

British Standard Methods of test for
Petroleum and its products

Part 12. Heat of combustion of liquid hydrocarbon fuels

(Identical with IP 12/73 (80))

Méthodes d'essai pour le pétrole et les produits pétroliers
Partie 12. Chaleur dégagée par la combustion des combustibles hydrocarburés liquides

Prüfmethoden für Erdöl und Erdölprodukte
Teil 12. Verbrennungswärme von flüssigen Kohlenwasserstoff-Kraftstoffen

Foreword

BS 2000 comprises a series of test methods for petroleum and its products that have been published previously by the Institute of Petroleum (IP) and have been accorded the status of British Standards. Each method should be read in conjunction with BS 2000 : Part 0 'General introduction', which gives details of the BSI/IP agreement for publication of the series, lists more than 50 methods scheduled to be published in this way in 1982, and provides general information on safety precautions, sampling and other matters.

The numbering of the other Parts follows that of the corresponding methods published in 'IP Standards for petroleum and its products, Part 1 Methods for analysis and testing'. BS 2000 : Part 12 is thus identical with IP 12/73, which was reapproved in 1980. IP 12/73 was previously published in A5 format as BS 4379* which has now been re-numbered and issued in the BS 2000 series. It is intended to issue further revisions when necessary in line with changes that may be made in subsequent editions of the IP method.

Caution. Attention is drawn to the safety precautions mentioned in Part 0 of this British Standard, and also to the specific precautionary directions indicated in Clause 6 and elsewhere in the text.

NOTE. The titles of the standards publications referred to in this Part of this British Standard are listed on the inside back cover.

WITHDRAWN

* Now withdrawn.

Method (identical with IP 12/73 (80))**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.

NOTE to 2.1. In this context, throughout the method, the term 'weight' should be replaced by 'mass'.

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 combustion² 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 ($\text{cal}_{\text{IT}}/\text{g}$) or British Thermal units per pound ($\text{Btu}_{\text{IT}}/\text{lb}$) the following relationships may be used:

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

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 A.1.

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

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 $\Delta H^{\circ}_{\text{K}_{298}}$ 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.

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.

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 are 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 (1 in) and thickness 0.05 to 0.075 mm (0.002 to 0.003 in). 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%w 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 over-charged with oxygen to a pressure greater than 40 bar (39.5 atm, 580 lb/in²).

NOTE to 5.1. Water complying with BS 3978 is suitable.

NOTES to 5.4. Firing cotton marketed in the United Kingdom as '13s/14 ends, scoured and bleached', is suitable.
BS 2000 : Part 107 (formerly BS 4350) is identical with IP 107.

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 (100°F) 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.

NOTE to 7.1. The flash point of the product under test may be determined in accordance with BS 2000 : Part 170 (formerly BS 3442 : Part 2).

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).

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.

NOTE to 8.1.1. A pipette complying with BS 1583 is suitable.

9. PROCEDURE

For liquid fuels of flash point below 38°C (100°F) 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 (100°F) 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.

NOTE to clause 9. See note to 7.1.

9.1. *Liquid Fuels of Flash Point Less than 38°C (100°F)*

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

NOTE to 9.1.1 and 9.1.2. A hypodermic syringe and a pipette, complying respectively with BS 1263 and BS 1583, are suitable.

opening somewhat larger than the diameter of the hypodermic syringe needle. Place a 4 × 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,

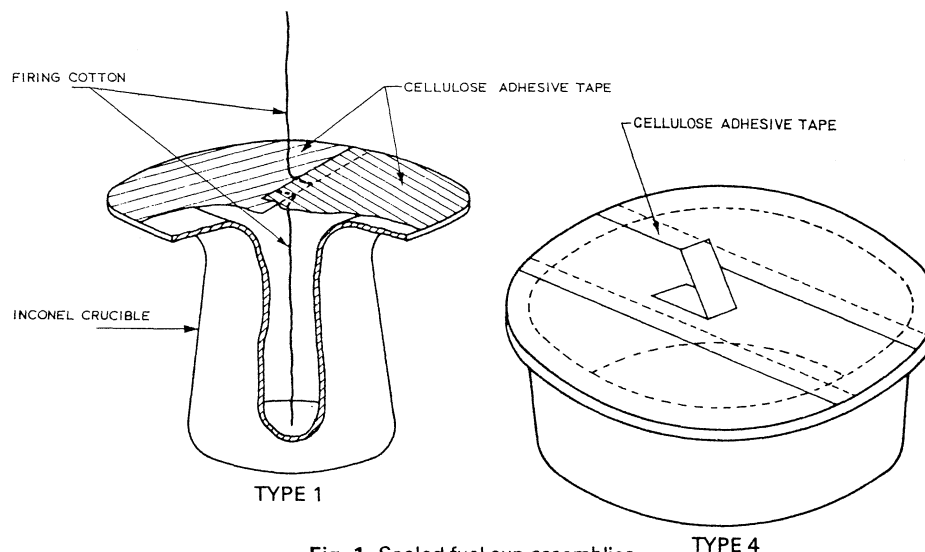


Fig. 1. Sealed fuel cup assemblies.

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 (100°F)* [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