



Designation: D240 – 19

Standard Test Method for Heat of Combustion of Liquid Hydrocarbon Fuels by Bomb Calorimeter¹

This standard is issued under the fixed designation D240; 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.

This standard has been approved for use by agencies of the U.S. Department of Defense.

1. Scope*

1.1 This test method covers the determination of the heat of combustion of liquid hydrocarbon fuels ranging in volatility from that of light distillates to that of residual fuels.

1.2 Under normal conditions, this test method is directly applicable to such fuels as gasolines, kerosines, Nos. 1 and 2 fuel oil, Nos. 1-D and 2-D diesel fuel and Nos. 0-GT, 1-GT, and 2-GT gas turbine fuels.

1.3 This test method is not as repeatable and not as reproducible as Test Method D4809.

1.4 The values stated in SI units are to be regarded as standard. The values in parentheses are for information only.

1.5 *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, health, and environmental practices and determine the applicability of regulatory limitations prior to use. For specific hazard statements, see Sections 7 and 9 and A1.10 and Annex A3.*

1.6 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

2. Referenced Documents

2.1 ASTM Standards:²

D129 Test Method for Sulfur in Petroleum Products (General High Pressure Decomposition Device Method)

¹ This test method is under the jurisdiction of ASTM Committee D02 on Petroleum Products, Liquid Fuels, and Lubricants and is the direct responsibility of Subcommittee D02.05 on Properties of Fuels, Petroleum Coke and Carbon Material.

Current edition approved Nov. 1, 2019. Published December 2019. Originally approved in 1957. Last previous edition approved in 2017 as D240 – 17. DOI: 10.1520/D0240-19.

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.

- D1018 Test Method for Hydrogen In Petroleum Fractions
D1266 Test Method for Sulfur in Petroleum Products (Lamp Method)
D1552 Test Method for Sulfur in Petroleum Products by High Temperature Combustion and Infrared (IR) Detection or Thermal Conductivity Detection (TCD)
D2622 Test Method for Sulfur in Petroleum Products by Wavelength Dispersive X-ray Fluorescence Spectrometry
D3120 Test Method for Trace Quantities of Sulfur in Light Liquid Petroleum Hydrocarbons by Oxidative Microcoulometry
D3701 Test Method for Hydrogen Content of Aviation Turbine Fuels by Low Resolution Nuclear Magnetic Resonance Spectrometry
D4294 Test Method for Sulfur in Petroleum and Petroleum Products by Energy Dispersive X-ray Fluorescence Spectrometry
D4809 Test Method for Heat of Combustion of Liquid Hydrocarbon Fuels by Bomb Calorimeter (Precision Method)
D5453 Test Method for Determination of Total Sulfur in Light Hydrocarbons, Spark Ignition Engine Fuel, Diesel Engine Fuel, and Engine Oil by Ultraviolet Fluorescence
D7171 Test Method for Hydrogen Content of Middle Distillate Petroleum Products by Low-Resolution Pulsed Nuclear Magnetic Resonance Spectroscopy
E1 Specification for ASTM Liquid-in-Glass Thermometers
E200 Practice for Preparation, Standardization, and Storage of Standard and Reagent Solutions for Chemical Analysis

3. Terminology

3.1 Definitions:

3.1.1 *gross heat of combustion, Q_g (MJ/kg), n*—the quantity of energy released when a unit mass of fuel is burned in a constant volume enclosure, with the products being gaseous, other than water that is condensed to the liquid state.

3.1.1.1 *Discussion*—The fuel can be either liquid or solid, and contain only the elements carbon, hydrogen, nitrogen, oxygen, and sulfur. The products of combustion, in oxygen, are gaseous carbon dioxide, nitrogen oxides, sulfur dioxide, and liquid water. In this procedure, 25 °C is the initial temperature

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

of the fuel and the oxygen, and the final temperature of the products of combustion.

3.1.2 *net heat of combustion, Q_n (MJ/kg), n*—the quantity of energy released when a unit mass of fuel is burned at constant pressure, with all of the products, including water, being gaseous.

3.1.2.1 *Discussion*—The fuel can be either liquid or solid, and contain only the elements carbon, hydrogen, nitrogen, oxygen, and sulfur. The products of combustion, in oxygen, are carbon dioxide, nitrogen oxides, sulfur dioxide, and water, all in the gaseous state. In this procedure, the combustion takes place at a constant pressure of 101.325 kPa (1 atm), and 25 °C is the initial temperature of the fuel and the oxygen, and the final temperature of the products of combustion.

3.1.3 The following relationships may be used for converting between units:

- 1 cal_{it} (International Table calorie) = 4.1868 J
- 1 Btu_{it} (International Table British thermal unit) = 1055.05585262 J and typically rounded to 1055.056 for practical use
- 1 cal_{it}/g = 0.0041868 MJ/kg
- 1 Btu_{it}/lb = 0.002326 MJ/kg

3.2 Definitions of Terms Specific to This Standard:

3.2.1 *energy equivalent, n*—(effective heat capacity or water equivalent) of the calorimeter is the energy required to raise the temperature one degree Celsius expressed as MJ/°C.

$$1 \text{ MJ/kg} = 1000 \text{ J/g} \quad (1)$$

In SI, the unit of heat of combustion has the dimension J/kg, but for practical use a multiple is more convenient. The MJ/kg is customarily used for the representation of heats of combustion of petroleum fuels. The net heat of combustion is related to the gross heat of combustion by the following equation:

$$Q_n (\text{net}, 25^\circ\text{C}) = Q_g (\text{gross}, 25^\circ\text{C}) - 0.2122 \times H \quad (2)$$

where:

- Q_n (net, 25 °C) = net heat of combustion at constant pressure, MJ/kg,
- Q_g (gross, 25 °C) = gross heat of combustion at constant volume, MJ/kg, and
- H = mass percent of hydrogen in the sample.³

NOTE 1—The energy unit of measurement employed in this test method is the joule with the heat of combustion reported in megajoules per kilogram.

4. Summary of Test Method

4.1 Heat of combustion is determined in this test method by burning a weighed sample in an oxygen bomb calorimeter under controlled conditions. The heat of combustion is computed from temperature observations before, during, and after combustion, with proper allowance for thermochemical and heat transfer corrections. Either isothermal or adiabatic calorimeter jackets can be used.

4.1.1 Temperatures can be measured in degrees Celsius.

³ Supporting data (derivation of equations) have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR: RR:D02-1346. Contact ASTM Customer Service at service@astm.org.

4.1.1.1 Temperatures can be recorded in either degrees Fahrenheit or ohms or other units when using electric thermometers. Use the same units in all calculations, including standardization.

4.1.2 Time is expressed in calculations in minutes and decimal fractions thereof. It may be measured in minutes and seconds.

4.1.3 Masses are measured in grams and no buoyancy corrections are applied.

5. Significance and Use

5.1 The heat of combustion is a measure of the energy available from a fuel. A knowledge of this value is essential when considering the thermal efficiency of equipment for producing either power or heat.

5.2 The heat of combustion as determined by this test method is designated as one of the chemical and physical requirements of both commercial and military turbine fuels and aviation gasolines.

5.3 The mass heat of combustion, the heat of combustion per unit mass of fuel, is a critical property of fuels intended for use in weight-limited craft such as airplanes, surface effect vehicles, and hydrofoils. The range of such craft between refueling is a direct function of the heat of combustion and density of the fuel.

6. Apparatus

6.1 *Test Room, Bomb, Calorimeter, Jacket, Thermometers, and Accessories*, as described in [Annex A1](#).

7. Reagents

7.1 *Benzoic Acid, Standard*⁴—Benzoic acid powder must be compressed into a tablet or pellet before weighing. Benzoic acid pellets for which the heat of combustion has been determined by comparison with the National Bureau of Standards sample are obtainable commercially for those laboratories not equipped to pellet benzoic acid.

7.2 *Gelatin Capsules*.

7.3 *Methyl Orange or Methyl Red Indicator*.

7.4 *Mineral Oil*.

7.5 *Oxygen*—Commercial oxygen produced from liquid air can be used without purification. If purification is necessary, see [A1.11 \(Warning\)](#)—Oxygen vigorously accelerates combustion. See [A3.2](#).

7.6 *Pressure-Sensitive Tape*—Cellophane tape 38 mm (1½ in.) wide, free of chlorine and sulfur.

7.7 *Alkali, Standard Solution*:

7.7.1 *Sodium Hydroxide Solution* (0.0866 mol/L)—Dissolve 3.5 g of sodium hydroxide (NaOH) in water and dilute to 1 L. Standardize with potassium acid phthalate and adjust to 0.0866 mol/L as described in Practice [E200](#) ([Warning](#))—Corrosive. Can cause severe burns or blindness.

⁴ Available from National Institute of Standards and Technology (NIST), 100 Bureau Dr., Stop 1070, Gaithersburg, MD 20899-1070, <http://www.nist.gov> as standard sample No. 39.

Evolution of heat produces a violent reaction or eruption upon too rapid mixture with water. See Annex A3.1.)

7.7.2 *Sodium Carbonate Solution* (0.03625 mol/L)—Dissolve 3.84 g of Na₂CO₃ in water and dilute to 1 L. Standardize with potassium acid phthalate and adjust to 0.03625 mol/L as described in Practice E200.

7.8 *2,2,4-Trimethylpentane (isooctane), Standard⁵*—(Warning—Extremely flammable. Harmful if inhaled. Vapors may cause flash fire. See Annex A3.3.)

8. Standardization

8.1 *Determine the Energy Equivalent of the Calorimeter*—Average not less than six tests using standard benzoic acid.⁶ These tests should be spaced over a period of not less than three days. Use not less than 0.9 g nor more than 1.1 g of standard benzoic acid (C₆H₅COOH). Make each determination according to the procedure described in Section 9 and compute the corrected temperature rise, *t*, as described in 10.1 or 10.2. Determine the corrections for nitric acid (HNO₃) and firing wire as described in 10.3 and substitute in the following equation:

$$W = (Q \times g + e_1 + e_2)/t \quad (3)$$

where:

W = energy equivalent of calorimeter, MJ/°C,
Q = heat of combustion of standard benzoic acid, MJ/g, calculated from the certified value,
g = weight of standard benzoic acid sample, g,
t = corrected temperature rise, as calculated in 10.1 or 10.2, °C,
*e*₁ = correction for heat of formation of nitric acid, MJ, and
*e*₂ = correction for heat of combustion of firing wire, MJ.

8.1.1 Repeat the standardization tests after changing any part of the calorimeter and occasionally as a check on both calorimeter and operating technique.

8.2 *Checking the Calorimeter for Use with Volatile Fuels*—Use 2,2,4-*trimethylpentane* to determine whether the results obtained agree with the certified value (47.788 MJ/kg, weight in air) within the repeatability of the test method. If results do not come within this range, the technique of handling the sample may have to be changed (Annex A1.8). If this is not possible or does not correct the error, run a series of tests using 2,2,4-*trimethylpentane* to establish the energy equivalent for use with volatile fuels.

8.3 *Heat of Combustion of Pressure-Sensitive Tape or Gelatin/Mineral Oil*—Determine the heat of combustion of either the pressure-sensitive tape or 0.5 g gelatin capsule/mineral oil in accordance with Section 9 using about 1.2 g of tape or 0.5 g gelatin capsule/mineral oil and omitting the sample. Make at least three determinations and calculate the heat of combustion as follows:

$$Q_{pst} = (\Delta t \times W - e_1)/1000 a \quad (4)$$

where:

*Q*_{pst} = heat of combustion of the pressure-sensitive tape or mineral oil, MJ/kg,
Δt = corrected temperature rise, as calculated in accordance with 10.1 or 10.2, °C,
W = energy equivalent of the calorimeter, MJ/°C,
*e*₁ = correction for the heat of formation of HNO₃, MJ, and
a = mass of the pressure-sensitive tape or gelatin capsule/mineral oil, g.

Average the determinations, and redetermine the heat of combustion of the tape or gelatin capsule/mineral oil whenever a new roll or batch is started.

9. Procedure

9.1 *Weight of Sample*—Control the weight of sample (including any auxiliary fuel) so that the temperature rise produced by its combustion will be equal to that of 0.9 g to 1.1 g of benzoic acid (Note 2). Weigh the sample to the nearest 0.1 mg.

NOTE 2—If the approximate heat of combustion of the sample is known, the required weight can be estimated as follows:

$$m = 26.454/Q_s \quad (5)$$

where:

m = mass of sample, g, and
*Q*_s = MJ/kg.

Some fuels contain water and particulate matter (ash) that will degrade calorimetric values. If the heat of combustion is required on a clean fuel, filter the sample to remove free water and insoluble ash before testing.

9.1.1 For highly volatile fluids, reduce loss with use of tape or gelatin capsule mineral oil.

NOTE 3—Acceptable procedures for handling volatile liquids include those described in the reports referenced at the end of this test method. References (1-6) describe glass sample holders: (7) describes a metal sample holder: (8) describes a gelatin sample holder.

9.1.2 *Tape*—Place a piece of pressure-sensitive tape across the top of the cup, trim around the edge with a razor blade, and seal tightly. Place 3 mm by 12 mm strip of tape creased in the middle and sealed by one edge in the center of the tape disk to give a flap arrangement. Weigh the cup and tape. Remove from the balance with forceps. Fill a hypodermic syringe with the sample. The volume of sample can be estimated as follows:

$$V = (W \times 0.00032)/(Q \times D) \quad (6)$$

where:

V = volume of sample to be used, mL,
W = energy equivalent of calorimeter, J/°C,
Q = approximate heat of combustion of the sample, MJ/kg, and
D = density, kg/m³, of the sample.

9.1.2.1 Add the sample to the cup by inserting the tip of the needle through the tape disk at a point so that the flap of tape will cover the puncture upon removal of the needle. Seal down the flap by pressing lightly with a metal spatula. Reweigh the

⁵ Obtainable from the National Institute of Standards Technology as standard sample No. 217b.

⁶ Jessup, R. S., "Precise Measurement of Heat of Combustion with a Bomb Calorimeter," NBS Monograph 7, U. S. Government Printing Office.

cup with the tape and sample. Take care throughout the weighing and filling operation to avoid contacting the tape or cup with bare fingers. Place the cup in the curved electrode and arrange the fuse wire so that the central portion of the loop presses down on the center of the tape disk.

9.1.3 *Gelatin/Mineral Oil*—Weigh the cup and gelatin capsule. The capsule should only be handled with forceps. Add the sample to the capsule. Reweigh the cup with capsule and sample. If poor combustion is expected with the capsule, add several drops of mineral oil on the capsule and reweigh the cup and contents. Place the cup in the curved electrode and arrange the fuse wire so that the central portion of the loop contacts the capsule and oil.

9.2 *Water in Bomb*—Add 1.0 mL of water to the bomb from a pipet.

9.3 *Oxygen*—With the test sample and fuse in place, slowly charge the bomb with oxygen to 3.0 MPa (30 atm) gauge pressure at room temperature (9.3.1). Do not purge the bomb to remove entrapped air. (**Warning**—Be careful not to overcharge the bomb. If, by accident, the oxygen introduced into the bomb should exceed 4.0 MPa, do not proceed with the combustion. An explosion might occur with possible violent rupture of the bomb. Detach the filling connection and exhaust the bomb in the usual manner. Discard the sample, unless it has lost no weight, as shown by reweighing.)

9.3.1 Lower or higher initial oxygen pressures can be used within the range from 2.5 MPa to 3.5 MPa, provided the same pressure is used for all tests, including standardization.

9.4 *Calorimeter Water*—Adjust the calorimeter water temperature before weighing as follows:

Isothermal jacket method	1.6 °C to 2.0 °C below jacket temperature
Adiabatic jacket method	1.0 °C to 1.4 °C below room temperature

This initial adjustment will ensure a final temperature slightly above that of the jacket for calorimeters having an energy equivalent of approximately 10.2 kJ/°C. Some operators prefer a lower initial temperature so that the final temperature is slightly below that of the jacket. This procedure is acceptable, provided it is used in all tests, including standardization.

9.4.1 Use the same amount (± 0.5 g) of distilled or deionized water in the calorimeter vessel for each test. The amount of water (2000 g is usual) can be most satisfactorily determined by weighing the calorimeter vessel and water together on a balance. The water can be measured volumetrically if it is measured always at the same temperature.

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

NOTE 4—Use a magnifier and estimate all readings (except those during

the rapid rise period) to the nearest 0.002 °C when using ASTM Bomb Calorimeter Thermometer 56C. Estimate Beckmann thermometer readings to the nearest 0.001 °C and 25 Ω resistance thermometer readings to the nearest 0.0001 Ω. Tap liquid thermometers with a pencil just before reading to avoid errors caused by the liquid sticking to the walls of the capillary.

NOTE 5—When the approximate expected rise is unknown, the time at which the temperature reaches 60 % of the total can be determined by recording temperatures at (45, 60, 75, 90, 105) s after firing and interpolating.

9.6 *Observations, Adiabatic Jacket Method* (Note 6)—Assemble the calorimeter in the jacket and start the stirrers. Adjust the jacket temperature to be equal to or slightly lower than the calorimeter, and run for 5 min to obtain equilibrium. Adjust the jacket temperature to match the calorimeter within ± 0.01 °C and hold for 3 min. Record the initial temperature and fire the charge. Adjust the jacket temperature to match that of the calorimeter during the period of rise, keeping the two temperatures as nearly equal as possible during the rapid rise, and adjusting to within ± 0.01 °C when approaching the final equilibrium temperature. Take calorimeter readings at 1 min intervals until the same temperature is observed in three successive readings. Record this as the final temperature. Time intervals are not recorded as they are not critical in the adiabatic method.

NOTE 6—These instructions supersede the instructions given in 9.5 when using jackets equipped for adiabatic temperature control.

9.7 *Analysis of Bomb Contents*—Remove the bomb and release the pressure at a uniform rate such that the operation will require not less than 1 min. Examine the bomb interior for evidence of incomplete combustion. Discard the test if unburned sample or sooty deposits are found.

9.7.1 Wash the interior of the bomb, including the electrodes and sample holder, with a fine jet of water and quantitatively collect the washings in a beaker. Use a minimum of wash water, preferably less than 350 mL. Titrate the washings with standard alkali solution, using methyl orange or methyl red indicator.

9.7.2 Remove and measure the combined pieces of unburned firing wire, and subtract from the original length. Record the difference as *wire consumed*.

9.7.3 Determine the sulfur content of the sample if it exceeds 0.1 %. Determine sulfur by analyzing the bomb washings remaining after the acid titration, using the procedure described in Test Methods D129. Alternatively, the sulfur content may be determined on the original sample using Test Methods D1266, D2622, D3120, D4294, or D5453. If the sulfur content of the original sample exceeds 0.22 %, the sulfur content may be determined using Test Method D1552.

10. Calculation

10.1 *Temperature Rise in Isothermal Jacket Calorimeter*—Using data obtained as prescribed in 9.5, compute the temperature rise, t , in an isothermal jacket calorimeter as follows:

$$t = t_c - t_a - r_1(b - a) - r_2(c - b) \quad (7)$$

where:

- t = corrected temperature rise,
- a = time of firing,

- b = time (to nearest 0.1 min) when the temperature rise reaches 60 % of total,
- c = time at beginning of period in which the rate of temperature change with time has become constant (after combustion),
- t_a = temperature at time of firing, corrected for thermometer error (10.1.1),
- t_c = temperature at time, c, corrected for thermometer error (10.1.1),
- r_1 = rate (temperature units per minute) at which temperature was rising during 5 min period before firing, and
- r_2 = rate (temperature units per minute) at which temperature was rising during the 5 min period after time c. If the temperature is falling, r_2 is negative and the quantity $-r_2(c - b)$ is positive.

10.1.1 All liquid-in-glass thermometers shall be corrected for scale error, using data from the thermometer certificate prescribed in Annex A1, A1.5.1, or A1.5.2. Beckmann thermometers also require a setting correction and an emergent stem correction (Annex A2, A2.1.2). Solid-stem ASTM Thermometers 56F and 56C do not require emergent stem corrections if all tests, including standardization are performed within the same 5.5 °C interval. If operating temperatures exceed this limit, apply a differential emergent stem correction (Annex A2, A2.1.1) to the correct temperature rise, t , in all tests, including standardization.

10.2 *Temperature Rise in Adiabatic Jacket Calorimeter*—Using data obtained as prescribed in 9.6, compute the temperature rise, t , in an adiabatic jacket calorimeter as follows:

$$t = t_f - t_a \quad (8)$$

where:

- t = corrected temperature rise,
- t_a = temperature when charge was fired, corrected for thermometer error (10.1.1), and
- t_f = final equilibrium temperature, corrected for the thermometer error (10.1.1).

10.3 *Thermochemical Corrections* (Annex A2)—Compute the following for each test:

- e_1 = correction for heat of formation of nitric acid (HNO_3), MJ = cm^3 of standard (0.0866 N) NaOH solution used in titration $\times 5/10^6$,
- e_2 = correction for heat of formation of sulfuric acid (H_2SO_4). MJ = $58.0 \times$ percentage of sulfur in sample \times mass of sample/ 10^6 ,
- e_3 = correction for heat of combustion and pressure-sensitive tape or gelatin capsule and mineral oil, MJ = mass of tape or capsule/oil, g \times heat of combustion of tape or capsule/oil, MJ/kg/ 10^6 , and
- e_4 = correction for heat of combustion of firing wire, MJ, = $1.13 \times$ millimetres of iron wire consumed/ 10^6 , = $0.96 \times$ millimetres of Chromel C wire consumed/ 10^6 .

10.4 *Gross Heat of Combustion*—Compute the gross heat of combustion by substituting in the following equation:

$$Q_g = (tW - e_1 - e_2 - e_3 - e_4) \times (1000/m) \quad (9)$$

where:

- Q_g = gross heat of combustion, at constant volume expressed as MJ/kg,
- t = corrected temperature rise (10.1 or 10.2), °C,
- W = energy equivalent of calorimeter, MJ/°C (8.1),
- e_1, e_2, e_3, e_4 = corrections as prescribed in 10.3, and
- m = mass of sample, g.

NOTE 7—The gross heat of combustion at constant pressure may be calculated as follows:

$$Q_{gp} = Q_g + 0.006145H \quad (10)$$

where:

- Q_{gp} = gross heat of combustion at constant pressure, MJ/kg, and
- H = mass percent of hydrogen in the sample. When the percentage of hydrogen in the sample is not known, the hydrogen content may be determined by Test Methods D1018, D3701, or D7171.

10.5 *Net Heat of Combustion*:

10.5.1 If the percentage of hydrogen, H , in the sample is known, the net heat of combustion may be calculated as follows:

$$Q_n = Q_g - 0.2122 \times H \quad (11)$$

where:

- Q_n = net heat of combustion at constant pressure, MJ/kg,
- Q_g = gross heat of combustion at constant volume, MJ/kg, and
- H = mass percent of hydrogen in the sample. When the percentage of hydrogen in the sample is not known, the hydrogen content may be determined by Test Methods D1018, D3701, or D7171.

10.5.2 If the mass percentage of hydrogen in aviation gasoline and turbine fuel samples is not determinable, the net heat of combustion may be calculated as follows:

$$Q_n = 10.025 + (0.7195)Q_g \quad (12)$$

where:

- Q_n = net heat of combustion at constant pressure, MJ/kg,
- Q_g = gross heat of combustion at constant volume, MJ/kg.

NOTE 8—Eq 12 is recommended only if the percentage of hydrogen is not determinable. It is based on Eq 11 and an empirical relation between Q_n and the percentage of hydrogen in aviation gasolines and turbine fuels, developed from data by Jessup and Cragoe.⁷

11. Report

11.1 Net heat of combustion is the quantity required in practical applications. The net heat should be reported to the nearest 0.005 MJ/kg.

NOTE 9—Usually the gross heat of combustion is reported for fuel oils

⁷ Jessup, R. S., and Cragoe, C. S., "Net Heat of Combustion of AN-F-28 Aviation Gasolines," Nat. Advisory Committee for Aeronautics, Technical Note No. 996, June 1945, and Joseph A. Coglianese and Ralph S. Jessup, "Relation Between Net Heat of Combustion and Aniline-Gravity Product of Aircraft Fuels," Nat. Institute of Standards Technology Report 2348, March 1953.

in preference to net heat of combustion to the nearest 0.005 MJ/kg.

11.2 To obtain the gross or net heat of combustion in cal (I.T.)/g or Btu/lb divide by the appropriate factor reporting to the nearest 0.5 cal/g or 1 Btu/lb.

$$Q_{\text{Btu}}/\text{lb} = (Q, \text{ MJ/kg})/0.002326 \quad (13)$$

$$Q_{\text{cal}}/\text{g} = (Q, \text{ MJ/kg})/0.0041868 \quad (14)$$

12. Precision and Bias⁸

12.1 *Precision*—The precision of this test method as obtained by statistical examination of interlaboratory test results is as follows:

12.1.1 *Repeatability*—The difference between successive test results obtained by the same operator with the same

⁸ Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR: RR:D02-38. The summary of cooperative test data from which these repeatability and reproducibility values were calculated was published for information as Appendix XII to the 1957 Report of Committee D02 on Petroleum Products and Lubricants. The summary of test data was also published from 1958 to 1966, inclusive, as Appendix III to ASTM Test Method D240.

apparatus under constant operating conditions on identical test material, would in the long run, in the normal and correct operation of the test method, exceed the values shown in the following table only in one case in twenty.

Repeatability	0.13 MJ/kg
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12.1.2 *Reproducibility*—The difference between two single and independent results, obtained by different operators working in different laboratories on identical test material, would in the long run, in the normal and correct operation of the test method, exceed the values shown in the following table only in one case in twenty.

Reproducibility	0.40 MJ/kg
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12.2 *Bias*—No general statement is made on bias for the standard since comparison with accepted reference materials (covering the range of values expected when the method is used) is not available.

13. Keywords

13.1 bomb calorimeter methods; gross heat of combustion; heat of combustion; heating tests; net heat of combustion

ANNEXES

(Mandatory Information)

A1. APPARATUS FOR HEAT OF COMBUSTION TEST

A1.1 *Test Room*—The room in which the calorimeter is operated must be free from drafts and not subject to sudden temperature changes. The direct rays of the sun shall not strike the jacket or thermometers. Adequate facilities for lighting, heating, and ventilating shall be provided. Thermostatic control of room temperature and controlled relative humidity are desirable.

A1.2 *Oxygen Bomb*—The oxygen bomb is to have an internal volume of 350 mL \pm 50 mL. All parts are to be constructed of materials which are not affected by the combustion process or products sufficiently to introduce measurable heat input or alteration of end products. If the bomb is lined with platinum or gold, all openings shall be sealed to prevent combustion products from reaching the base metal. The bomb must be designed so that all liquid combustion products can be completely recovered by washing the inner surfaces. There must be no gas leakage during a test. The bomb must be capable of withstanding a hydrostatic pressure test to a gauge pressure of 3000 psi (20 MPa) at room temperature, without stressing any part beyond its elastic limit. (See **Note 3**.)

A1.3 *Calorimeter*—The calorimeter (**Note A1.1**) vessel shall be made of metal (preferably copper or brass) with a tarnish-resistant coating, and with all outer surfaces highly polished. Its size shall be such that the bomb will be completely immersed in water when the calorimeter is assembled. It shall have a device for stirring the water thoroughly and at a uniform rate, but with minimum heat input. Continuous stirring

for 10 min shall not raise the calorimeter temperature more than 0.01 °C starting with identical temperatures in the calorimeter, room, and jacket. The immersed portion of the stirrer shall be coupled to the outside through a material of low heat conductivity.

Note A1.1—As used in this test method, the term *calorimeter* designates the bomb, the vessel with stirrer, and the water in which the bomb is immersed.

A1.4 *Jacket*—The calorimeter shall be completely enclosed within a stirred water jacket and supported so that its sides, top, and bottom are approximately 10 mm from the jacket wall. The jacket can be arranged so as to remain at substantially constant temperature, or with provision for rapidly adjusting the jacket temperature to equal that of the calorimeter for adiabatic operation. It must be constructed so that any water evaporating from the jacket will not condense on the calorimeter.⁹

A1.4.1 A double-walled jacket with a dead-air insulation space may be substituted for the constant-temperature water jacket if the calorimeter is operated in a constant-temperature (± 2 °F) (± 1 °C) room. The same ambient conditions must be maintained for all experiments, including standardization.

⁹ The sole source of supply of the apparatus known to the committee at this time is Parr Instrument Co., 211 Fifty-Third St., Moline, IL 61265. If you are aware of alternative suppliers, please provide this information to ASTM Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee,¹ which you may attend.

A1.5 Thermometers—Temperatures in the calorimeter and jacket shall be measured with the following thermometers or combinations thereof:

A1.5.1 Etched Stem, Liquid-in-Glass, ASTM Bomb Calorimeter Thermometer having a range from 66 °F to 95 °F or 19 °C to 35 °C, 18.9 °C to 25.1 °C, or 23.9 °C to 30.1 °C, as specified, and conforming to the requirements for Thermometer 56F, 56C, 116C, or 117C, respectively, as prescribed in Specification E1. Each of these thermometers shall have been tested for accuracy at intervals no larger than 2.5 °F or 2.0 °C over the entire graduated scale. Corrections shall be reported to 0.005 °F or 0.002 °C, respectively, for each test point.

A1.5.2 Beckmann Differential Thermometer, range 6 °C reading upward as specified and conforming to the requirements for Thermometer 115C as prescribed in Specification E1. Each of these thermometers shall be tested for accuracy at intervals no larger than 1 °C over the entire graduated scale and corrections reported to 0.001 °C for each test point.

A1.5.3 Calorimetric Type Platinum Resistance Thermometer, 25 Ω.

A1.6 Thermometer Accessories—A magnifier is required for reading liquid-in-glass thermometers to one tenth of the smallest scale division. This shall have a lens and holder designed so as not to introduce significant errors due to parallax.

A1.6.1 A Wheatstone bridge and galvanometer capable of measuring resistance of 0.0001 Ω are necessary for use with resistance thermometers.

A1.7 Timing Device—A watch or other timing device capable of measuring time to 1 s is required for use with the isothermal jacket calorimeter.

A1.8 Sample Holder—Nonvolatile samples shall be burned in an open crucible of platinum (preferred), quartz or acceptable base metal alloy. Base metal alloy crucibles are acceptable if after a few preliminary firings the weight does not change significantly between tests.

A1.9 Firing Wire—Use a 100 mm length of No. 34 B & S gauge iron wire or Chromel C resistance wire. Shorter lengths may be used if the same length is employed in all tests, including standardization tests. Platinum wire may be used if the ignition energy is small and reproducible.

A1.10 Firing Circuit—A 6 V to 16 V alternating or direct current is required for ignition purposes with an ammeter or pilot light in the circuit to indicate when current is flowing. A step-down transformer connected to a 115 V 50/60 Hz lighting circuit of storage batteries can be used (**Warning**—The ignition circuit switch shall be of the momentary contact type, normally open, except when held closed by the operator.).

A1.11 Oxygen Purifying Device—Commercial oxygen produced from liquid air can generally be used without purification. Oxygen prepared by electrolysis of water should not be used without purification, as it can contain enough hydrogen to affect results by 1 % or more. Combustible impurities can be removed from oxygen by passing it over copper oxide (CuO) at about 500 °C.

A2. CORRECTIONS

A2.1 Thermometer Corrections¹⁰

A2.1.1 The differential emergent stem correction for solid stem calorimetric thermometers (56F and 56C) may be computed from the following equation:

$$\text{Differential stem correction} = K(t_c - t_a)(t_a + t_c - L - T) \quad (\text{A2.1})$$

where:

K = differential expansion coefficient of the liquid and the glass of which the thermometer is made; for mercury-in-glass, the value is 0.00016 for Celsius thermometers; for organic liquid-in-glass, the value is 0.001 for Celsius thermometers,

L = scale reading to which the thermometer was immersed,

T = mean temperature of emergent stem,

t_a = initial temperature reading, and

t_c = final temperature reading.

A2.1.2 Differential emergent stem correction for a Beckman thermometer immersed to the zero of the scale may be computed as follows:

$$\text{Differential stem correction} = K(t_c - t_a)(S + t_c + t_a - T) \quad (\text{A2.2})$$

where:

S = setting (temperature at zero reading) of the thermometer.

K , T , t_c , and t_a as defined in A2.1.1.

A2.1.3 Setting correction for a Beckmann thermometer may be computed as follows:

$$\text{Setting correction} = \text{factor} \times (t_c - t_a) \quad (\text{A2.3})$$

where:

Factor is obtained from Table A2.1 and t_c and t_a as defined in A2.1.1.

A2.2 Thermochemical Corrections

A2.2.1 Heat of Formation of Nitric Acid—A correction of 5 J is applied for each cubic centimetre of standard

¹⁰ For a complete discussion of those corrections, see the American Institute of Physics Symposium, *Temperature, Its Measurement and Control in Science and Industry*, Reishold Publishing Corp., New York, NY, 1941.

TABLE A2.1 Correction Factors

Setting	Factor
15	-0.0015
20	0.0000
25	+0.0015
30	+0.0029
35	+0.0043
40	+0.0056

(0.0866 mol/L) NaOH solution used in the acid titration. This is based on the assumption that (1) all of the acid titrated is HNO₃ and (2) the heat of formation of 0.1 M HNO₃ under the test conditions is 57.8 kJ/mole. When H₂SO₄ is also present, part of the correction for H₂SO₄ is contained in the *e*₁ correction, and the remainder in the *e*₂ correction.

A2.2.2 Heat of Formation of Sulfuric Acid—A correction of 5.80 kJ is applied to each gram of sulfur in the sample. This is based upon the heat of formation of 0.17 M H₂SO₄, which is -301.4 kJ/mole. But, a correction equal to 2 × 57.8 kJ/mole of sulfur was applied for H₂SO₄ in the *e*₁ correction. Thus, the additional correction necessary is:

$$301.4 - (2 \times 57.8) = 185.8 \text{ kJ/mole or } 5.80 \text{ kJ/g of sulfur} \quad (\text{A2.4})$$

A2.2.2.1 The value of 5.80 kJ/g of sulfur is based on a fuel oil containing a relatively large amount of sulfur since as the percentage of sulfur decreases, the correction decreases and consequently a larger error can be tolerated. For this calculation 0.8 % S, 99.2 % CH₂ was taken as the empirical composition of fuel oil. If a 0.6 g sample of such a fuel oil is burned in a bomb containing 1 cm³ of water, the H₂SO₄ formed will be approximately 0.17 mol/L.

A2.2.2.2 Using data from National Institute of Standards Technology *Circular No. 500*, the heat of reaction SO₂ (g) + ½ O₂ (g) + 651 H₂O (1) – H₂SO₄·650 H₂O (1) at constant volume and 3 MPa is -301.4 kJ/mole.

A2.2.3 Heat of Combustion of Fuse Wire—The following heats of combustion are accepted:

Iron wire, No. 34 B & S gauge = 1.13 J/mm
Chromel C wire No. 34 B & S gauge = 0.96 J/mm

A2.2.4 Heat of Combustion of Pressure-Sensitive Tape—The correction for the heat of combustion of the tape (as determined in accordance with 8.3) assumes complete combustion of the tape.

A3. WARNING STATEMENTS

A3.1 Sodium Hydroxide

Warning—Corrosive. Can cause severe burns or blindness. Evolution of heat produces a violent reaction or eruption upon too rapid mixture with water.

Before using, secure information on procedures and protective measures for safe handling.

Do not get in eyes, on skin, on clothing.

Avoid breathing dusts or mists.

Do not take internally.

When handling, use chemical safety goggles or face shield, protective gloves, boots, and clothing.

When mixing with water, add slowly to surface of solution to avoid violent spattering. In the preparation of solutions do not use hot water, limit temperature rise, with agitation, to 10 °C/min or limit solution temperature to a maximum of 90 °C. No single addition should cause a concentration increase greater than 5 %.

A3.2 Oxygen

Warning—Oxygen vigorously accelerates combustion.

Do not exceed the sample size limits.

Do not use oil or grease on regulators, gauges, or control equipment.

Use only with equipment conditioned for oxygen service by carefully cleaning to remove oil, grease, and other combustibles.

Keep combustibles away from oxygen and eliminate ignition sources.

Keep surfaces clean to prevent ignition or explosion, or both, on contact with oxygen.

Always use a pressure regulator. Release regulator tension before opening cylinder valve.

All equipment and containers used must be suitable and recommended for oxygen service.

Never attempt to transfer oxygen from cylinder in which it is received to any other cylinder.

Do not mix gases in cylinders.

Do not drop cylinder. Make sure cylinder is secured at all times.

Keep cylinder valve closed when not in use.

Stand away from outlet when opening cylinder valve.

Keep cylinder out of sun and away from heat.

Keep cylinder from corrosive environment.

Do not use cylinder without label.

Do not use dented or damaged cylinders.

For technical use only. Do not use for inhalation purposes.

Use only in well-ventilated area.

See compressed gas association booklets G-4 and G-4.1 for details of safe practice in the use of oxygen.

A3.3 2,2,4-Trimethylpentane

Warning—Extremely flammable. Harmful if inhaled.

Vapors may cause flash fire.

Keep away from heat, sparks, and open flame.

Keep container closed.

Use with adequate ventilation.

Avoid buildup of vapors and eliminate all sources of ignition, especially nonexplosion-proof electrical apparatus and heaters.

Avoid prolonged breathing of vapor or spray mist.

Avoid prolonged or repeated skin contact.

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SUMMARY OF CHANGES

Subcommittee D02.05 has identified the location of selected changes to this standard since the last issue (D240 – 17) that may impact the use of this standard. (Approved Nov. 1, 2019.)

(1) Revised subsection 3.1.1.1.

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