



Designation: D240 – 14

# Standard Test Method for Heat of Combustion of Liquid Hydrocarbon Fuels by Bomb Calorimeter<sup>1</sup>

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 ( $\epsilon$ ) 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 and health 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.

## 2. Referenced Documents

### 2.1 ASTM Standards:<sup>2</sup>

- D129 Test Method for Sulfur in Petroleum Products (General High Pressure Decomposition Device Method)
- D1018 Test Method for Hydrogen in Petroleum Fractions
- D1266 Test Method for Sulfur in Petroleum Products (Lamp Method)
- 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

<sup>1</sup> 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.

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<sup>2</sup> 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.

- 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, 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 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, oxygen, nitrogen, 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

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

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<sub>it</sub> (International Table calorie) = 4.1868 J
- 1 Btu<sub>it</sub> (International Table British thermal unit) = 1055.05585262 J and typically rounded to 1055.056 for practical use
- 1 cal<sub>it</sub>/g = 0.0041868 MJ/kg
- 1 Btu<sub>it</sub>/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:

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

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.<sup>3</sup>

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.

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

<sup>3</sup> Supporting data (derivation of equations) have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR: D02-1346.

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*<sup>4</sup>—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. 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 Na<sub>2</sub>CO<sub>3</sub> 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), Standard*<sup>5</sup>—**(Warning)**—Extremely flammable. Harmful if inhaled. Vapors may cause flash fire. See Annex **A3.3**.)

<sup>4</sup> 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.

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

## 8. Standardization

8.1 *Determine the Energy Equivalent of the Calorimeter*—Average not less than six tests using standard benzoic acid.<sup>6</sup> 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 (C<sub>6</sub>H<sub>6</sub>COOH). 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 (HNO<sub>3</sub>) 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*<sub>1</sub> = correction for heat of formation of nitric acid, MJ, and
- e*<sub>2</sub> = 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*<sub>pst</sub> = heat of combustion of the pressure-sensitive tape or mineral oil, MJ/kg,
- $\Delta t$  = corrected temperature rise, as calculated in accordance with 10.1 or 10.2, °C,
- W* = energy equivalent of the calorimeter, MJ/°C,
- e*<sub>1</sub> = correction for the heat of formation of HNO<sub>3</sub>, 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*<sub>s</sub> = 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 MJ 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/m<sup>3</sup>, 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 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

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

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 ( $\pm 0.5$  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  $\Omega$  resistance thermometer readings to the nearest 0.0001  $\Omega$ . 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  $\pm 0.01$  °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  $\pm 0.01$  °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, D1266, D2622, D3120, D4294, or D5453.

## 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