal Samples for Analysis<sup>2</sup>
- D 3173 Test Method for Moisture in the Analysis Sample of Coal and Coke<sup>2</sup>
- D 3177 Test Method for Total Sulfur in the Analysis Sample of Coal and Coke<sup>2</sup>
- D 3180 Practice for Calculating Coal and Coke Analyses from As-Determined to Different Bases<sup>2</sup>
- D 4239 Test Methods for Sulfur in the Analysis Sample of Coal and Coke Using High Temperature Tube Furnace Combustion Methods<sup>2</sup>
- D 5142 Test Methods for Proximate Analysis of the Analysis Sample of Coal and Coke by Instrumental Procedures<sup>2</sup>
- E 1 Specification for ASTM Thermometers<sup>4</sup>

E 144 Practice for Safe Use of Oxygen Combustion Bombs<sup>5</sup>

E 178 Practice for Dealing with Outlying Observations<sup>6</sup>

### 3. Terminology

#### 3.1 Definitions:

3.1.1 *adiabatic calorimeter*—a calorimeter which has a jacket temperature adjusted to follow the calorimeter temperature so as to maintain zero thermal head.

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

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

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

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

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

3.1.7 *isoperibol calorimeter*—a calorimeter which has a jacket of uniform and constant temperature.

3.1.8 *net calorific value (net heat of combustion at constant pressure),  $Q_p$  (net)*—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.

#### 3.2 Definitions of Terms Specific to This Standard:

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

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

<sup>1</sup> 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.

Current edition approved April 10, 2003. Published June 2002. Originally published in 1995. Last previous edition approved in 2002 as D 5865–02.

<sup>2</sup> *Annual Book of ASTM Standards*, Vol 05.06.

<sup>3</sup> *Annual Book of ASTM Standards*, Vol 11.01.

<sup>4</sup> *Annual Book of ASTM Standards*, Vol 14.03.

<sup>5</sup> *Annual Book of ASTM Standards*, Vol 14.04.

<sup>6</sup> *Annual Book of ASTM Standards*, Vol 14.02.

3.2.2.1 *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.

NOTE 1—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 should be avoided.

#### 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 D 388.

#### 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 Bomb*—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 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 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 bomb 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 bomb. 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  $\pm 0.1^\circ\text{C}$  (isoperibol) or at the same temperature  $\pm 0.1^\circ\text{C}$  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 *Automated Calorimeters*—Platinum resistance or linear thermistor thermometers shall be capable of measuring to the nearest 0.0001°C. Thermometer calibration shall be traceable to a recognized certifying agency.

##### 6.6.2 *Manual Calorimeters:*

6.6.2.1 *Platinum Resistance or Linear Thermistor Thermometers* shall be capable of measuring to the nearest 0.0001°C. Thermometer calibration shall be traceable to a recognized certifying agency.

6.6.2.2 *Liquid-in-Glass Thermometers*—Conforming to the requirements for thermometers 56C, 116C, or 117C as prescribed in Specification E 1. Thermometers 56C shall be calibrated at intervals no larger than 2.0°C over the entire graduated scale. The maximum difference in correction between any two calibration points shall be no more than 0.02°C. Thermometers 116C and 117C shall be calibrated at intervals no larger than 0.5°C over the entire graduated scale. The maximum difference in correction between any two calibration points shall not be more than 0.02°C.

6.6.2.3 *Beckman Differential Thermometer*—(Glass enclosed scale, adjustable), having a range of approximately 6°C in 0.01°C subdivisions reading upward and conforming to the requirements for Thermometer 115C, as prescribed in Specification E 1. The thermometer shall be calibrated at intervals no larger than 1°C over the entire graduated scale. The maximum difference in the correction between any two calibration points shall be less than 0.02°C.

6.6.2.4 *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 weight 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 gage) 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 gage), 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- 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 bomb; 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.<sup>7</sup>

## 7. Reagents

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

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.<sup>8</sup>

7.3 *Benzoic Acid—Standard (C<sub>6</sub>H<sub>5</sub>COOH)*—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 (Na<sub>2</sub>CO<sub>3</sub>) or other suitable standard solution. Dissolve 3.757 g of sodium carbonate, 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 calorie) in the acid titration.

## 8. Hazards

8.1 The following precautions are recommended for safe calorimeter operation. Additional precautions are noted in Practice E 144. 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 bomb shall not exceed the bomb manufacturer's specifications.

8.1.2 Inspect the bomb 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 gage used in regulating the oxygen feed to the bomb. Valves, gages, and gaskets shall meet industry safety codes. Suitable reducing valves and adapters for 3- to 4-MPa (300- to 500-psig) discharge pressure can be obtained 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.

8.1.4 During ignition of a sample, the operator shall not extend any portion of the body over the calorimeter.

8.1.5 Do not fire the bomb if the bomb has been dropped or turned over after loading.

8.1.6 Do not fire the bomb if there is evidence of gas leakage when the bomb is submerged in the calorimeter vessel.

8.1.7 For manually operated calorimeters, the ignition switch shall be depressed only long enough to fire the charge.

## 9. Sample

9.1 The analysis sample is the material pulverized to pass 250- $\mu$ m (No. 60) sieve, prepared in accordance with either Practice D 346 for coke or Method D 2013 for coal.

## 10. Determination of the Heat Capacity of the Calorimeter

10.1 *Sample*—Weigh 0.8 to 1.2 g of benzoic acid into a sample holder. Record sample weight to the nearest 0.0001 g.

### 10.2 Preparation of Bomb:

10.2.1 Rinse the bomb with water to wet internal seals and surface areas of the bomb or precondition the calorimeter according to the manufacturer's instructions. Add 1.0 mL of water to the bomb before assembly.

10.2.2 Connect a measured fuse in accordance with manufacturer's guidelines.

10.2.3 Assemble the bomb. Admit oxygen to the bomb to a consistent pressure of between 2 and 3 MPa (20 and 30 atm). The same pressure is used for each heat capacity run. Control oxygen flow to the bomb so as not to blow material from the sample holder. If the pressure exceeds the specified pressure, detach the filling connection and exhaust the bomb. Discard the sample.

### 10.3 Preparation of Calorimeter:

10.3.1 Fill the calorimeter vessel with water at a temperature not more than 2°C below room temperature and place the assembled bomb in the calorimeter. Check that no oxygen bubbles are leaking from the bomb. If there is evidence of leakage, remove and exhaust the bomb. Discard the sample.

10.3.2 The mass of water used for each test run shall be  $M \pm 0.5$  g where  $M$  is a fixed mass of water. Devices used to supply the required mass of water on a volumetric basis shall

<sup>7</sup> Request Research Report: D05-1025, available from ASTM Headquarters.

<sup>8</sup> *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.



be adjusted when necessary to compensate for change in the density of water with temperature.

10.3.3 With the calorimeter vessel positioned in the jacket start the stirrers.

10.4 *Temperature Observations Automated Calorimeters:*

10.4.1 *Stabilization*—The calorimeter vessel’s temperature shall remain stable over a period of 30 s before firing. The stability shall be  $\pm 0.001^\circ\text{C}$  for an adiabatic calorimeters and  $\pm 0.001^\circ\text{C/s}$  or less for an isoperibol calorimeter.

10.4.2 *Extrapolation Method*—Fire the charge, record the temperature rise. The test can be terminated when the observed thermal curve matches a thermal curve which allows extrapolation to a final temperature with a maximum uncertainty of  $\pm 0.002^\circ\text{C}$ .

10.4.3 *Full Development Method*—Fire the charge and record the temperature rise until the temperature has stabilized for a period of 30 s in accordance with the stability requirements specified in 10.4.1.

10.5 *Temperature Observations Manual Calorimeters:*

10.5.1 When using ASTM Thermometers 56C, estimate all readings to the nearest  $0.002^\circ\text{C}$ . When using ASTM Thermometers 115C, 116C, or 117C, estimate readings to  $0.001^\circ\text{C}$  and 25- $\Omega$  resistance thermometer readings to the nearest  $0.0001 \Omega$ . Tap or vibrate mercury thermometers just before reading to avoid errors caused by mercury sticking to the walls of the capillary.

10.5.2 Allow 5 min for the temperature of the calorimeter vessel to stabilize. Adjust the jacket temperature to match the calorimeter vessel temperature within  $0.01^\circ\text{C}$  and maintain for 3 min.

10.5.3 Fire the charge. Record the time as  $a$  and the temperature as  $t_a$ .

10.5.4 For adiabatic calorimeters adjust the jacket temperature to match that of the calorimeter vessel temperature during the period of the rise. Keep the two temperatures as equal as possible during the period of rapid rise. Adjust to within  $0.01^\circ\text{C}$  when approaching the final stabilization temperature. Record subsequent readings at intervals no greater than 1 min until three successive readings do not differ by more than  $\pm 0.001^\circ\text{C}$ . Record the first reading after the rate of change has stabilized as the final temperature  $t_c$  and the time of this reading as  $c$ . For isoperibol calorimeters, when approaching the final stabilization temperature, record readings until three successive readings do not differ by more than  $0.001^\circ\text{C}$  per min. Record the first reading after the rate of change has stabilized as the final temperature as  $t_c$  and the time of this reading as  $c$ .

10.5.5 Open the calorimeter and remove the bomb. Release the pressure at a uniform rate such that the operation will not be less than 1 min. Open the bomb and examine the bomb interior. Discard the test if unburned sample or sooty deposits are found.

10.6 *Thermochemical Corrections (see Appendix X1):*

10.6.1 *Acid Correction (see X1.1)*—One may use either the titration (10.6.1.1) or calculated titration (10.6.1.2) procedure for coal and coke samples.

10.6.1.1 *Titration Method*—Wash the interior of the bomb with distilled water containing the titration indicator (see 7.5) until the washings are free of acid and combine with the rinse

of the capsule. Titrate the washings with the standard solutions (see 7.6) using a titration indicator, or a pH or millivolt meter. The number of millilitres of standard  $\text{Na}_2\text{CO}_3$  used in the titration shall be taken as  $e1$ .

10.6.1.2 *Calculated Titration Method*—Each calorimeter system shall be tested at several energy levels with benzoic acid pellets weighing 0.8, 1.0, and 1.2 g. This range corresponds to the optimum energy levels of 5000 through 8000 calories. Two runs shall be made at each weight. Plot millilitres of titrant ( $y$ ) versus temperature rise, degree C ( $x$ ), for each calibration and use linear regression to determine the formula for the line  $y = m(x) + b$  (see Fig. 1). The resulting formula for a line is the equation for determining the calculated millilitres of titrant ( $e1$ ). The calculated titrant =  $m(x) + b$  where  $m$  and  $b$  have been determined by linear regression. The temperature rise ( $x$ ) for each test shall be plotted on the graph to determine the calculated acid correction ( $e1$ ) or determined from the equation  $y = mx + b$ . Example:

Sample wt., g	Measured Titration (y)	Temperature Rise (x)
0.7643	7.8	7.7443
0.8104	7.0	8.2188
1.0392	11.0	10.5114
1.0506	10.3	10.6420
1.1539	10.5	11.6584
1.2562	13.0	12.6491

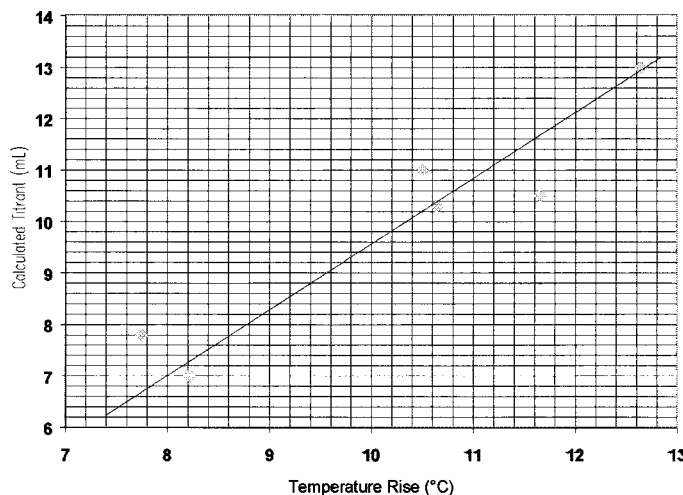
$$y = m(x) + b \quad (1)$$

Using regression analysis, the above data yield the following data: slope = 1.0826, intercept =  $-1.1496$ , and the equation for the millilitres of titrant =  $y = 1.0826x - 1.1496$ .

With any given temperature rise ( $x$ ), the value  $y$  ( $e1$ ) may be determined.<sup>9</sup>

NOTE 2— $m$  above represents the slope of the line, whereas in other references in this method  $m$  represents mass.

<sup>9</sup> Request Research Report: D05-1028, “Interlaboratory Study for the Use of Calculated Nitric Acid Correction” available from ASTM Headquarters.



**FIG. 1 Titration Versus Temperature Rise**

NOTE 3—Regression analysis to determine the equation for the millilitres of titrant ( $e1$ ) is to be done without forcing the data through zero.

10.6.2 *Fuse Correction (see X1.3)*—Determine the fuse correction using one of the two alternatives:

10.6.2.1 Measure the combined pieces of unburned ignition fuse and subtract from the original length to determine the fuse consumed in firing according to Eq 2.

$$e2 = K_l \times l \quad (2)$$

where:

- $e2$  = the correction for the heat of combustion of the firing fuse,
- $l$  = the length of fuse consumed during combustion,
- $K_l$  = 0.96 J/mm (0.23 cal/mm) for No. 34 B&S gage Chromel C,
- $K_l$  = 1.13 J/mm (0.27 cal/mm) for No. 34 B&S gage iron wire, and
- $K_l$  = 0.00 J/mm for platinum or palladium wire provided the ignition energy is constant.

or;

10.6.2.2 Weigh the combined pieces of unburned fuse and subtract from the original weight to determine the weight in milligrams of the fuse consumed in firing ( $m$ ). Remove any ball of oxidized metal from the ends before weighing.

$$e2 = K_m \times m \quad (3)$$

where:

- $e2$  = the correction for the heat of combustion of the firing fuse,
- $m$  = the weight in mg of fuse consumed during combustion,
- $K_m$  = 5.9 J/mg (1.4 cal/mg) for No. 34 B&S gage Chromel C,
- $K_m$  = 7.5 J/mg (1.8 cal/mg) for No. 34 B&S gage iron wire, and
- $K_m$  = 0.00 J/mg for platinum or palladium wire provided the ignition energy is constant.

When cotton thread is used, employ the correction in J recommended by the instrument manufacturer.

10.7 *Calculation of the Corrected Temperature Rise*—Compute the corrected temperature rise,  $t$ , as follows:

$$t = t_c - t_a + C_e + C_r + C_s \quad (4)$$

where:

- $t$  = corrected temperature rise, °C;
- $t_a$  = initial temperature reading at time of firing;
- $t_c$  = final temperature reading;
- $C_e$  = thermometer, emergent stem correction (see Eq A1.4);
- $C_r$  = radiation correction (see Eq A1.2); and
- $C_s$  = thermometer setting correction (see Eq A1.3).

10.7.1 The temperature rise in isoperibol calorimeters require a radiation correction.

10.7.2 Beckman differential thermometers require a setting correction and an emergent stem correction.

10.7.3 Solid-stem ASTM Thermometers 56C do not require emergent stem corrections if all tests are performed within the same 5.5°C interval. If the operating temperature range is beyond this limit, a differential emergent stem correction shall be applied.

10.8 *Calculation of the Heat Capacity*—Calculate the heat capacity ( $E$ ) of the calorimeter using the following equation:

$$E = [(H_c \times m) + e1 + e2]/t \quad (5)$$

where:

- $E$  = the calorimeter heat capacity, J/°C;
- $H_c$  = heat of combustion of benzoic acid, as stated in the certificate, J/g;
- $m$  = mass of benzoic acid, g;
- $e1$  = acid correction from 10.6.1 from either the titration method (10.6.1.1) or the calculated titration (10.6.1.2);
- $e2$  = fuse correction from 10.6.2, J; and
- $t$  = corrected temperature rise from 10.7, °C.

10.8.1 Using the procedures described in 10.1-10.8 complete a total of ten acceptable test runs. An individual test shall be rejected only if there is evidence of incomplete combustion.

10.8.2 The relative standard deviation of the heat capacity of ten acceptable test runs shall be 0.15 % or less of the average energy equivalent. If after considering the possibility of outliers using criterion established in Practice E 178, this limit is not met, one should review operation of the calorimeter for any assignable cause which should be corrected before repeating the series. Table 1 summarizes a series of heat capacity runs. This table would be applicable regardless of the unit of measure for the heat capacity.

## 11. Heat Capacity Checks

11.1 The heat capacity value shall be checked a minimum of once a month, after changing any part of the calorimeter, or after changing the oxygen supply. Two procedures are available for heat capacity check: Standard Method and Rolling Average Method.

NOTE 4—Although it is only required to check the heat capacity once a month, this may be inadequate. A more frequent check of heat capacity values is recommended for laboratories making a large number of tests on a daily basis. The frequency of the heat capacity check should be determined to minimize the number of tests that would be affected by an undetected shift in the heat capacity values.

### 11.2 Standard Method:

11.2.1 A single new heat capacity test value shall not differ from the existing heat capacity value by more than ±0.17 %. If

**TABLE 1 Heat Capacity Runs**

Note—Variance =  $s^2 = \{(\text{Sum Column C} - [(\text{Sum Column B})^2/10])/9\} = 89.51$ .  
Standard Deviation =  $s = \sqrt{s^2} = 9.46$ .  
Relative Standard Deviation =  $(s/\text{Average}) \times 100 = 0.09 \%$ .

Run Number	Column A Heat Capacity, J/°C	Column B Difference From Average	Column C (Column B) <sup>2</sup>
1	10 257.7	+4.2	17.6
2	10 249.3	-4.2	17.6
3	10 270.2	+16.7	278.9
4	10 253.5	0.0	0
5	10 245.1	-8.4	70.6
6	10 249.3	-4.2	17.6
7	10 240.9	-12.6	158.8
8	10 266.0	+12.5	156.3
9	10 257.7	+4.2	17.6
10	10 245.1	-8.4	70.6
SUM		-0.2	805.6
AVERAGE	E = 10 253.5		

this requirement is met, the existing heat capacity value is acceptable. For example: existing heat capacity value is 2402 cal/°C.  $2402 \text{ cal/}^\circ\text{C} \times 0.0017 = 4.1 \text{ cal/}^\circ\text{C}$ . If single test value is within 4.1 cal/°C of the 2402 cal/°C value, then the existing heat capacity value is still acceptable.

11.2.2 If the requirements given in 11.2.1 are not met, an additional heat capacity test shall be run. The difference between the two new heat capacity values shall not exceed 0.21 % of the existing heat capacity value. The average of the two new heat capacity values shall not differ from the existing heat capacity value by more than  $\pm 0.13$  %. If this requirement is met, the existing heat capacity value is acceptable.

11.2.3 If the requirements given in 11.2.2 are not met, two more heat capacity tests shall be run. The range of the four new test values shall not exceed 0.33 % of the existing heat capacity value. The average of the four new heat capacity values shall not differ from the existing heat capacity value by more than  $\pm 0.08$  %. If this requirement is met, the existing heat capacity value is acceptable.

11.2.4 If the requirements given in 11.2.3 are not met, a fifth and sixth heat capacity test shall be run. The range of the six new test values shall not exceed 0.42 % of the existing heat capacity value. The average of the six new heat capacity values shall not differ from the existing heat capacity value by more than  $\pm 0.08$  %. If these requirements are met, do not change the existing heat capacity value.

11.2.5 If the requirements given in 11.2.4 are not met, four more heat capacity tests shall be run. The range of the ten new test values shall not exceed 0.50 % of the existing heat capacity value. The average of the ten new heat capacity values shall not differ from the existing heat capacity value by more than  $\pm 0.04$  %. If this requirement is met, the existing heat capacity value is acceptable.

11.2.6 If requirements given in 11.2.5 are not met, the average value from the ten new test values shall be used to determine a new heat capacity value provided the relative standard deviation of the ten values does not exceed 0.15 %.

11.2.7 The summary of the numerical requirements at each step in checking the heat capacity is given in Table 2.

### 11.3 Rolling Average Method:

11.3.1 A single new heat capacity value shall not differ from the existing heat capacity value by more than  $\pm 0.17$  %.

11.3.2 Values that serve to confirm existing heat capacity values will be included with the original 10 calibration tests until a total of 20 tests are made. These tests will comprise a database for calculating the mean heat capacity value provided the relative standard deviation of the 20 values does not exceed

0.15 %. Any new calibration check beyond the 20 tests will replace the oldest value in the heat capacity database of 20 tests. A maximum relative standard deviation of 0.15 % shall be maintained for the heat capacity database of 20 tests.

11.3.3 When using a rolling average, the heat capacity data must be continually evaluated for four indications of out-of-control conditions: first, seven consecutive results are higher than the mean; second, seven consecutive results are lower than the mean; third, seven consecutive results are continually increasing; and fourth, seven consecutive results are continually decreasing.

11.3.4 Out-of-control trends indicate that the calorimeter operation is suspect and causes should be identified. Whether or not causes are identified, the calorimeter should be recalibrated according to the procedure in Section 10.

## 12. Procedure for Coal and Coke Samples

12.1 Weigh 0.8 to 1.2 g of sample into a sample holder. Record the weight to the nearest 0.0001 g (see 12.6.3).

12.2 Follow the procedures as described in 10.2-10.5 for determination of heat capacity. For the calorific value of coke, it is necessary to use 3-MPa (30-atm) pressure for both standardization and analysis. The starting temperature for determinations shall be within  $\pm 0.5^\circ\text{C}$  of that used in the determination of the heat capacity.

12.2.1 For coke, place a clean combustion capsule in the center of a quartz disk and press the capsule to make an impression in the disk. Cut slits from the outside edge of the disk to the impression. Insert the quartz disk in the combustion capsule so that the slit portion will cover the sides of the capsules.

12.3 Carry out a moisture determination in accordance with Test Method D 3173 or Test Methods D 5142 on a separate portion of the analysis sample preferably on the same day but not more than 24 h apart from the calorific value determination so that reliable corrections to other bases can be made.

12.4 Conduct the sulfur analysis in accordance with Test Methods D 3177 or D 4239. From the weight % sulfur, calculate the sulfur corrections (see X1.2):

$$e_3 = 55.2 \text{ J/g} \times S \times m \quad (13.18 \text{ cal/g} \times S \times m) \quad (6)$$

where:

$e_3$  = a correction for the difference between the heat of formation of  $\text{H}_2\text{SO}_4$  from  $\text{SO}_2$  with respect to the formation of  $\text{HNO}_3$ , J;

$S$  = wt % sulfur in the sample; and

$m$  = mass of sample from 12.1, g.

12.4.1 When titration method is used (see 10.6.1.1), the sulfur correction is

$$e_3 = 55.18 \text{ J/g} \times S \times m \text{ or } (13.18 \text{ cal/g} \times S \times m) \quad (7)$$

12.4.2 When the calculated titration method is used (see 10.6.1.2), the sulfur correction is

$$e_3 = 94.51 \text{ J/g} \times S \times m \text{ or } (22.57 \text{ cal/g} \times S \times m) \quad (8)$$

12.5 For eight mesh samples, analyze coals susceptible to oxidation within 24 h of preparation.

12.6 Coal or coke that do not burn completely can be treated as follows:

12.6.1 Use a crucible liner of the type recommended in 6.11.

**TABLE 2 Numerical Requirements**

Number of Check Runs	Maximum Range $((E_{n\max} - E_{n\min})/E_e) \times 100$	Maximum Difference $((E_{nav} - E_e)/E_e) \times 100$
1	...	$\pm 0.17$
2	0.21	$\pm 0.13$
4	0.33	$\pm 0.08$
6	0.42	$\pm 0.08$
10	0.50	$\pm 0.04$

$E_e$  is the existing heat capacity value.

$E_{n\min}$  is the minimum reading in group of heat capacity check runs.

$E_{n\max}$  is the maximum reading in a group of heat capacity check runs.

$E_{nav}$  is the average of the group of heat capacity check runs.