BS 2000 :
Part 12 : 1993

Methods of test for

Petroleum and its products

Part 12. Determination of specific energy

(Identical with IP 12/79(80))

Confirmed
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British Standards

Foreword

This British Standard, having been prepared under the direction of the Petroleum Standards Policy Committee, was published under the authority of the Standards Board and comes into effect on 28 February 1993.

This British Standard supersedes BS 2000 : Part 12 : 1982, which is withdrawn.

BS 2000 comprises a series of test methods for petroleum and its products that are published by the Institute of Petroleum (IP) and have been accorded the status of a British Standard. Each method should be read in conjunction with the preliminary pages of `IP Standard methods for analysis and testing of petroleum and related products' which gives details of the BSI/IP agreement for publication of the series, provides general information on safety precautions, sampling and other matters, and lists the methods published as Parts of BS 2000.

The numbering of the Parts of BS 2000 follows that of the corresponding methods published in `IP Standard methods for analysis and testing of petroleum and related products'. Under the terms of the agreement between BSI and the Institute of Petroleum, the revised version of BS 2000 : Part 12 will be published by the IP (in `Standard methods for analysis and testing of petroleum and related products' and as a separate publication). BS 2000 : Part 12 : 1993 is thus identical with IP 12/79, which was reapproved in 1980. Square brackets marked in the margin of this IP Standard indicate text that differs from the previous edition.

IP 12 was previously published as a British Standard as BS 4379 (now withdrawn) which was subsequently renumbered and issued in the BS 2000 series.

Committee reference PTC/13

IP 12/79
(1980)

BS 2000: Part 12: 1993

Determination of specific energy

1. SCOPE

1.1. This method provides for the determination of the gross heat of combustion of liquid fuels, and formulae are given for calculating the net heat of combustion.

2. SUMMARY OF METHOD

2.1. A weighed quantity of the sample is burned in oxygen in a bomb calorimeter under controlled conditions. The heat of combustion is calculated from the weight of the sample and the rise in temperature, with proper allowance for heat transfer and for the formation of nitric and sulphuric acids in the bomb, no account being taken of other minor products formed. The value so obtained is the gross heat of combustion at constant volume.

2.2. The bomb calorimeter is calibrated by the combustion of benzoic acid.

2.3. Either isothermal or adiabatic calorimeter jackets may be used.

3. DEFINITIONS

3.1. *Gross Heat of Combustion*[1] – The gross heat of combustion of a fuel at constant volume is the number of heat units measured as being liberated at 25°C when unit weight of the fuel is burned in oxygen saturated with water vapour in a bomb under standard conditions. The resultant materials in the bomb are considered as being gaseous oxygen, carbon dioxide, sulphur dioxide, nitrogen, liquid water in equilibrium with its vapour and saturated with carbon dioxide, other compounds in solution, and solid ash. The gross heat of combustion[2] is represented by the symbol Q_g.

3.2. *Net Heat of Combustion*[1] – The heat of combustion of a fuel at constant pressure is the number of heat units measured as being liberated at 25°C when unit weight of fuel is burned in oxygen at constant pressure such that the heat released is equal to the gross heat of combustion of the fuel at constant pressure less the latent heat of evaporation at 25°C and constant pressure of the water both originally contained in the fuel and formed by its combustion. The net heat of combustion is represented by the symbol Q_n.

3.3. *Unit of measurement* – The unit of measurement employed in this method is the joule. If the results are required in terms of calories per gram (cal_{IT}/g) or British Thermal units per pound (Btu_{IT}/lb) the following relationships may be used:

$$1\ \text{cal}_{IT}/\text{g} = 4.1868\ \text{J/g (exactly)}$$
$$1\ \text{Btu}_{IT}/\text{lb} = 2.326\ \text{J/g (exactly)}$$

4. APPARATUS

4.1. The room in which the calorimeter equipment is located shall be free from draughts and sudden changes in temperature.

4.2. *Calorimeter Bomb* – conforming to the specification given in Annex A1.

4.3. *Calorimeter Vessel* – metal vessel polished on the outside, preferably at least 75 mm higher than the bomb, preferably of such cross-sectional area that 2 litres of water just covers the bomb.

4.3.1. *Stirrer* – A mechanical device for stirring the water in the calorimeter vessel at a uniform rate. The stirring shall be thorough, but not so rapid as to cause appreciable heating of the water. Continuous stirring of the water in the calorimeter vessel of the isothermal jacketed apparatus for 10 min after thermal equilibrium has been established shall not cause an increase in temperature of more than 0.01°C. With the adiabatic jacketed apparatus continuous stirring of the water in the calorimeter vessel for 10 min after thermal equilibrium has been established shall not cause an increase in temperature of more than 0.002°C. The portion of the stirrer immersed in the calorimeter vessel shall be connected to the outside portion with material of low heat conductivity.

4.3.2. *Water Jacket* – a double walled metal vessel containing water, fitted with a lid and leaving an air gap of preferably 10 mm all around the calorimetric vessel.

4.3.2.1. The isothermal jacket shall be arranged so as to remain at a uniform temperature (maximum variation 0.05°C) during the test.

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[1] The definitions of gross and net heat of combustion are based on BS 526 or ASTM D2382, Sec. 3, 'Definitions of the Calorific Value of Fuel'.

[2] Users of this method desiring to calculate $\Delta H^{\circ}k_{298}$ 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. See, for example, E. J. Prosen, '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' (US 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. In any comparison of measurements on pure compounds with those cited in these compilations, the user of this method should realize that impurities of various kinds, including water and foreign hydrocarbons, may cause significant effects on the values obtained from particular samples of material.

4.3.2.2. Adiabatic calorimeters shall be capable of circulating water continuously through both jacket and lid. The system shall be fitted with heating and cooling devices such that the temperature of the jacket water is rapidly adjusted to that of the water in the calorimeter vessel with a sensitivity sufficiently good to satisfy the requirements of 9.5.2.

4.4. *Fuel Cup* – a range of fuel cups that may be used is illustrated in Annex A2.

4.5. *Ignition System* – conforming to the specifications given in Annex A5.

4.6. *Thermometers* – conforming to the specifications given in Annex A3.

4.6.1. *Thermometer Reading Eyepiece* – magnifying type with adjustable focus, for use with mercury-in-glass thermometers.

4.7. *Oxygen Charging Equipment* – conforming to the specification given in Annex A4.

5. MATERIALS AND REAGENTS

5.1. *Water* – unless otherwise indicated, references to water shall be understood to mean distilled or demineralized reagent water.

5.2. *Oxygen* – under pressure in cylinders, free from combustible material.

5.3. *Ignition Wire* – 0.1 ± 0.03 mm dia. platinum wire. The same diameter and length of wire should be used in the calibration and determination.

5.4. *Firing Cotton* (if required) – a strand of wick as specified for use with ASTM D1266–IP 107, dried at 100 to 105°C and stored over silica gel until required. The heat of combustion of each batch of firing cotton must be determined.

5.5. *Sodium Hydroxide Solution* – approx. 0.1 *N*, accurately standardized.

5.6. *Benzoic Acid* – powder or pellet form, of thermochemical standard of purity and of a heat of combustion certified by the National Physical Laboratory or the National Bureau of Standards. Powdered material shall be compressed into pellets.

5.7. *Cellulose Adhesive Tape* – plain transparent cellulose film of width not less than 25 mm and thickness 0.05 to 0.075 mm. Use only cellulose-based film. The heat of combustion of each batch of tape must be determined.

5.8. *Indicator* – the following alternatives may be used:

5.8.1. *Methyl Purple Solution* – aqueous solution containing approximately 0.1% active constituent, or

5.8.2. *Methyl Red Solution* – 60% alcohol–aqueous solution containing approximately 0.1% indicator.

6. SAFETY PRECAUTIONS

6.1. The weight of sample shall be such that the heat developed during the combustion shall in no case exceed 90 J/ml bomb capacity; and the total weight of sample, together with any combustible material such as cellulose tape, shall be calculated in advance, so that the given limit is not exceeded.

6.2. Provision must be made to ensure that the oxygen filling pressure does not exceed the safety limit (see Annex A4 concerning oxygen charging equipment).

The operator shall not go near the calorimeter until at least 20 sec have elapsed from the time of firing.

6.3. The bomb must be completely submerged in water during firing and the charge must not be ignited if there is any evidence of gas leakage. Also, do not fire the bomb if it has been accidentally overcharged with oxygen to a pressure greater than 40 bar (39.5 atm, 580 lb/in^2).

6.4. Because of the risk of explosion, it is strongly recommended that the firing point and the oxygen cylinder be situated outside the room or safety enclosure containing the calorimeter, but in any case firing shall be by remote control in order to minimize the risk of injury to the operator (see Annex A5 concerning Ignition Systems).

7. SAMPLE

7.1. Take samples of liquid fuels of flash point less than 38°C directly into a container of not less than 200 ml capacity, fill the container as completely as possible and close immediately after taking the sample. Store samples in a refrigerator at below 4°C until required. The fuel shall be transferred to the fuel cup at a temperature as near as possible to the storage temperature.

7.2. If results are required on a dry basis, determine the water content independently and correct the result accordingly.

8. STANDARDIZATION

8.1. *Determination of Effective Heat Capacity, Energy Equivalent or Water Equivalent* – using tweezers, place in the weighed fuel cup (Type 2 or 3 of Annex A2 Fig. 4) the approximate weight of benzoic acid derived from the relation:

$$m = \frac{90 \times \text{Bomb capacity in ml}}{26\,500}$$

where *m* is the approx. weight of benzoic acid, in g.

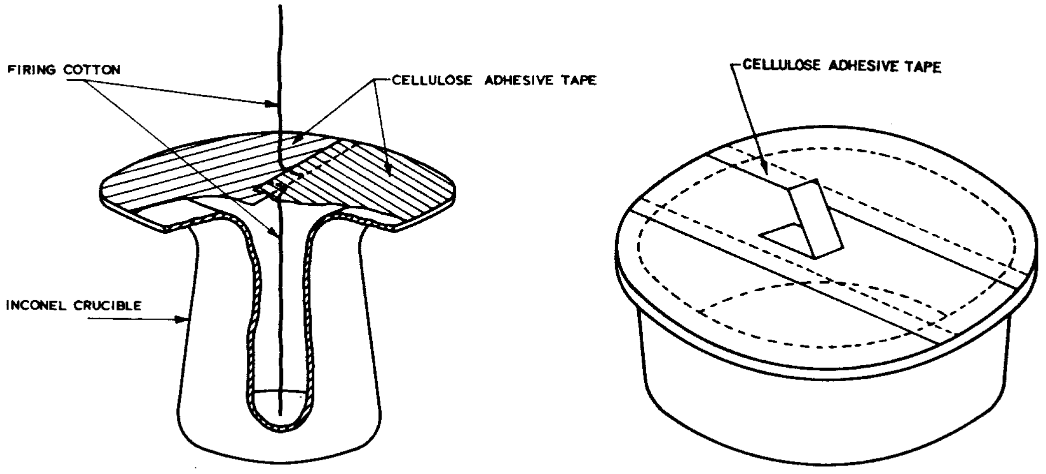
8.1.1. Weigh the fuel cup and its contents to the nearest 0.1 mg to find the weight of benzoic acid. Pipette 1 ml of water into the bomb (to saturate the oxygen used for combustion with water vapour). Place the fuel cup in the circular ring support attached to the terminals of the bomb.

8.1.2.1. Attach a measured length of ignition wire (approx. 100 mm, see Section 5.3) across the bomb terminals so as to form a U-shape loop and arranged so that the central portion of the loop is in contact with the benzoic acid; or

8.1.2.2. Attach a measured length of ignition wire (approx. 100 mm, see Section 5.3) across the bomb terminals under light tension. Weigh a suitable length of dry firing cotton and tie it at the centre of the ignition wire. Insert the free end of the firing cotton into the crucible so that it is in contact with the benzoic acid.

8.1.3. Close the bomb securely.

8.1.4. Admit oxygen slowly to a gauge pressure of 30 bar (29.6 atm, 430 psig).



TYPE 1

TYPE 4

Fig. 1. Sealed fuel cup assemblies.

8.1.5. Determine the effective heat capacity of the bomb by making not less than 5 combustions of the certified benzoic acid using the standard quantity of water. The standard quantity of water is such that the cover of the bomb (but not terminals) is immersed and the effective heat capacity of the system is approx. 10 500 joules/°C. If necessary, make preliminary combustions of benzoic acid to establish the correct weight of water. Once established this shall be the standard quantity of water, weighed to within 0.5 g, to be used in all subsequent determinations.

8.1.6. When using isothermal apparatus follow the details of procedure described in 9.4 and 9.6. When using adiabatic apparatus follow the details of procedure described in 9.5 and 9.6. Calculate the effective heat capacity as described in 10.1 to 10.4.

9. PROCEDURE

For liquid fuels of flash point below 38°C proceed as in 9.1.1 or 9.1.2 and continue the determination as in 9.4, 9.6, and 9.7 when using isothermal apparatus or as in 9.5, 9.6, and 9.7 when using adiabatic apparatus. For liquid fuels of flash point above 38°C proceed as in 9.2.1 or 9.2.2 and continue the determination as in 9.4, 9.6, and 9.7 when using isothermal apparatus or as in 9.5, 9.6, and 9.7 when using adiabatic apparatus.

9.1. *Liquid Fuels of Flash Point Less than 38°C.*

9.1.1. *Fuel Cup Type 1 or 4 Annex A2 Fig. 4* – Weigh the fuel cup to 0.1 mg. Cover the cup with the cellulose adhesive tape, trim around the edge with a razor blade, and seal tightly. Puncture the tape with a large needle to make an opening somewhat larger than the diameter of the hypodermic syringe needle. Place a 4 x 12 mm strip of tape, creased in the middle and sealed along one side, in the centre of the tape disk to give a flap arrangement which will cover the hole when finally sealed down, as shown in Fig. 1, Type 4. Weigh the cup and tape, and remove from the balance with forceps. Add the required weight [Note 1] of sample with a hypodermic syringe through the hole in the tape. Seal the flap down over the hole by pressing lightly with a metal spatula. Allow the temperature to reach equilibrium (7.1) and reweigh the cup, tape, and sample. Care must be taken throughout the weighing and filling operation to avoid contacting the tape or cup with bare fingers. Place the cup in the curved electrode and attach a measured length of ignition wire (see 5.3) across the bomb terminals such that the central portion of the loop presses down on the centre of the tape disk. Pipette 1 ml of water into the bomb and immediately close the bomb securely; or, alternatively

9.1.2. *Fuel Cup Type 1 or 4 of Annex A2 Fig. 4* – Weigh the fuel cup to the nearest 0.1 mg. Cover the fuel cup top with two pieces of cellulose adhesive tape, such that they slightly overlap as shown in Fig. 1, Type 1. Fix one end of a weighed length of firing cotton into the overlap, the other end being free for attachment to the ignition wire. Weigh the fuel cup and the attached tape and firing cotton to the nearest 0.1 mg. Charge the fuel cup by lifting the lip of the sealing tape and introducing the required weight [Note 1] of liquid fuel with a hypodermic syringe. Replace the tape to seal the fuel cup, allow the temperature to reach equilibrium (Section 7.1) and weigh the fuel cup and its contents to the nearest 0.1 mg. Pipette 1 ml of water into the bomb. Place the fuel cup in the circular ring support attached to the terminals of the bomb. Attach a measured length of ignition wire (see Section 5.3) across the bomb terminals under light tension. Tie the free end of the firing cotton to the centre of the ignition wire and with a pin make about six small holes in the tape sealing the mouth of the fuel cup. Immediately close the bomb securely.

9.2. *Liquid Fuels of Flash Point Greater than 38°C [Note 2].*

9.2.1. *Fuel Cup Type 2, 3, or 4 of Annex A2 Fig. 4* – Place the required weight [Note 1] of liquid fuel in the weighed fuel cup. Weigh the fuel cup and its contents to the nearest 0.1 mg. Pipette 1 ml of water into the bomb. Place the fuel cup in the circular ring support attached to the terminals of the bomb. Attach a length of ignition wire across the bomb terminals under light tension. Weigh a suitable length of dry firing cotton and tie it at the centre of the ignition wire. Dip the free end of the firing cotton into the contents of the fuel cup and immediately close the bomb securely; or, alternatively

9.2.2. *Fuel Cup Type, 2, 3, or 4 of Annex A2 Fig. 4* – Place the required weight [Note 1] of sample in the weighed fuel cup. Weigh the cup and sample to 0.1 mg. Place the cup in the curved electrode and arrange the fuse wire so that the central portion of the loop just dips into the contents of the cup. Pipette 1 ml of water into the bomb. Immediately close the bomb securely.

NOTE 1: The weight of the sample shall be controlled such that

$$M = \frac{90 \times \text{Bomb capacity in ml}}{Q_g}$$

where M = required wt of sample in g, and
Q_g = approx. heat of combustion of the sample in J/g.

NOTE 2: Liquid fuels having flash point in the range 38 to 60°C may tend to lose a small proportion of their more volatile components on exposure to the atmosphere. Weigh the sample into the fuel cup and seal immediately in the bomb whilst avoiding exposure to draughts.

9.3. Admit oxygen slowly to a gauge pressure of 30 bar (29.6 atm, 430 psig).

9.4. *Isothermal Jacket Calorimeters* – Fill the water jacket with water at a temperature within 3°C of room temperature and ensure that it remains constant throughout. Fill the calorimeter vessel with the standard quantity of water (see 8.1.5) weighed to within 0.5 g. The initial temperature of the bomb and calorimeter shall be:

- (i) in the range 15 to 32°C;
- (ii) above the dew point;
- (iii) approx. 2.5°C below the temperature of the water jacket and preferably within 2°C of the temperature of standardization (see Note 9).

9.4.1. Place the prepared bomb, **CAUTION:** see Section 6, in the calorimeter vessel, check that there is no leakage of oxygen, confirm that the firing leads are dead, and make the appropriate electrical connexions. Put the covers in position, arrange the thermometer and stirrer so that they do not touch the bomb or vessel, and start the stirrer.

9.4.2. When the temperature is rising steadily and at least 5 min after starting the stirrer, record a series of temperature readings [Note 3] at 1 min intervals for 5 min, from which the temperature at the end of the sixth minute, i.e. time of firing, will later be found by extrapolation. The rate of temperature rise in the 5 min period before firing shall be constant [Note 4].

9.4.3. At the end of the sixth minute fire the charge by closing the firing circuit for not longer than 2 sec. **CAUTION:** see 6.2.

DO NOT GO NEAR THE BOMB UNTIL AT LEAST 20 SECONDS HAVE ELAPSED FROM THE TIME OF FIRING

9.4.4. Record the temperatures at 45, 60, 75, 90, and 105 sec after the time of firing. By interpolation between these readings the time at which the temperature rise reached 60% of its final value will later be found [Note 5].

9.4.5. After the rapid rise period (about 4 to 5 min) record the temperature at 1 min intervals on each completed min after the time of firing. Continue these readings until the difference between successive readings has been constant for 5 min [Note 5]. From this series determine the time at the beginning of the period in which the rate of temperature change with time is constant. Determine also the rate of change of temperature with time.

9.4.6. The temperature rise shall be between 2.5 and 3.5°C and the final temperature shall not be more than 1°C (and preferably not more than 0.5°C) above that of the jacket.

NOTE 3: Temperatures should be read to 0.001°C. This will not be possible during the rapid period, and the most accurate readings which are practicable at this time should be recorded. Mercury-in-glass thermometers shall be tapped lightly before reading, particularly when the temperature is falling, to prevent errors caused by sticking of the mercury. A convenient method of effecting this is to mount a small buzzer directly on top of the thermometer, and operate it for a few moments before each reading. Use an eyepiece to facilitate thermometer reading.

NOTE 4: The rate of temperature change with time shall be considered constant if the variation in the rate does not exceed 0.001°C/min. The rate of change of temperature shall be calculated as the mean of the relevant recordings.

NOTE 5: When the approx. heat of combustion of the fuel is known to within 1500 joule/g, the expected temperature rise may be determined from the relation:

$$t = \frac{MQ_g}{W}$$

where Q_g = approx. gross heat of combustion, in J/g,
M = weight of sample in g, and
W = effective heat capacity of calorimeter in J/°C.

Calculate the temperature at the 60% point by adding to the temperature at the time of firing, 60% of the expected temperature rise. Start an additional stopwatch at the time of the first reading of the series of temperature recordings made before firing. Stop the stopwatch when the calculated 60% temperature rise is attained and record the time.

9.5. *Adiabatic Calorimeters* – Fill the calorimeter vessel with the standard quantity of water, weighed to within 0.5 g (see 8.1.5), the temperature of which shall be within the range of 15 to 32°C, shall be above the dew point and preferably within 2°C of the temperature of standardization (see Note 9). Ensure that the jacket is filled with water at a temperature close to, and preferably equal to or slightly below, that of the calorimeter vessel. Place the prepared bomb in the calorimeter vessel, check that there is no leakage of oxygen, confirm that the firing leads are dead and make the appropriate electrical connexions. Place the covers in position, arrange the stirrer, thermometer, and temperature regulating device in position so that they do not touch the bomb or calorimeter walls. Switch on the calorimeter stirrer, jacket stirrer, heaters, and cooling coil and run the apparatus for 5 min to attain equilibrium.

9.5.1. If, at the start, the bomb is markedly different in temperature from the calorimeter vessel, more than 5 min may be required to reach equilibrium.

9.5.2. Check that the apparatus is at equilibrium by recording the temperature to the nearest 0.001°C [Note 3] at 1 min intervals. Successive readings shall not differ by more than 0.001°C and shall not show any progressive tendency. When four successive readings have complied with the requirements consider the apparatus to be at equilibrium and record the temperature to the nearest 0.001°C as the firing temperature (t_a, see 10.3). Fire the charge by closing the firing circuit for not longer than 2 sec. **CAUTION:** see 6.2.

DO NOT GO NEAR THE BOMB UNTIL AT LEAST 20 SECONDS HAVE ELAPSED FROM THE TIME OF FIRING

9.5.3. Record the temperature to the nearest 0.001°C at 1 min intervals until the same temperature is recorded for three successive readings. Record this value as the final temperature t_f (see 10.3) [Note 6].

9.6. Fifteen minutes after the ignition, remove the bomb from the calorimeter, dry the outside of the bomb and release the pressure uniformly at such a rate that the operation takes at least 1 min. Open the bomb and examine the inside for traces of unburned oil or soot; if either is found discard the determination [Note 7].

9.6.1. Rinse out the interior of the bomb, including the fuel cup, with a fine jet of distilled water, and collect the washings, which shall not exceed a volume of 350 ml, in a beaker. Add a few drops of indicator and titrate with the sodium hydroxide solution to determine the quantity of nitric and sulphuric acids formed in the combustion.

NOTE 6: If a constant temperature is not obtained within 15 min of firing the apparatus should be considered suspect.

NOTE 7: The combustion of highly leaded fuels may cause appreciable corrosion inside a stainless steel bomb, but this is not to be taken as a reason for rejecting the test result.

9.7. When the sulphur content of the sample is unknown, filter the neutralized washings through a medium texture filter paper such as a Whatman No. 40, and determine the sulphur content as prescribed in ASTM D129–IP 61.

10. CALCULATION AND REPORT

10.1. Correct all temperatures for thermometer errors according to the certificate.

10.2. *Temperature Rise in Isothermal Jacket Calorimeter* – Using data obtained as prescribed in Section 9.4, compute the temperature rise, Δt, in an isothermal jacket calorimeter as follows:

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

where

Δt = corrected temperature rise, in °C;

a = time for firing, in min;

b = time (to nearest 0.1 min) when the temperature rise reaches 60% of the total, in min;

c = time at beginning of period in which the rate of temperature change with time has become constant (after combustion), in min;

t_a = temperature at time of firing, in °C;

t_c = temperature at time, c, in °C;

r_1 = rate at which the temperature was rising during the 6 min period before firing, in °C/min;

r_2 = rate at which the temperature was rising during the 5 min period after time c in °C/min. If the temperature was falling, r_2 is negative and the quantity $[-r_2(c-b)]$ is positive.

10.3. *Temperature Rise in Adiabatic Jacket Calorimeter* – Using data obtained as prescribed in 9.5 and 10.1, compute the temperature rise, Δt in an adiabatic jacket calorimeter as follows:

$$\Delta t = t_f - t_a$$

where

Δt = corrected temperature rise, in °C;

t_a = temperature at time of firing, in °C;

t_f = final maximum recorded temperature, in °C.

10.4. *Effective Heat Capacity of the Calorimeter* – Calculate the effective heat capacity of the calorimeter, W in joules/°C as follows:

$$W = \frac{[Q_B + 1.2(25-t_f)]m + e_1 + e_2}{\Delta t} - D_T$$

[Notes 8 and 9]

where

Q_B = certified calorific value of the benzoic acid in J/g (see 5.6);

m = weight of benzoic acid, in g;

Δt = corrected temperature rise, in °C;

e_1 = correction for the heat of formation of acids in J (1 ml 0.1 N NaOH = 5.9 J);

e_2 = correction for heat of combustion of firing cotton in J (if used) (heat of combustion of batch × weight of cotton);

D_T = correction for test temperature variation [see Note 9] in J/°C. (Apply this correction in whole numbers.)

NOTE 8: The term $[Q_B + 1.2(25-t_f)]$ relates the certified heat of combustion of benzoic acid at 25°C to the final temperature of the calorimeter.

NOTE 9: The term D_T is an approximation which is applied to adjust the effective heat capacity of the system at the mean temperature, T, of the determination to the reference temperature of 25°C, and is only necessary when the mean temperature of the bomb standardization and the determination differ by more than 3°C. It is calculated as follows:

$$D_T = \alpha M_w - \beta\left(M_s + \frac{M_B}{4}\right) \text{ J/degC}$$

where

M_w = weight of water in the system, in kg;

M_s = weight of stainless steel in the system, in kg;

M_B = weight of bronze and brass in the system, in kg.

The values α and β are obtained from the graph in Fig. 2. The mean temperature T in °C is given by the relation

$$T = \frac{t_a + t_f}{2}$$

where

t_a = temperature at the time of firing in °C;

t_f = final maximum recorded temperature in °C.

Plot the calculated values of D_T in J/°C against values of T between 15 and 35°C.

10.5 *Gross Heat of Combustion* – Calculate the gross heat of combustion at constant volume and at 25°C, in J/g from the equation:

$$Q_g = \frac{\Delta t \times (W + D_T) - e_1 - e_2 - e_3 - e_4}{M}$$

where

W = effective heat capacity of the system at 25°C, in J/°C;

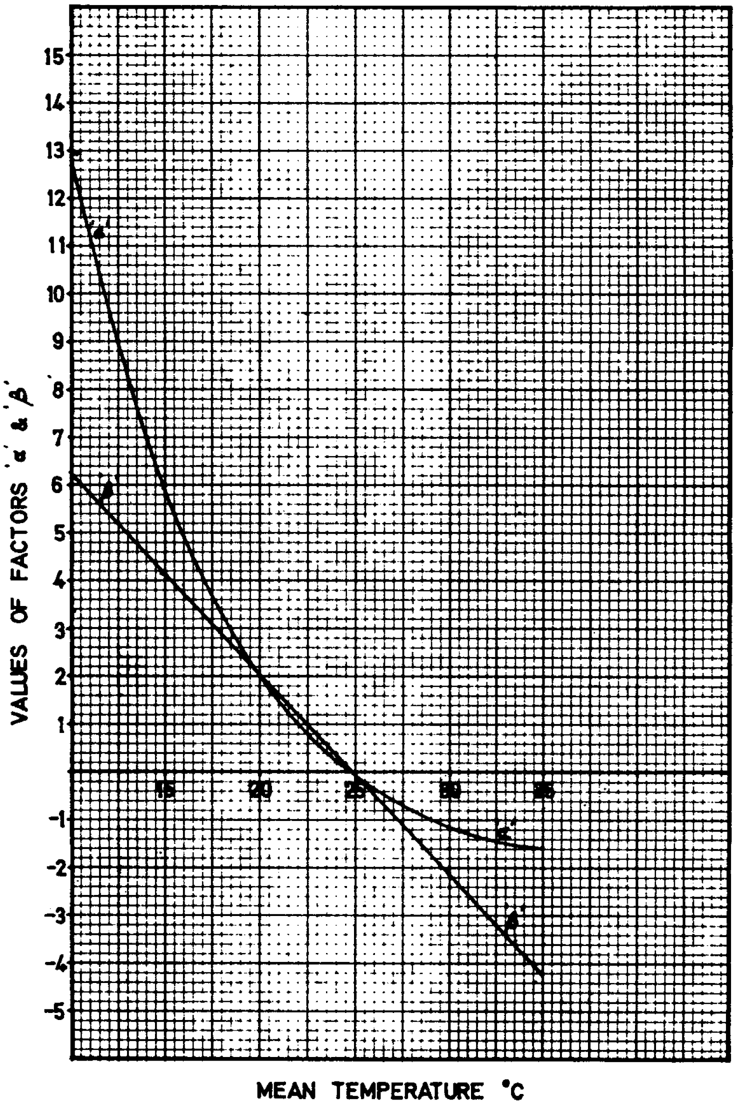


Fig. 2. Values of α and β for calculating D_T.

D_T = correction at the mean temperature, T, obtained from the data plotted as described in Note 9, in J/°C (apply this correction in whole numbers);

Δt = corrected temperature rise, in °C;

e_1 = correction for the heat of formation of acids, in joules (1 ml 0.1 N NaOH = 5.9 J);

e_2 = correction for firing cotton (if used) in joules (heat of combustion of batch × weight of cotton used);

e_3 = supplementary correction for the sulphur content of the sample, in joules ($58.6 \times \%S \times$ wt of sample, in g);

e_4 = correction for cellulose tape, if used, in joules (heat of combustion of batch × wt of tape used);

M = weight of sample, in g.

10.6. *Net Heat of Combustion* – Calculate the net heat of combustion (Q_n) in joules/g from the following equation:

$$Q_n = Q_g - 212.19\text{H}$$

where H is the hydrogen content of the sample, in percent weight.

The following equation may be used for the calculation of net heat of combustion of aviation gasoline and turbine fuel when the hydrogen content of the sample is not known:

$$Q_n = 10\,023 + 0.7195 Q_g \text{ [Note 10].}$$

NOTE 10: This equation is only recommended if the percentage of hydrogen is not known. It is based on the previous equation and an empirical relationship between Q_n and the percentage of hydrogen in aviation gasoline and turbine fuels, developed from data by R. S. Jessup and C. S. Gragoe, 'Heat of Combustion of AN-F-28 Aviation Gasoline', National Advisory Committee of Aeronautics, Tech. Note 996, June 1945, and J. A. Cogliano and R. S. Jessup, 'Relationship between Net Heat of Combustion and Aniline Gravity Product of Aircraft Fuels', National Bureau of Standards Report 2348, March 1953.

10.7. To obtain the gross or net heat of combustion in cal_{IT}/g or Btu_{IT}/lb divide Q_g or Q_n by the appropriate factor given in Section 3.

10.8. Report the result as the Gross or Net Heat of Combustion to the nearest 20 J/g, or to the nearest 10 Btu_{IT}/lb or to the nearest 5 cal_{IT}/g.

11. PRECISION

The following criteria should be used for judging the acceptability of results (95% confidence).

11.1. *Repeatability* – Duplicate results by the same operator should be considered suspect if they differ by more than

$$276\ \text{J/g}\ (119\ \text{Btu}_{\text{IT}}/\text{lb},\ 66\ \text{cal}_{\text{IT}}/\text{g})$$

11.2. *Reproducibility* – The results submitted by each of two laboratories should not be considered suspect unless the two results differ by more than

$$773\ \text{J/g}\ (332\ \text{Btu}_{\text{IT}}/\text{lb},\ 185\ \text{cal}_{\text{IT}}/\text{g})$$

11.2.1. The precision estimates have been derived by statistical analysis of inter-laboratory test results and were first published in 1971.

11.2.2. In the light of a cooperative programme carried out by the ASTM/IP, it is apparent that this method should be carried out by experienced operators. Under these circumstances a greatly improved precision can be expected.

ANNEX A

APPARATUS FOR DETERMINATION OF THE HEAT OF COMBUSTION OF LIQUID FUELS

A1. IP STANDARD BOMB SPECIFICATION CONFORMING TO BS 4791: 1972

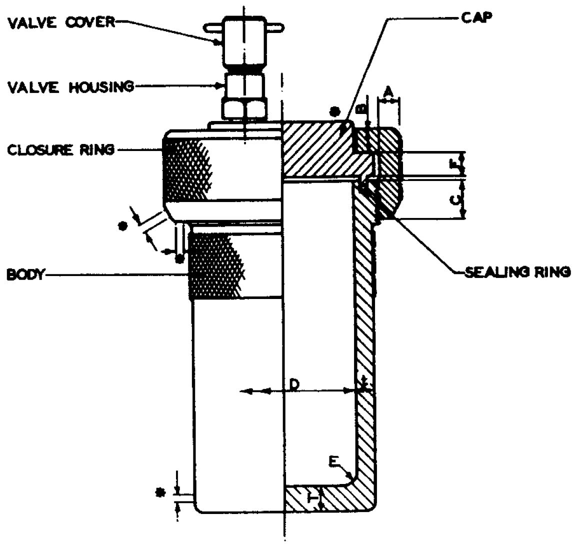
A1.1. *General* – This specification covers the essential constructional features and materials, and testing of bombs to be used for determining the heat of combustion of liquid fuels, or their sulphur content, in accordance with IP standard methods.

A1.2. *General Design* – the proportions of the bomb shall conform to Fig. 3.

It shall have an internal diameter of not less than 55 mm and a capacity of 325 ± 25 ml. The weight of the bomb shall not exceed 3.25 kg. It shall be so constructed that it does not leak, and can be easily drained. All parts enclosing the gas space shall be constructed of materials which are not affected sufficiently by the combustion process or products to introduce measurable heat input or alteration of the end products. The electrodes shall be made of heat and corrosion resistant material, e.g. platinum or its alloys, suitable steels or nickel chrome, and so placed that when the oil cup is in position its base shall be not less than 90 mm from the underside of the bomb lid. The closure of the bomb shall be so designed that in normal operation the bomb can be sealed and opened by hand without the use of tools of any type. The calorimeter bomb seal shall be so designed that after hand-tightening an increase of pressure in the bomb will tighten the seal and prevent leakage.

A1.3. *Materials* – The bomb cap and body shall be machined from solid or hollow forgings or bar. They shall not be fabricated from components welded or brazed together.

For a bomb designed to the minimum dimensions and dimensional ratios given in Table 1, the material



* PERMISSIBLE POSITION FOR ENGRAVING

Fig. 3. Typical bomb for heat of combustion (for values of labelled dimensions see Table 1).

TABLE 1. Dimensions of Bomb Body, Cap and Closure Ring

Detail	Symbol (see Fig. 3)	Requirement
Body		
External diameter		to be uniform within 0.03 mm
Internal diameter	D	shall be not less than 55 mm
Capacity of the combustion chamber		325 ± 25 ml
Thickness of side wall	t	not less than 0.10 D
Thickness of base	T	not less than 0.165 D
Internal radius	E	not less than t
Closure Ring		
Dimensions of closure ring when made of aluminium bronze:		
Thickness of wall	A	not less than 0.14 D
Thickness of flange	B	not less than 0.17 D
Screw Thread		
Nominal pitch thread form, and fit		ISO metric threads 1.5 mm or 2 mm pitch shall be used with a 6H/6g (medium) fit complying with BS 3643. ISO inch (unified) threads complying with BS 1580 Unified Threads, are acceptable during the period of change to metrication. In this case a 16 tpi 2A/2B (medium) fit shall be used. The roots shall be radiused: they shall not encroach upon the minimum wall thickness.
Length of engagement	C	not less than 0.25 D
Cap		
Thickness of cap flange	F	not less than 0.10 D
Total thickness of cap		not less than 0.25 D
Crucible Position Related to Cap		
Base of crucible to underside of cap		not less than 90 mm
Total Mass		shall not exceed 3.25 kg

shall have the following mechanical properties:

Tensile strength not less than 550 MN/m^2.
Yield stress not less than 210 MN/m^2.
Elongation at break not less than 30%.
Izod impact value not less than 68 Nm.

The material from which the *bomb cap and body* are made shall, in addition, be certified to have passed a suitable test for resistance to intercrystalline corrosion. If steel is used it shall be subject to the ring test and 90° bend test, described in BS 1501–6 and BS 970.

The appropriate British Standards for suitable materials are listed below:

BS 1501–6	Steels for use in the chemical, petroleum, and allied industries.
BS 970	Wrought steels in the form of bars, billets and forgings, up to 152.5 mm ruling section, for automobile and general engineering purposes.
BS 1503–845	Grade B for Ti for forgings.
BS 1506–845	For bars.

The *closure ring* shall be made of material capable of withstanding the pressures generated by the combustion process and chosen to minimize galling or seizing of the thread engaging the bomb body. It shall be machined from solid or hollow forgings or bar. It shall not be fabricated from components welded or brazed together.

For a bomb designed to the minimum dimensions and dimensional ratios given in Table 1, the material shall have the following mechanical properties:

Tensile strength not less than 525 MN/m^2.
Elongation at break not less than 25%.

Aluminium bronze to BS 2872 Grade CA 103 and BS 2874 Grade CA 103 have been proved by experience to be suitable.

The appropriate British Standards are listed below:

BS 2872: 1969	Copper and copper alloys. Forging stock and forgings.
BS 2874: 1969	Copper and copper alloys. Rods and sections (other than forging stock).

A1.4. *Finish* – The surface of all pressure parts shall have a smooth machined or ground finish throughout. No stamping or engraving shall be allowed except in the positions indicated in Fig. 3, but this restriction does not apply to the use of electric pencils. If a knurled surface is provided, the metal thickness shall be increased locally by at least the depth of knurling.

A1.5. *Pressure Test in Accordance with BS 4791* – After completion, each bomb shall be tested under a water pressure of 300 bar, which shall be maintained in the bomb for a period of 10 min without leakage. After removal of the test pressure, the external diameter of the bomb body shall not show an increase exceeding 0.1% of the diameter measured, and the threads shall be examined for galling. The performance of the bomb under this test shall be attested by certificate.

NOTE 11: The British Standards Institution, Maylands Avenue, Hemel Hempstead, Herts, is prepared to accept bombs for examination for compliance with the pressure test.

A1.6. *Marking*

A1.6.1. Each bomb body, lid, and closure ring shall be indelibly marked with:

(*a*) a reference (e.g. BS 1506–845B) identifying the material used in its construction;

(*b*) the manufacturer's serial number.

A1.6.2. Each bomb assembly shall be indelibly marked with test pressure to which it was subjected; and the date on which the pressure test was made.

A1.7. *Certificates* – The manufacturer or supplier of the bomb shall supply to the purchaser a copy of the steelmaker's certificate for the steel from which the bomb has been made, and also a certificate that the bomb has been made wholly in accordance with this specification, with the following information:

A1.7.1. The reference number of the BS steel used in the construction of the bomb.

A1.7.2. The maker's serial number, and the date of manufacture of the bomb.

A1.7.3. The name of the testing body, the test pressure to which the bomb was subjected, and the date on which the pressure test was made.

A1.7.4. A certificate to the effect that a prototype closure ring made of material corresponding to that used in the manufacture of production closure rings has withstood a total load (W) as defined below, applied in such a way as to simulate operating conditions without undergoing a permanent change of shape at any point greater than 0.05 mm, where

$W = 34.3\ S^2$ newtons,
S = OD of the gasket or sealing ring in mm.

A2. FUEL CUPS

A2.1. The fuel cups illustrated in Fig. 4 are suitable for use in this method.

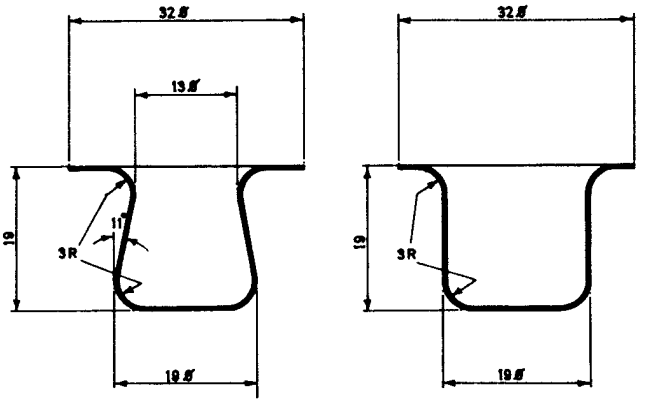
A3. THERMOMETERS

A3.1. Temperatures in the jacket and in the calorimeter, respectively, shall be measured with thermometers conforming to any of the following types:

A3.1.1. *Mercury-in-Glass, Bomb Calorimetry Thermometers* – having a 6°C range conforming to the requirements for thermometers in BS 791 or those given in ASTM Specification E1 for the ASTM 116C and ASTM 117C thermometers. Each of these thermometers shall have been tested for accuracy at intervals of 0.5°C or less over the entire graduated scale. Corrections shall be reported to 0.002°C or better for each test point.

A3.1.2. *Platinum Resistance, Quartz Crystal or Thermistor Thermometers* – with elements enclosed in a metal sheath and connected to suitable electrical measuring equipment may be used in this method provided the temperature measuring system meets or exceeds the following minimum requirements:

Readability, the last digit must be readable to	0.001°C.
Repeatability, in temperature rise measurements over the same 3°C range	±0.001°C.

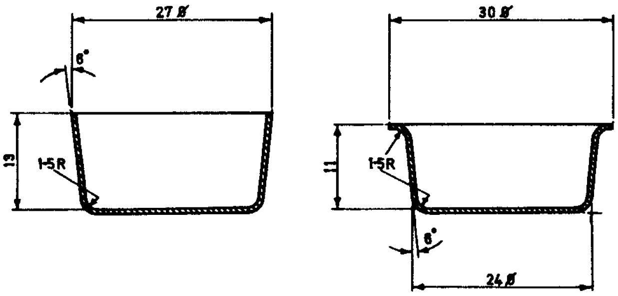


TYPE 1

MATERIAL	THICKNESS	APPROX WEIGHT
INCONEL BS3072	0·46	8·3 g

TYPE 2

MATERIAL	THICKNESS	APPROX WEIGHT
INCONEL BS3072	0·46	8·3g



TYPE 3

MATERIAL	THICKNESS	APPROX WEIGHT
TYPE 310 STAINLESS STEEL	0·8	9g
HASTALLOY C	0·7	9g
PLATINUM 3½ % Rh	0·35	11g

TYPE 4

MATERIAL	THICKNESS	APPROX WEIGHT
PLATINUM 3½% Rh	0·35	11g

Fig. 4. Fuel cups.

Absolute accuracy, the error in any single temperature reading shall not exceed	±0.150°C.

A4. OXYGEN CHARGING EQUIPMENT

A4.1. The valves, gauges, filling tube and fittings used in the oxygen charging system must meet industry safety codes and must be rated for use at input pressures up to 206 bar (3000 psig) and discharge pressures up to 55 bar (800 psig). Separate gauges should be provided to show the supply pressure and the bomb pressure. The bomb gauge should be not less than 75 mm in diameter and preferably graduated from 0 to 55 bar (atm) in 1 bar (atm) sub-divisions. Both gauges must be absolutely oil-free and must never be tested in a hydraulic system containing oil. The charging equipment should include either a pressure reducing valve which will limit the discharge pressure to a maximum of 40 bar (600 psig) or a relief valve set to discharge at 40 bar (600 psig) in case the bomb should accidentally be overcharged. Means should also be provided for releasing the residual pressure in the filling tube after the bomb valve has been closed.

A5. IGNITION SYSTEM

A5.1. The ignition current should be drawn either from a stepdown transformer connected to an alternating current line or from a storage battery. The firing voltage must not exceed 24 volts and should be held to the lowest practicable level recommended by the manufacturer. An ammeter or a pilot light may be used in the circuit to indicate when current is flowing, and the circuit must be controlled by a double-pole, momentary contact switch which remains normally open, except when held closed by the operator.

The switch shall be held in the closed position for not more than 2 sec.