



Designation: **D4809 – 13 D4809 – 18**

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

This standard is issued under the fixed designation D4809; 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 hydrocarbon fuels. It is designed specifically for use with aviation turbine fuels when the permissible difference between duplicate determinations is of the order of 0.2 %. It can be used for a wide range of volatile and nonvolatile materials where slightly greater differences in precision can be tolerated.

1.2 In order to attain this precision, strict adherence to all details of the procedure is essential since the error contributed by each individual measurement that affects the precision shall be kept below 0.04 %, insofar as possible.

1.3 Under normal conditions, ~~the~~^{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.

1.4 Through the improvement of the calorimeter controls and temperature measurements, the precision is improved over that of Test Method **D240**.

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

1.6 *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 ~~health~~ environmental practices and determine the applicability of regulatory limitations prior to use.* For specific warning statements, see Section 7, 10.6, A1.7.1, and Annex A3.

1.7 *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

[ASTM D4809-18](#)

2.1 *ASTM Standards:*² [www.astm.org/catalog/standards/sist/fc66cf9a-5536-47a7-840a-d3db67577fb0/astm-d4809-18](#)

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

D240 Test Method for Heat of Combustion of Liquid Hydrocarbon Fuels by Bomb Calorimeter

D1018 Test Method for Hydrogen In Petroleum Fractions

D1193 Specification for Reagent Water

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

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

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

¹ This test method is under the jurisdiction of ASTM Committee **D02** on Petroleum Products—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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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.

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

E1 Specification for ASTM Liquid-in-Glass Thermometers

E144 Practice for Safe Use of Oxygen Combustion Vessels

E200 Practice for Preparation, Standardization, and Storage of Standard and Reagent Solutions for Chemical Analysis

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<https://standards.itih.ai/catalog/standards/sist/fc66cf9a-5536-47a7-840a-d3db67577fb0/astm-d4809-18>

3. Terminology

3.1 Definitions:

3.1.1 *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 products at 25°C. Gross heat of combustion (see **Note 1**) is represented by the symbol Q_g .³

NOTE 1—Users of this test method desiring to calculate ΔH° for a pure compound should note that corrections must 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. In any comparison of measurements on pure compounds with those cited in these compilations³, 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.

3.1.1 *net gross heat of combustion—combustion, Q_g (MJ/kg)³, n* —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 the quantity of energy released when a unit mass of the fuel is burned in oxygen at a constant pressure of 0.101 MPa, 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 combustion in a constant volume enclosure, with the products being gaseous, other than water that is represented by the symbol condensed Q_n and is related to the gross heat of combustion by the following equation: to the liquid state.

$$Q_n(\text{net}, 25^\circ\text{C}) = Q_g(\text{gross}, 25^\circ\text{C}) - 0.2122 \times H \quad (1)$$

where:

$Q_n(\text{net}, 25^\circ\text{C})$ = net heat of combustion at constant pressure, MJ/kg,
 $Q_g(\text{gross}, 25^\circ\text{C})$ = gross heat of combustion at constant volume, MJ/kg, and
 H = mass % of hydrogen in the sample.

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 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)^{4,5}, n* —the quantity of energy released when a unit mass of fuel is burned at constant pressure, with all 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 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 *energy equivalent (effective heat capacity or water equivalent) equivalent), n* —the energy equivalent of the calorimeter expressed as joules per degree Celsius, J/°C.

NOTE 1—The energy equivalent may be expressed in any energy unit and any temperature unit so long as the value is used consistently throughout the calculations.

3.2 Units:

3.2.1 *Temperatures* are measured in degrees Celsius.

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

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

³ 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, DC, 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.

⁴ Supporting data (derivation of equations) have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D02-1346. Contact ASTM Customer Service at service@astm.org.

⁵ Jessup, R. S., “Precise Measurement of Heat of Combustion with a Bomb Calorimeter,” *NBS Monograph 7*, U.S. Government Printing Office.

3.2.4 The energy unit of measurement employed in this test method is the joule with the heat of combustion reported in megajoules per kilogram (Note 32).

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

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.

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

$$\begin{aligned} 1 \text{ cal (International Table calorie)} &= 4.1868 \text{ J}^A \\ 1 \text{ Btu (British thermal unit)} &= 1055.06 \text{ J} \\ 1 \text{ cal (I.T.)}/\text{g} &= 0.0041868 \text{ MJ}/\text{kg}^A \\ 1 \text{ Btu}/\text{lb} &= 0.002326 \text{ MJ}/\text{kg}^A \\ 1 \text{ atm} &= 0.101325 \text{ MPa} \end{aligned}$$

^A Conversion factor is exact.

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 increase is measured by a temperature reading instrument which allows the precision of the test method to be met. 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.

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 10.5.1.

6.3 *Heavy-Duty Analytical Balance*, having a sensitivity of 0.05 g as specified in 10.7.2.

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.⁶ 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 D1193, Type IV or better.

7.3 *Benzoic Acid*⁷—The acid must be pelleted before use.

7.4 *Firing Wire*—0.127 mm (No. 36 gage) platinum wire, No. 34 B & S gage iron wire or Chromel C resistance 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**—Oxygen vigorously accelerates combustion. (See A3.1.)) Oxygen prepared by electrolysis of water cannot be used without purification as it can contain some hydrogen. Combustible impurities may be removed by passage over copper oxide at 500°C.

⁶ *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 Obtainable from the National Institute of Standards and Technology, Clopper and Quince Orchard Roads, Gaithersburg, MD 20899, as Standard Sample 39i. If you are aware of alternative suppliers, please provide this information to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee,¹ which you may attend.

7.7 *Pressure-Sensitive Tape*—Cellophane tape 38 mm wide, free of chlorine and sulfur.⁸

7.8 *Alkali, Standard Solutions—Solutions.*

7.8.1 *Sodium Hydroxide Solution* (~~0.0866~~ (0.0866 *N*))—Dissolve ~~3.5 g~~ 3.5 g of sodium hydroxide (NaOH) in water and dilute to 1 L. (**Warning**—Corrosive. Can cause severe burns or blindness. Evolution of heat produces a violent reaction or eruption upon too rapid mixture with water (see water. See Annex A3.2.)). Standardize with potassium acid phthalate and adjust to 0.0866 *N* as described in Practice E200, or alternative use.

7.8.2 *Sodium Carbonate Solution* (~~0.0725~~ (0.0725 *N*))—Dissolve 3.84 g of Na₂CO₃ in water and dilute to 1 L.

7.9 *2,2,4-Trimethylpentane*—(isooctane), *Standard Standard*.⁹ (**Warning**—Extremely flammable. Harmful if inhaled. Vapors may cause flash fire. (See Annex A3.3.)).

8. Preparation of Apparatus

8.1 *Arrangement of Apparatus*—Install the thermometers as recommended by the manufacturer of the calorimeter. Position the liquid-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 is helpful, but not necessary to have liquid-in-glass calorimetric thermometers in both the bucket and jacket for quick temperature observations. Thermistors can be taped to these thermometers. If the thermistors are taped to the thermometers, it can be done 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.

8.2 *Calorimeter Jacket Controller and Auxiliary Equipment*—Adjust the jacket controller, valves, heater, etc., and so forth, as recommended by the calorimeter manufacturer.

9. Standardization

9.1 *Energy Equivalent of the Calorimeter*—Benzoic acid shall be used as the primary ~~standard~~ standard. (**Warning**—Oxygen vigorously accelerates combustion. See A3.1.) Choose a sample mass so that the temperature rise is approximately equivalent to an energy change of ~~30 000 J~~ 30 000 J. Initially determine the energy equivalent by averaging six determinations made using benzoic acid over a period of at least ~~3~~ three days.

9.1.1 A relative standard deviation (RSD) of 0.1 % or less for the six determinations must be achieved. If not, continue to run until six determinations establish a value that has a RSD of 0.1 % or better. If this degree of precision cannot be achieved, review the procedure, critical measurements, mechanical operations and everything that may contribute to scatter in the results. After establishing an energy equivalent value, determine the value at frequent intervals using benzoic acid (every ~~1~~ one or ~~2~~ two days of testing) with the average of the last six determinations being used for the energy equivalent as long as the last six determinations have a RSD of 0.1 % or less.

9.1.2 If any part of the equipment is changed or any part of the procedure is altered, redetermine the value. Make each determination in accordance with Section 10. Determine the correction for nitric acid (HNO₃) as described in 11.3 and substitute in the following equation:

$$W = (Q_b \times m + e_1) / \Delta t \quad (2)$$

where:

W = energy equivalent of calorimeter, J/°C,

m = mass of benzoic acid, g,

Δt = corrected temperature rise, as calculated in accordance with 11.1 or 11.2, °C,

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 mass given for NBS Standard 39i. Multiply kilojoules per gram mass by 1000 to obtain joules per gram (Note 5).

Q_b = heat of combustion of benzoic acid, J/g calculated from the certified value in kilojoules per gram mass given for NBS Standard 39i. Multiply kilojoules per gram mass by 1000 to obtain joules per gram (Note 4).

NOTE 3—2,2,4-trimethyl pentane may be used for checking the energy equivalent of the system for use with volatile fuels.

⁸ Cellophane tape Scotch Brand No. 610, available from 3M Co., meets the specification requirements. If you are aware of alternative suppliers, please provide this information to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee,¹ which you may attend.

⁹ Obtainable from the National Institute of Standards and Technology, Clopper and Quince Roads, Gaithersburg, MD 20899, as Standard Sample No. 217b. If you are aware of alternative suppliers, please provide this information to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee,¹ which you may attend.

NOTE 4—Multiply the heat evolved by combustion of the standard sample by the following factor.¹⁰

$$1 + 10^{-6} [197 (P - 3.04) + 42 ((m/V) - 3)] \quad (3)$$

$$+ 30 ((M_w/V) - 3) - 45 (t - 25)]$$

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$$+ 30 ((M_w/V) - 3) - 45 (t - 25)]$$

where:

P = initial absolute pressure of oxygen, MPa at temperature t ,

m = mass of benzoic acid, g,

M_w = mass of water placed in bomb before combustion, g,

V = internal volume of bomb, L, and

t = ~~temperature to which the combustion reaction is referred, °C (final temperature of the calorimeter).~~

t = ~~temperature to which the combustion reaction is referred, °C (final temperature of the calorimeter).~~

9.2 *Heat of Combustion of Pressure-Sensitive Tape*—Determine the heat of combustion of the pressure-sensitive tape in accordance with Section 10 using about 1.2 g of tape and omitting the sample. Make at least three determinations and calculate the heat of combustion as follows:

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

where:

Q_{pst} = heat of combustion of the pressure-sensitive tape, J/g

Δt = corrected temperature rise, as calculated in accordance with 11.1 or 11.2, °C,

W = energy equivalent of the calorimeter, J/°C,

e_1 = correction for the heat of formation of HNO₃, J, and

a = mass of the pressure-sensitive tape, g.

9.2.1 Average the determinations, and redetermine the heat of combustion of the tape whenever a new roll is started.

10. Procedure

10.1 Turn on the apparatus. Make all electrical connections and open the water lines.

10.2 Before beginning, be sure that the bomb and its fittings are completely dry, inside and out.

10.3 Measure a piece of firing wire 100 mm long and attach the wire to the bomb electrodes forming a U-shaped loop.

10.4 Pipet 1.0 cm³ of water into the bomb and cover with a watch glass.

10.5 *Mass of Sample:*

10.5.1 Weigh the sample cup to 0.01 mg on a semimicro analytical balance. Place a piece of pressure-sensitive type (Note 65) across the top of the cup, trim around the edge with a razor blade, and seal tightly. Place a 33-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 necessary to produce a temperature rise equivalent to approximately 30 000 J–30 000 J can be estimated as follows:

$$V = (W \times 0.0032) / (Q \times D) \quad (5)$$

where:

V = volume of sample to be used, cm³,

W = energy equivalent of the calorimeter, J/°C,

Q = approximate heat of combustion of the sample, MJ/kg, and

D = density, g/cm³, of the sample.

NOTE 5—For relatively high-boiling samples, such as non-volatile (i.e., in other words, IBP above +180°C) kerosine-type jet fuels, it is not necessary to use tape.

10.5.2 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.

10.6 *Bomb Assembly*—Assemble the bomb and tighten the cover securely. Connect the bomb to the oxygen cylinder and slowly admit oxygen until a pressure of 3.0 MPa is attained. Do not purge the bomb to remove entrapped air. Disconnect the bomb from

¹⁰ See NBS Monograph 7, p. 12.