



Standard Test Method for Heat of Combustion of Hydrocarbon Fuels by Bomb Calorimeter (High-Precision Method)¹

This standard is issued under the fixed designation D 2382; 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 Department of Defense. Consult the DoD Index of Specifications and Standards for the specific year of issue which has been adopted by the Department of Defense.

1. Scope

1.1 This test method covers the determination of the heat of combustion of hydrocarbon fuels. It is designed specifically for use with aviation turbine fuels when the permissible difference between duplicate determinations is of the order of 0.1 % (Note 1). It can be used for a wide range of volatile and nonvolatile materials where slightly greater differences in precision can be tolerated.

NOTE 1—In order to attain this accuracy, strict adherence to all details of the procedure is essential since the error contributed by each individual measurement that affects the accuracy shall be kept below 0.02 %, insofar as possible.

1.2 *This standard may involve hazardous materials, operations, and equipment. This standard does not purport to address all of the safety problems 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 7.6, 7.8, Note 6, 11.6 and Note A1.1.

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

2. Referenced Documents

2.1 ASTM Standards:

- D 129 Test Method for Sulfur in Petroleum Products (General Bomb Method)²
- D 240 Test Method for Heat of Combustion of Liquid Hydrocarbon Fuels by Bomb Calorimeter²
- D 1018 Test Method for Hydrogen in Petroleum Fractions²
- D 1193 Specification for Reagent Water³
- D 1266 Test Method for Sulfur in Petroleum Products (Lamp Method)²
- D 1552 Test Method for Sulfur in Petroleum Products (High-Temperature Method)²

¹ This test method is under the jurisdiction of ASTM Committee D-2 on Petroleum Products and Lubricants and is the direct responsibility of Subcommittee D02.05 on Properties of Fuels, Petroleum Coke and Oil Shale.

Current edition approved Oct. 31, 1988. Published December 1988. Originally published as D 2382 – 65 T. Last previous edition D 2382 – 83.

² Annual Book of ASTM Standards, Vol 05.01.

³ Annual Book of ASTM Standards, Vol 11.01.

- D 2622 Test Method for Sulfur in Petroleum Products by X-Ray Spectrometry⁴
- D 3701 Test Method for Hydrogen Content of Aviation Turbine Fuels by Low Resolution Nuclear Magnetic Resonance Spectrometry⁴
- D 4294 Test Method for Sulfur in Petroleum Products by Energy-Dispersive X-Ray Fluorescence Spectroscopy⁴
- E 1 Specification for ASTM Thermometers⁵
- E 144 Practice for Safe Use of Oxygen Combustion Bombs⁶
- E 200 Practice for Preparation, Standardization, and Storage of Standard Solutions for Chemical Analysis⁷

3. Terminology

3.1 The energy unit of measurement employed in this test method is the joule with the heat of combustion reported in megajoules per kilogram (Note 2).

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

NOTE 2—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.

3.1.1 The following relationships may be used for converting to other units:

- 1 cal (Thermochemical) = 4.1840 J⁴
- 1 Btu (Thermochemical) = 1054.35 J
- 1 cal (I.T.)/g = 0.0041868 MJ/kg⁴
- 1 Btu/lb = 0.002326 MJ/kg⁴

⁴ Conversion factor is exact.

3.2 *Gross Heat of Combustion*, expressed as megajoules per kilogram. The gross heat of combustion at constant volume of a liquid or solid fuel containing only the elements carbon, hydrogen, oxygen, nitrogen, and sulfur is the quantity of heat liberated when a unit mass of the fuel is burned in oxygen in an enclosure of constant volume, the products of combustion being gaseous carbon dioxide, nitrogen, sulfur dioxide, and liquid water, with the initial temperature of the fuel and the oxygen and the final temperature of the

⁴ Annual Book of ASTM Standards, Vol 05.02.

⁵ Annual Book of ASTM Standards, Vols 05.03 and 14.03.

⁶ Annual Book of ASTM Standards, Vol 14.02.

⁷ Annual Book of ASTM Standards, Vol 15.05.

products at 25°C. Gross heat of combustion⁸ is represented by the symbol Q_g .

3.3 *Net Heat of Combustion*, expressed as megajoules per kilogram. The net heat of combustion at constant pressure of a liquid or a solid fuel containing only the elements carbon, hydrogen, oxygen, nitrogen, and sulfur is the quantity of heat liberated when a unit mass of the fuel is burned in oxygen at a constant pressure of 0.101 MPa (1 atm), the products of combustion being carbon dioxide, nitrogen, sulfur dioxide, and water, all in the gaseous state, with the initial temperature of the fuel and the oxygen and the final temperature of the products of combustion at 25°C. The net heat of combustion⁹ is represented by the symbol Q_n and 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 % of hydrogen in the sample.

3.4 *Energy Equivalent (Effective Heat Capacity or Water Equivalent)*—The energy equivalent of the calorimeter expressed as joules per ohm is the energy required to raise the temperature of the calorimeter 1 Ω.

3.5 *Temperatures* are measured in ohms (see Note 3).

NOTE 3—The conversion of resistance in ohms to temperature in degrees Celsius is not strictly a straight-line function, but if the mean temperature of the experiment is kept within reasonable limits (the mean value of the initial and final resistance within 0.1 Ω of a previously established value), no significant error is introduced.⁹

3.6 *Time* is expressed in minutes and decimal fractions thereof. It may be measured in minutes or seconds, or both.

3.7 *Masses* are measured in grams. No buoyancy corrections are applied except to obtain the mass of benzoic acid.

4. Summary of Test Method

4.1 The heat of combustion is determined by burning a weighed sample in an oxygen-bomb calorimeter under controlled conditions. The temperature is measured by means of a platinum resistance thermometer. The heat of combustion is calculated from temperature observations before, during, and after combustion, with proper allowance for thermochemical and heat-transfer corrections. Either

isoperibol or adiabatic calorimeters may be used.

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 mass heat of combustion, that is, the heat of combustion per unit mass of fuel, is measured by this procedure. Its magnitude is particularly important to weight-limited vehicles such as airplanes, surface effect vehicles, and hydrofoils as the distance such craft can travel on a given weight of fuel is a direct function of the fuel's mass heat of combustion and its density.

5.3 The volumetric heat of combustion, that is, the heat of combustion per unit volume of fuel, can be calculated by multiplying the mass heat of combustion by the density of the fuel (mass per unit volume). The volumetric heat of combustion, rather than the mass heat of combustion, is important to volume-limited craft such as automobiles and ships, as it is directly related to the distance traveled between refuelings.

5.4 The high-precision procedure employed in this test method roughly halves the repeatability and reproducibility associated with Test Method D 240, the earlier bomb calorimeter method. The greater precision permits improved measures of the thermal efficiency of heat devices.

6. Apparatus

6.1 *Test Room, Bomb, Calorimeter, Jacket, Thermometers, and Accessories*, as described in Annex A1.

6.2 *Semimicro Analytical Balance*, having a sensitivity of 0.01 mg as specified in 11.5.1.

6.3 *Heavy-Duty Analytical Balance*, having a sensitivity of 0.05 g as specified in 11.7.2.

7. Reagents and Materials

7.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.¹⁰ Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

7.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean reagent water conforming to Specification D 1193, Type IV or better.

7.3 *Benzoic Acid*¹¹—The acid must be pelleted before use.

7.4 *Firing Wire*—0.127 mm (No. 36 gage) platinum wire, cut in 100-mm lengths.

7.5 *Methyl Red Indicator*.

7.6 *Oxygen*—Commercial oxygen produced from liquid air can be used without purification (**Warning**—See Note 4.)

⁸ Users of this test method desiring to calculate ΔH_{c298}° for a pure compound should note that corrections shall be applied to the value of Q_g for buoyancy of air, heat capacities of reaction components, reduction to a constant-pressure process, and deviations of the reaction from the thermodynamic standard state. See, for example, Prosen, E. J., "Experimental Thermochemistry," F. D. Rossini, editor, Interscience Publishers, 1956, pp. 129–148. Reliable values for heats of combustion of pure compounds are given in National Bureau of Standards Circular C-461, "Selected Values of Properties of Hydrocarbons" (U. S. Government Printing Office, Washington, D. C., 1947) and in F. D. Rossini, et al., "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds," Carnegie Press, Pittsburgh, Pa., 1953. These compilations were prepared by F. D. Rossini, et al, as part of American Petroleum Institute Research Project 44. In any comparison of measurements on pure compounds with those cited in these compilations, the user of this test method should realize that impurities of various kinds, including water and foreign hydrocarbons may cause significant effects on the values obtained for particular samples of material.

⁹ See Jessup, R. S., "Precise Measurement of Heat of Combustion with a Bomb Calorimeter," *NBS Monograph 7*, U. S. Government Printing Office.

¹⁰ "Reagent Chemicals, American Chemical Society Specifications," Am. Chemical Soc., Washington, D.C. For suggestions on the testing of reagents not listed by the American Chemical Society, see "Anal. Standards for Laboratory U.K. Chemicals," BDH Ltd., Poole, Dorset, New York, NY, and the "United States Pharmacopeia."

¹¹ Obtainable from the National Bureau of Standards, Washington, D.C. 20234, as Standard Sample 39i.

Oxygen prepared by electrolysis of water cannot be used without purification as it can contain some hydrogen. Combustible impurities can be removed by passage over copper oxide at 500°C.

NOTE 4: **Warning**—Oxygen vigorously accelerates combustion. See Annex A3.1.

7.7 *Pressure-Sensitive Tape*—Cellophane tape 38 mm (1½ in.) wide.¹²

7.8 *Sodium Hydroxide Solution (0.0866 N)*—Dissolve 3.5 g of sodium hydroxide (NaOH) in water and dilute to 1 L (**Warning**—See Note 5). Standardize with potassium acid phthalate and adjust to 0.0866 N as described in Practice E 200.

NOTE 5: **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 A3.2.

8. Calibration Apparatus

8.1 *Calibration of Resistance Bridge*—The Mueller-type bridge should have its calibration checked at periodic intervals against a suitable external certified resistance.

8.2 *Calibration of Platinum Resistance Thermometer*—The platinum resistance thermometer is provided with three calibration constants determined by the manufacturer. These are as follows: the resistance, R_0 , at the ice point; the fundamental coefficient, c , of the coil; and delta (δ) in the Callender equation. If the thermometer is properly constructed, the constants c and δ will not significantly change with time. The value of R_0 can change slightly. Because of this tendency to change and because R_0 is to be determined with the Mueller bridge used in the test, this value is given only to three decimal places. R_0 is to be determined initially by determining the ice point¹³ in duplicate on three different days and averaging the results, and check periodically (once every three months). If the value of R_0 changes significantly (0.001 Ω), the calibration of the bridge shall be checked. If the bridge has not changed a recalibration of the platinum resistance thermometer is necessary.

9. Preparation of Apparatus

9.1 *Arrangement of Apparatus* (Note 6)—Install the platinum resistance thermometer in the bucket so that at least 152 mm (6 in.) of the sheath is immersed. Position the mercury-in-glass thermometer so that the bulb is halfway to the bottom of the bucket and locate the thermistor with its sensing element at about the midpoint of the thermometer bulb. Mount these elements so that exactly the same length is immersed each time the calorimeter is used. Install a thermistor in the water jacket with the element immersed to the same depth as in the bucket. It will be helpful, but not necessary to have mercury-in-glass calorimetric thermometers in both the bucket and jacket for quick temperature observations. Tape the thermistors to these thermometers and mount the platinum resistance thermometer separately.

¹² Cellophane tape Scotch Brand No. 600 or 610, available from the Minnesota Mining and Manufacturing Co., meets the specification requirements.

¹³ The ice point should be determined in accordance with the procedure described in "Notes to Supplement Resistance Thermometer Certificates," National Bureau of Standards (1949).

If the thermistors are taped to the thermometers, do it in such a manner that the sensing elements are at the midpoint of the thermometer bulbs. The thermometer bulbs and temperature-sensing elements shall not touch the bomb, bucket, or water jacket.

NOTE 6—This arrangement applies to the use of the Parr equipment for adiabatic measurements.

9.2 *Calorimeter Controller and Heater*—Turn on the water heater and allow about 10 min for it to come to operating temperature. Assemble an oxygen bomb and place it in the calorimeter bucket with 2100 g of water. Place the bucket in the calorimeter jacket and close the cover. Start the calorimeter stirrer and controller. Lower the thermometers into place. Open the two throttling valves on the controller about one turn and add hot or cold water with the manual control until the galvanometer spot moves toward the center zero point. Allow the system to operate under automatic control and make adjustments with the throttling valves until the spot swings uniformly back and forth within not more than ten divisions on either side of the zero point. Use the mercury-in-glass thermometers and the balance control potentiometer to bring the bucket and jacket temperatures into balance, then using the platinum resistance thermometer adjust the balance control potentiometer so that the temperature of the bucket remains constant or lowers slightly (not more than 0.001 Ω in 5 min). The two valves (or plugcocks) on the water inlet to the calorimeter shall be used for coarse adjustment when a full flow of hot or cold water is admitted to the jacket. Close the hot-water valve sufficiently to prevent an excessive temperature over-shoot during periods of rapid temperature rise. Close the cold-water valve far enough to prevent flooding when a full flow of cold water is admitted to the jacket.

10. Standardization

10.1 *Energy Equivalent of the Calorimeter*—Benzoic acid shall be used as the primary standard (Note 7). Choose a sample mass so that the temperature rise is approximately 0.32 Ω (3.2°C average temperature rise). Initially determine the energy equivalent by averaging six determinations made using benzoic acid over a period of at least 3 days. Then determine it at frequent intervals using benzoic acid (every 1 or 2 days) with the average of the last six determinations being used for the energy equivalent. If any part of the equipment is changed or any part of the procedure is altered, the value should be redetermined. Make each determination in accordance with Section 11. Determine the correction for nitric acid (HNO₃) as described in 12.4 and substitute in the following equation:

$$W = (Q_b \times m + e_1) / \Delta t \quad (3)$$

where:

W = energy equivalent of calorimeter, J/ Ω ,

m = mass of benzoic acid, (in vacuum) g, (Note 8),

Δt = corrected temperature rise, as calculated in accordance with 12.2 or 12.3, Ω ,

e_1 = correction for heat of formation of nitric acid, J, and

Q_b = heat of combustion of benzoic acid, J/g calculated from the certified value in kilojoules per gram (determined in vacuum) given for NBS Standard 39i. Multiply kilojoules per gram mass by 1000 to obtain joules per gram (Note 9).