

Methods of test for

Petroleum and its products

Part 12. Determination of specific energy

(Identical with IP 12/79(80))

Confirmed January 2010

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This British Standard supersedes BS 2000 : Part 12 : 1982, which is withdrawn.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IP 12 was previously published as a British Standard as BS 4379 (now withdrawn) which was subsequently renumbered and issued in the BS 2000 series.

Compliance with a British Standard does not of itself confer immunity from legal obligations.

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Determination of specific energy

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.

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 combustion² is represented by the symbol Q_g .

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 ΔH°_{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.

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:

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

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

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.

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/in²).

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).