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Standard Test Method for
Gross Calorific Value of Coal and Coke[1]

This standard is issued under the fixed designation D5865; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope*

1.1 This test method pertains to the determination of the gross calorific value of coal and coke by either an isoperibol or adiabatic bomb calorimeter.

1.2 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this 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]

D121 Terminology of Coal and Coke
D346 Practice for Collection and Preparation of Coke Samples for Laboratory Analysis
D388 Classification of Coals by Rank
D1193 Specification for Reagent Water
D2013 Practice for Preparing Coal Samples for Analysis
D3173 Test Method for Moisture in the Analysis Sample of Coal and Coke
D3177 Test Methods for Total Sulfur in the Analysis Sample of Coal and Coke
D3180 Practice for Calculating Coal and Coke Analyses from As-Determined to Different Bases
D4239 Test Method for Sulfur in the Analysis Sample of Coal and Coke Using High-Temperature Tube Furnace Combustion
D7582 Test Methods for Proximate Analysis of Coal and Coke by Macro Thermogravimetric Analysis
E144 Practice for Safe Use of Oxygen Combustion Bombs
E178 Practice for Dealing With Outlying Observations
E882 Guide for Accountability and Quality Control in the Chemical Analysis Laboratory
E2251 Specification for Liquid-in-Glass ASTM Thermometers with Low-Hazard Precision Liquids

3. Terminology

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

3.2 *Definitions:*

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

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

3.2.3 *British thermal unit [Btu]*—is the amount of heat required to raise the temperature of one pound - mass [lbm] of liquid water at one atmosphere pressure one degree Fahrenheit at a stated temperature. The results of combustion calorimetric tests of fuels for steam power plants may be expressed in terms of the 1956 International Steam Table calorie (I.T. cal) which is defined by the relation, 1 I.T. cal = 4.1868 J. The Btu used in modern steam tables is defined by the means of the relation, 1 I.T. cal / g = 1.8 I.T. Btu / lb. Thus, 1 I.T. Btu / lb = 2.326 J / g.

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

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

3.2.5 *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.

3.2.6 *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.

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

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

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

3.3 *Definitions of Terms Specific to This Standard:*
3.3.1 *corrected temperature rise*—the calorimeter temperature change caused by the process that occurs inside the bomb corrected for various effects.

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

3.3.2.1 *Discussion*—

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

4. Summary of Test Method

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

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

5. Significance and Use

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

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

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

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

6. Apparatus and Facilities

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

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

6.6 *Thermometers:*

6.6.1 *Platinum resistance or thermistor thermometers*—shall be capable of measuring to the nearest 0.0001°C. These types of thermometers consist of two major subsystems. The first and most obvious is the temperature sensing probe itself. The second and equally important aspect is the measurement subsystem. For both subsystems, the relationship between the thermometer resistance and temperature shall be well characterized. The absolute temperature shall be known to ± 0.1 C at the temperature of the calorimetric measurement.

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

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

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

6.7 *Sample Holder*—An open crucible of platinum, quartz, or base metal alloy. Before use in the calorimeter, heat treat base metal crucibles for a minimum of 4 h at 500°C to ensure the crucible surface is completely oxidized. Base metal alloy crucibles are acceptable, if after three preliminary firings, the 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 gauge) diameter or smaller. Nickel-chromium alloy (Chromel C) alloy, cotton thread, or iron wire are acceptable. Platinum or palladium wire, 0.10-mm diameter (No. 38 B&S gauge), can be used provided constant ignition energy is supplied. Use the same type and length (or mass) of ignition fuse for calorific value determinations as used for standardization.

6.9 *Ignition Circuit*—A 6- 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.[3]

7. Reagents

7.1 *Reagent Water*—Conforming to conductivity requirements for Type II of Specification D1193 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.[4]

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

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[3] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D05-1025.

[4] *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.

7.6 *Standard Solution*—Sodium carbonate (Na_2CO_3) or other suitable standard solution. A convenient standard solution may be prepared as follows. Dissolve 3.706 g of sodium carbonate, dried for 24 h at 105°C, in water and dilute to 1 L. The resulting concentration (0.0699 N) assumes the energy of formation of HNO_3 under bomb conditions is -59.7 kJ/mol (-14.3 kcal/mole) (see X1.1). One milliliter of this solution is equivalent to 4.2 J (1.0 cal) in the acid titration. Alternatively, 1.0 ml of a 0.1000 N base solution is equivalent to 6.0 J (1.4 cal) in the acid titration. In general, one milliliter of an arbitrary standard titrant solution is equivalent to its concentration (equivalents / liter or normality [N]) times 59.7 J (14.3 cal).

8. Hazards

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

8.1.1 The mass of sample and any combustion aid as well as the pressure of the oxygen admitted to the 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 gauge used in regulating the oxygen feed to the bomb. Valves, gauges, 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 gauge annually for accuracy or after any accidental over pressures that reach maximum gauge 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-µm (No. 60) sieve, prepared in accordance with either Practice D346 for coke or Method D2013 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 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 ±0.001°C for an adiabatic calorimeters and ±0.001°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 ±0.002°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 S56C, estimate all readings to the nearest 0.002°C. When using ASTM Thermometers S116C, or S117C, estimate readings to 0.001°C and 25- resistance thermometer readings to the nearest 0.0001 . Tap or vibrate liquid-in-glass thermometers just before reading to avoid errors caused by liquid 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°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°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 ±0.001°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°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 *Bomb depressurization*—~~Open the calorimeter and remove the bomb. Release the pressure~~ When the thermochemical corrections will be made by titration, the depressurization and subsequent rinse collection shall be done in a manner ensuring at least 80% recovery of the acidic combustion products. An effective measure of the recovery is offered by the recovery factor described in the following section.[5] Depressurization at a ~~uniform~~ rate such that the operation ~~will~~is 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.~~one minute provides effective recovery and does not require validation. There are no special requirements related to the bomb depressurization if the calculated nitric acid procedure is used.

10.5.5.1 Determine the recovery factor from the slope of the straight line resulting from the regression analysis of the titration results (mg of sulfur vs. meq) using three or more samples with at least two different sulfur concentrations that span the range of sulfur values typically encountered in the laboratory. One equivalent of sulfuric acid (1000 meq) is formed from 16.03 grams of sulfur. A plot of sulfur (mg) vs. milliequivalents (meq) of titrant used to neutralize the bomb rinsings has a theoretical slope of 16.03. The milliequivalents of titrant is the product of milliliters of base used and its concentration (normality). The mass of sulfur in the sample in milligrams is the product of the sulfur concentration in weight percent in the analysis sample, the sample mass and ten. A slope of 16 implies 100% recovery. Increasing values are indicative of diminished recovery. For example, a value of 20 indicates 80% recovery (16.03 × 100 / 20 = 80%).

10.5.6 After depressurization, open the bomb and examine the bomb interior carefully for signs of unburned material or sooty deposits. Discard the test result if either is observed.

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 product of the volume of titrant used in milliliters, the concentration of the standard solution (normality) and 59.7 J (14.3 cal) shall be taken as e1.

10.6.1.2 *Calculated Nitric Acid Method*—For test samples that contain no nitrogen, the nitric acid formed in the bomb during the combustion process is derived from the nitrogen in the air that occupies the bomb prior to pressurizing it with oxygen. The quantity of nitric acid formed is a function of the volume of the bomb, the oxygen filling pressure and the quantity of energy released in the bomb during a test. For a given bomb and filling pressure, the relationship between the amount of nitric acid formed and the energy released can be determined using the following procedure. The calorimeter should be tested using one-gram pellets of benzoic acid when the bomb volume is nominally 340 milliliters. If the bomb volume differs significantly from 340 ml, the sample weight used should be adjusted as required in order to comply with the bomb manufacturer's safe operating guidelines. Tests should be run in duplicate. Determine the nitric acid correction by titrating the bomb washings as outlined in 10.6.1.1. Divide the correction obtained (*e1*) by the amount of energy released in the bomb for the corresponding test. The energy contribution from the ignition fuse (*e2*) is usually small (<1% of the total energy released) and may be ignored. The average value of this ratio is used to establish a factor (NAF) that allows the nitric acid correction to be determined for any arbitrary energy release.

$$e1 = (NAF)*energy\ released\ for\ the\ test \tag{1}$$

Example:

The nitric acid correction for a 340-ml oxygen bomb is found to be 41.9 J (10.0 calories) when the released energy corresponds to that liberated by one gram of benzoic acid, 26.45 kJ (6318 calories). The ratio of these quantities is 1.58 J per 1000 joules of released energy or 1.58 calories per 1000 calories of released energy. The nitric acid correction for any calorimetric test can then be expressed as follows:

$$e1 = 1.58*energy\ released\ for\ the\ test\ (kJ\ or\ kcal) \tag{2}$$

For a given calorimeter, the energy released in the bomb during a test for the purposes of calculating the nitric acid correction

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[5] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D05-1028, ~~" Interlaboratory~~ "Interlaboratory Study for the Use of Calculated Nitric Acid ~~Correction".~~ Correction."

(e1) may be expressed as the product of the temperature rise for the test and the effective calorimeter heat capacity or calorimeter calibration factor.[6]

$$e1 = (1.58/1000)*E*t \tag{3}$$

The calculated nitric acid method can be applied to samples containing up to 2% nitrogen without introducing a significant error in the resulting heat of combustion value.

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 4.

$$e2 = K_l \times l \tag{4}$$

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 gauge Chromel C,
K_l = 1.13 J/mm (0.27 cal/mm) for No. 34 B&S gauge 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.

$$e2 = K_m \times m \tag{5}$$

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 gauge Chromel C,
K_m = 7.5 J/mg (1.8 cal/mg) for No. 34 B&S gauge 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:

$$t = t_c - t_a + C_e + C_r \tag{6}$$

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 A1.6 or Eq A1.8);
C_r = radiation correction (see Eq A1.1 or Eq A1.2).

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

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

$$E = [(H_c \times m) + e1 + e2]/t \tag{7}$$

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 precision of ten acceptable calibration test runs shall have a relative standard deviation (RSD) no greater than 0.17%. If after considering the possibility of outliers using criteria established in Practice E178, this limit is not met, one should review operation of the calorimeter for any assignable cause. Operating deficiencies should be corrected before performing additional

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[6] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D05-1028, "Interlaboratory Study for the Use of Calculated Nitric Acid Correction".

calibration measurements as required. Table 1 provides an example summary of a series of calibration tests. The formulas used to arrive at the mean value and relative standard deviation are independent of the units used for the calibration measurements.

10.9 *Valid Working Range for the Calibration of the Calorimeter:*

10.9.1 It is a generally accepted principle of reliable analysis that instruments should be calibrated over the full range of measurement and that measurements be restricted to the range calibrated. It is not good practice to report extrapolated data obtained outside the range of calibration. The range or reliable calibration can be considered as the range of reliable measurement and vise versa.

10.9.2 It should be possible to vary the amount of benzoic acid calibrant by at least ±25% without observing a significant trend in the values obtained for the effective heat capacity or instrument calibration factor. The working limits for the instrument calibration shall be determined and defined in terms of the corrected temperature rise. All subsequent measurements shall be kept within these limits.

10.9.3 A convenient way to check a previously calibrated instrument is to use benzoic acid as an unknown. The mean value for the heat of combustion from duplicate runs using 0.7 g and 1.3 g sample masses, respectively, should be within 56 J/g or 24 Btu / lb of the accepted heat of combustion value.

10.9.4 For any given instrument, examination of the applicable range of the instrument calibration should be carried out when the instrument is new, moved to a different location or subject to major repair.

11. Calibration Verification

11.1 The calorimeter calibration shall be checked on a regular basis. Renewed determination of the heat capacity is required whenever significant alterations have been made to the instrument or to the test conditions. The optimum frequency for checking the heat capacity or instrument calibration will depend on the stability of the measurement system and the risk involved when the system departs from statistical control. Since all data obtained during the period last-known-in-control to first-known-out-of-control are suspect, such intervals may need to be minimized.

11.1.1 There are several empirical approaches to deciding on how frequently the instrument calibration should be checked. The experience of the laboratory may indicate the expected frequency of occurrence of trouble, in which case reference sample measurements, at least three in number, should be equally spaced within such an interval. Another approach is the "length of run" concept. In this, recognizable breaks in the production (of data) process are identified which could cause significant changes in precision or bias. Such breaks could include change of work shift; rest periods; change, modification, or adjustment of apparatus; use of new calibration standards; significantly long down-times; use of a new lot of reagents. At least three reference samples should be measured during any of these periods when the periods are considered to be potentially significant.

11.1.2 Periodic checks of the instrument calibration are a risk-reducing procedure. However, if it involves more than ten percent of a laboratory's measurement effort, either the quality control process may need improvement or too much effort is being exerted in this direction. If less than five percent of effort is devoted to such measurements, the laboratory may be taking too high a risk of producing unacceptable data, or may not even know the quality of the data it is producing. The above statements are made with a laboratory making a significant number of high-quality routine measurements in mind. If a laboratory's program involves occasional or one-of-a-kind measurements, the amount of quality assurance effort required, including the number of measurements of reference materials to be made may be significantly more than that indicated above.

11.1.3 Two complementary procedures are offered for calorimeter calibration verification: Control Chart Method and Rolling Average Method.

11.2 *Control Chart Method for Calibration Verification:*

TABLE 1 Calibration Measurments

Run Number	Column A Heat Capacity J/C	Column B Difference from Average Squared
1	10258	20
2	10249	20
3	10270	272
4	10254	0
5	10245	72
6	10249	20
7	10241	156
8	10266	156
9	10258	20
10	10245	72
Sum	102535	811
Average	10254	Sum Column A /10
Variance (s^2)	90	Sum Column B /9
Standard Deviation(s)	9	Sqrt (Variance)
Relative Standard Deviation (RSD)	0.09%	s/Average * 100

11.2.1 A control chart is a graphical way to interpret test data. In its simplest form, a selected reference sample is measured periodically and the results are plotted sequentially (or time-ordered) on a graph. Limits for acceptable values are defined and the measurement system is assumed to be in control (variability is stable and due to chance alone) as long as the results stay within these limits. The residence of the values within expected limits is accepted as evidence that the precision of measurement remains in control. The monitored precision of measurement and the accuracy of measurement of the reference sample may be transferred, by inference, to all other appropriate measurements made by the system while it is in a state of control.

11.2.2 A control chart can be realized by sequentially plotting individual measurement values. The central line is the most probable value for (that is, the grand average) of all the measurements or the accepted measurement value. The limits LWL to UWL (lower and upper warning limits) define the area in which 95 percent of the plotted points are expected to lie. The limits LCL to UCL (lower and upper control limits) define the area in which almost all (99.7%) of the plotted points are expected to lie when the system is in a state of statistical control. It should be clear that when more than 5 percent of the points (one in twenty) lie outside of the warning limits or when values fall outside of the control limits the system is behaving unexpectedly and corrective actions, and even rejection of data, may be required.

11.2.3 Results are expected to scatter with a normal distribution within the limits. Systematic trends or patterns in the data plots may be early warning of incipient problems and are cause for concern; hence techniques to identify such should be practiced.

11.2.4 Control charts, including the factors for calculating control limits are discussed more thoroughly elsewhere (see Guide E882 and (1)[7]. The central line is either the known value for the test sample (for example, certified value), or the mean of 10 sets of independent measurements. Control limits are then calculated according to the following relationships.

UCL	Mean or accepted value + 3 * sigma / sqrt(N)
UWL	Mean or accepted value + 2 * sigma / sqrt(N)
Central Line	Mean of the 10 most recent measurements or the
X(bar)	accepted value.
LWL	Mean or accepted value – 2 * sigma / sqrt(N)
LCL	Mean or accepted value – 3 * sigma / sqrt(N)

For the above limits, N represents the number of repetitive measurements of the reference sample, the mean of which is plotted on an Xbar chart. For an X chart (single measurement of the reference sample) N = 1. The standard deviation of the measurement process is sigma. Sigma is taken as 0.10% of the mean of the ten most recent measurements or 0.10% the accepted value if tests are being performed using a reference material, for example benzoic acid, run as an unknown. Table 2 illustrates important selected control limits for calorimeter operation when benzoic acid is used as a test sample.

11.3 *Rolling Average Method:*

11.3.1 The mean value of the ten most recent calorimeter calibration or heat capacity measurements is used to support the calibration of the calorimeter system. A single new value, incorporated into the average of the ten most recent measurements, discarding the oldest measurement in the existing series of ten measurements first, must meet the precision requirements outlined in 10.8.2.

11.4 *Recommended Test Substances:*

11.4.1 By international agreement in the 1920's, benzoic acid was selected as the chemical standard to be used in calibrating bomb calorimeters. Today, it remains as the sole chemical primary standard for this type of calibration.

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[7] The boldface numbers in parentheses refer to a list of references at the end of this standard.

TABLE 2 Calorimeter Control Limits When Benzoic Acid is Used as a Test Sample

NOTE 1—Accepted heat of combustion taken as 26454 J/g
Process sigma is 0.10% RSD
Control limits based on 99% confidence (3 sigma) values
Values are in J/g except as noted.

Number of Observations in a Group	UCL for the range (High-Low) within the Group	UCL for the RSD within the Group	Maximum Permissible Deviation of the Group Mean from the Accepted Value or Grand Mean
1	...	...	79.4
2	97.5	0.2606	56.1
3	115.3	0.2276	45.8
4	124.3	0.2088	39.7
5	130.1	0.1964	35.5
6	134.3	0.1874	32.4
7	137.6	0.1806	30.0
8	140.4	0.1751	28.1
9	142.7	0.1707	26.5
10	144.7	0.1669	25.1
15	151.8	0.1554	20.5
20	156.7	0.1470	17.7
25	160.2	0.1420	15.9

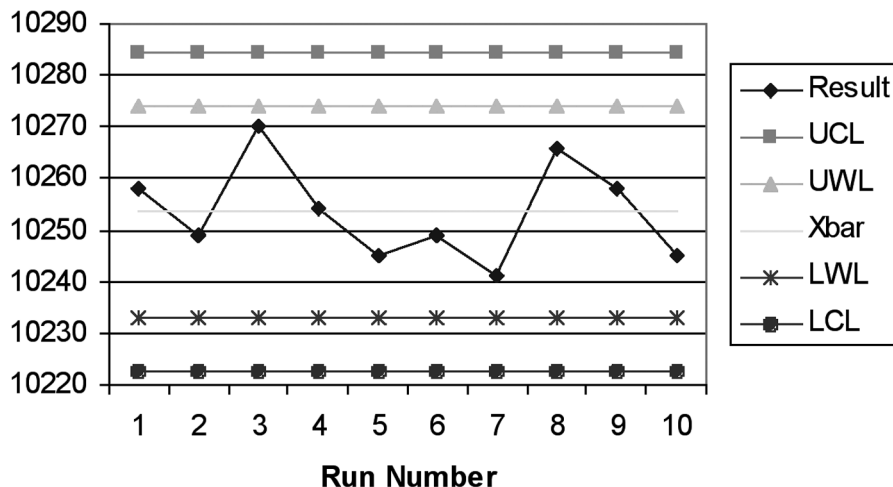## Calorimeter Heat Capacity X Chart

FIG. 1 Example of X Chart for Calibration Runs
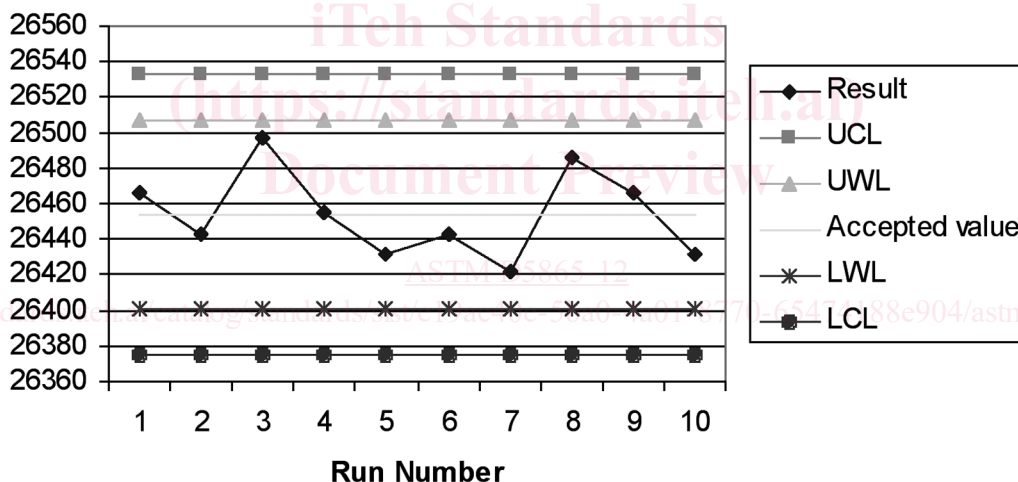
Benzoic Acid Check Sample X Chart

FIG. 2 Example of X Chart for Check Sample Runs

11.4.1.1 In general, the calibration of an analysis instrument consists of the evaluation of its response function in terms of the composition of the analyte. The instrument responds to some property of the analyte, the value of which needs to be quantified by use of known substances. It is tacitly assumed that the instrument will respond analogously to the standard and test samples. With this in mind, the confidence in the measurement process is influenced by the uncertainty in composition of known samples and the soundness of the analogy.

11.4.1.2 It is desirable to perform check experiments in order to demonstrate confidence in the ability to make measurements on unknowns that are not only acceptably precise but also acceptably accurate. This is especially true in instances where conditions in the calibration and combustion tests differ appreciably. For example, large differences in the rates of combustion between the calibrant and the unknown or significant differences in combustion chemistries may give rise to systematic errors that are difficult to detect. The use of test substances in such check experiments can help demonstrate that the techniques and procedures used in determining heats of combustion of unknown materials are reasonably free of persistent errors.

11.4.2 For work with solid samples, the following test substances are recommended.

Substance	$-\Delta u_B / Jg^{-1A}$
Acetanilide CAS 103-84-4 CH3CONHC6H5 MWT 135.17 Density 1.22 g/cc	31279 **(2)**
Tris (hydroxymethyl) aminomethane CAS 77-86-1 (HOCH2)3-CNH2 MWT 121.14 Density = 1.35 g/cc	20058 **(3)**

[A] Mass against stainless steel weights (8 g/cc) in air (0.0012 g/cc).

11.4.2.1 Both acetanilide and tris (hydroxymethyl) aminomethane are available in high purity, are non-hygroscopic and have very low vapor pressure. Acetanilide is available from NIST as a micro-analytical standard for CHON compounds (SRM 141). Tris (hydroxymethyl) aminomethane is also available from NIST as an acidimetric standard (SRM 723).

11.4.2.2 Both materials are commercially available. When the aforementioned materials are used as secondary thermochemical standards or test substances for combustion calorimetry, ensure that the minimum stated purity is at least 99.9%.

11.4.2.3 Crystalline tris (hydroxymethyl) aminomethane is difficult to form into a durable pellet. Its relatively low heat of combustion value allows this material to be weighed directly into the combustion crucible and combusted in this form. When a consumable metal fuse wire is used, the wire loop shall be in direct contact with the granular sample.

11.4.2.4 Acetanilide is easily formed into a 12.5 mm diameter pellet and shall be burned in this form due to its higher heat of combustion value.

11.4.2.5 The nitric acid correction for tests involving the recommended test substances is approximately 50% higher than what's typically obtained for benzoic acid calibrant samples. This is a consequence of the single nitrogen atom associated with each of the test materials. About 10% of this nitrogen gives rise to aqueous nitric acid during the high pressure combustion process. The remainder appears as elemental nitrogen in the combustion products. The additional correction is accounted for transparently when the titration method is used to arrive at the acid correction. When the calculated nitric acid method is used, the nitric acid factor (NAF) shall be increased by 50% when applied to tests involving these test substances.

11.5 *Use of Laboratory Control Materials:*

11.5.1 A laboratory control material (LCM) is similar to a certified reference material in that it is a homogeneous matrix that offers key characteristics similar to the samples being analyzed. A true LCM is one that is prepared and stored in a stable condition strictly for use in-house by a single laboratory. Alternately, the material may be prepared by a central laboratory and distributed to others (so-called regional or program control materials). Unlike CRMs, the heat of combustion of LCMs are not certified but are based upon a statistically valid number of replicate analyses by one or several laboratories. In practice, this material can be used to assess the performance of a single laboratory, as well as to determine the degree of comparability among different laboratories.

11.5.2 A significant amount of work is involved with the production and maintenance of any LCM. For example, materials related issues such as stability, homogenization techniques and proper conditions for storage must be addressed. For smaller laboratories, the time and effort involved supporting the use of true LCMs may not be justified. In such cases, the use of CRMs is preferred.

11.5.3 Routine analysis of CRMs or LCMs represent an important aspect of a performance-based QA philosophy. At least one CRM or LCM must be analyzed along with each batch of 20 or fewer samples (that is, QA samples should comprise a minimum of 5% of each set of samples). For CRMs, the certified heat of combustion value will be known to the analyst(s) and will be used to provide an immediate check on performance before proceeding with a subsequent sample batch. Performance criteria for both precision and accuracy must be established for the analysis of CRMs or LCMs using a given instrumental technique. If the laboratory fails to meet either the precision or accuracy control limit criteria for a given analysis of the CRM or LCM, the data for the entire batch of samples is suspect. Potential operating deficiencies must be checked / corrected and the CRM or LCM may have to be reanalyzed to confirm the results. If the values are still outside the control limits in the repeat analysis, the laboratory is required to find and eliminate the source(s) of the problem and repeat the analysis of that batch of samples until control limits are met, before final data are reported.

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 ±0.5°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.