

ISO

INTERNATIONAL ORGANIZATION FOR STANDARDIZATION

ISO RECOMMENDATION R 1928

SOLID MINERAL FUELS

DETERMINATION OF GROSS CALORIFIC VALUE
BY THE CALORIMETRIC BOMB METHOD,
AND CALCULATION OF NET CALORIFIC VALUE

1st EDITION

April 1971

COPYRIGHT RESERVED

The copyright of ISO Recommendations and ISO Standards belongs to ISO Member Bodies. Reproduction of these documents, in any country, may be authorized therefore only by the national standards organization of that country, being a member of ISO.

For each individual country the only valid standard is the national standard of that country.

Printed in Switzerland

Also issued in French and Russian. Copies to be obtained through the national standards organizations.

BRIEF HISTORY

The ISO Recommendation R 1928, *Solid mineral fuels — Determination of gross calorific value by the calorimetric bomb method, and calculation of net calorific value*, was drawn up by Technical Committee ISO/TC 27, *Solid mineral fuels*, the Secretariat of which is held by the British Standards Institution (BSI).

Work on this question led to the adoption of Draft ISO Recommendation No. 1928, which was circulated to all the ISO Member Bodies for enquiry in December 1969. It was approved, subject to a few modifications of an editorial nature, by the following Member Bodies :

Australia	Iran	Thailand
Belgium	Netherlands	Turkey
Canada	Portugal	U.A.R.
Chile	Romania	United Kingdom
Czechoslovakia	South Africa, Rep. of	U.S.A.
Denmark	Spain	U.S.S.R.
France	Sweden	Yugoslavia
Greece	Switzerland	

The following Member Bodies opposed the approval of the Draft :

Germany
Poland

This Draft ISO Recommendation was then submitted by correspondence to the ISO Council, which decided to accept it as an ISO RECOMMENDATION.

CONTENTS

	Page
1. Scope	5
2. Definitions	5
3. Principle	6
4. Reagents	6
5. Apparatus	7
6. Sample	8
7. Procedure	8
8. Corrections	12
9. Calculation and expression of results	13
10. Precision of the method	14
11. Calculation of net calorific value	14
Annex — Determination of effective heat capacity of the calorimeter	16
Appendix Y — Examples to illustrate a method of calculating results	18
Appendix Z — Additional calculations	21

SOLID MINERAL FUELS

**DETERMINATION OF GROSS CALORIFIC VALUE
BY THE CALORIMETER BOMB METHOD,
AND CALCULATION OF NET CALORIFIC VALUE**

1. SCOPE

This ISO Recommendation describes the determination of the gross calorific value of a solid fuel at constant volume in an adiabatic, an isothermal, or a static bomb calorimeter.

The result obtained by this method is the gross calorific value of the analysis sample at constant volume, the water of the combustion products being condensed to liquid at the calorimeter temperature. In practice, fuel is burned at constant (atmospheric) pressure and the water is not condensed but is removed, as vapour, with the flue gases. Under these conditions the operative heat of combustion is the net calorific value of the fuel at constant pressure. The net calorific value at constant volume may also be used; formulae for calculating both values are given.

2. DEFINITIONS

2.1 Unit of heat : The absolute joule (J).

$$\begin{aligned} 1 \text{ J} &= 1 \text{ newton metre (N}\cdot\text{m)} \\ &= 1 \times 10^7 \text{ ergs} \\ &= 0.238\,846 \text{ International Table calories (cal}_{\text{IT}}) \\ (1 \text{ cal}_{\text{IT}} &= 4.1868 \text{ J}) \end{aligned}$$

2.2 Unit of temperature : The kelvin (K)

1 K = a temperature interval of 1 degree Celsius.

The international reference temperature for thermochemistry of 25 °C is used as the reference temperature for calorific value, though the temperature dependence of the calorific value of coal or coke is small [about 1 J/(g.K)].

2.3 Gross calorific value at constant volume. The number of heat units measured as being liberated when unit mass of solid fuel is burned in oxygen in a bomb under standard conditions; the materials after combustion are taken to consist of the gases oxygen, carbon dioxide, sulphur dioxide and nitrogen, liquid water in equilibrium with its vapour and saturated with carbon dioxide, and solid ash.

2.4 Net calorific value at constant volume. The number of heat units which would be liberated if unit mass of the fuel were burned in oxygen under conditions of constant volume, the residual materials being taken as oxygen, carbon dioxide, sulphur dioxide, nitrogen, water vapour and ash, all at 25 °C.

2.5 Net calorific value at constant pressure. The number of heat units which would be liberated if unit mass of the fuel were burned in oxygen under conditions of constant pressure, the residual materials being taken as oxygen, carbon dioxide, sulphur dioxide, nitrogen, water vapour and ash, all at 25 °C.

2.6 Effective heat capacity of the system. The heat required to cause unit rise of temperature in the calorimeter system under the conditions of a calorimetric determination.

3. PRINCIPLE

3.1 Gross calorific value

A weighed portion of the sample of solid fuel is burned in oxygen in a bomb calorimeter under standardized conditions. The gross calorific value is calculated from the temperature rise of the water in the calorimeter vessel and the mean effective heat capacity of the system. Allowances are made for the heat released by the ignition fuse, for thermochemical corrections and, where appropriate, for heat losses from the calorimeter to the water jacket.

3.2 Net calorific value

The net calorific value at constant volume and the net calorific value at constant pressure of a fuel are obtained by calculation from the gross calorific value at constant volume determined on the analysis sample. The calculation of the net calorific value at constant volume requires a knowledge of the moisture and hydrogen contents of the analysis sample; the calculation of the net calorific value at constant pressure requires, in addition, a knowledge of the oxygen content of the analysis sample.

4. REAGENTS

- 4.1 *Oxygen* at a pressure capable of filling the bomb to 30 bar and free from combustible matter (oxygen made by the electrolytic process may contain up to 4 % of hydrogen and is therefore unsuitable).

4.2 Fuse :

Firing wire : nickel-chromium 0.16 to 0.20 mm diameter *or*
platinum 0.06 to 0.10 mm diameter

Cotton : white cellulose cotton.

- 4.3 *Paste*. Fused aluminosilicate cement passing a 63 μm test sieve and suitable for use up to a temperature of 1400 °C, mixed with water.

- 4.4 *Alumina*. Fused alumina of analytical reagent quality, passing a 180 μm sieve and retained on a 106 μm sieve.

4.5 Reagent solutions

- 4.5.1 *Barium hydroxide* solution 0.1 N.

- 4.5.2 *Sodium carbonate* solution 0.1 N.

- 4.5.3 *Sodium hydroxide* solution 0.1 N.

- 4.5.4 *Hydrochloric acid* solution 0.1 N.

4.6 Coloured indicators

- 4.6.1 *Screened methyl orange indicator* solution, 1 g/l.

Dissolve 0.25 g of methyl orange and 0.15 g of xylene cyanol FF in 50 ml of 95 % (V/V) ethanol and dilute to 250 ml with water.

- 4.6.2 *Phenolphthalein* solution, 10 g/l.

Dissolve 2.5 g of phenolphthalein in 250 ml of 95 % (V/V) ethanol.

- 4.7 *Thermochemical standard*. Dry benzoic acid of thermochemical standard certified by a national testing authority.

After pelleting the benzoic acid, the pellets should be dried before use by exposing them for at least 3 days in a desiccator containing magnesium perchlorate. Alternatively, transfer about 1.2 g of the benzoic acid into a crucible, previously weighed to 0.1 mg, and heat at 121 to 126 °C for 1 hour; after cooling in a desiccator, reweigh the crucible and contents to 0.1 mg to obtain the mass of dry benzoic acid taken.

The heat of combustion of the benzoic acid listed in the certificate for the conditions of use should be adopted in calculating the effective heat capacity of a calorimeter.

5. APPARATUS

- 5.1 *Bomb*, capable of withstanding safely the pressures developed during combustion. The design should permit complete recovery of all liquid products. The materials of construction should resist corrosion by the acids produced by the combustion of coal or coke.

NOTE. – Bomb parts should be inspected regularly for wear and corrosion; particular attention should be paid to the condition of the threads of the main closure.

- 5.2 *Calorimeter*, made of metal, highly polished on the outside and capable of holding sufficient water to cover completely the flat upper surface of the bomb while the water is being stirred.

- 5.3 *Stirrer*, driven at a constant speed. The stirrer shaft should contain a non-conducting section below the cover of the water jacket to minimize the transmission of heat to or from the system. If a cover is used for the calorimeter vessel, the non-conducting section should be above this cover.

NOTE. – For isothermal and static bomb calorimeters the rate of stirring should ensure that the length of the chief period (see clause 7.2) in determinations of effective heat capacity using benzoic acid (see Annex) does not exceed 10 minutes.

- 5.4 *Water jacket*, which may be an adiabatic, isothermal or static type, enclosing the calorimeter vessel with an air-gap of approximately 10 mm separating the vessel and water jacket.

The adiabatic water jacket should have either electrode or immersion heaters capable of supplying energy at a rate sufficient to maintain the temperature of the water in the jacket within 0.1 K of that of the calorimeter vessel after the charge has been fired. When in balance at 25 °C, the temperature drift of the calorimeter vessel should not exceed 0.0005 K/min.

The isothermal water jacket should be provided with a means of keeping its temperature constant to ± 0.1 K.

The static water jacket should have a thermal capacity big enough to restrict changes of temperature of the water in it. From the time of firing the charge to the end of the after-period or during a period of 15 minutes, whichever is the greater, with a cooling constant (d) of 0.0020 (see clause 8.2), the rise in temperature of the water in the jacket should be less than 0.16 K; with a cooling constant (d) of 0.0030, the rise in temperature should be less than 0.11 K.

NOTE. – For an insulated metal jacket this can be ensured by making the capacity at least 12.5 litres, contained in a wide annular jacket.

- 5.5 *Temperature measuring instrument*, capable of indicating temperatures which when corrected have an accuracy of 0.002 K, so that temperature intervals of 2 to 3 K can be determined with an accuracy of 0.004 K. It should be calibrated against a known standard by a national testing authority, at intervals not larger than 0.5 K over the range of use or, for mercury-in-glass thermometers, over the whole graduated scale.

- (1) Resistance thermometers composed of a platinum resistance, resistance bridge and galvanometer may be used.
- (2) Mercury-in-glass thermometers which conform to the following ISO Recommendations are suitable :

ISO/R 651, *Solid stem calorimeter thermometers*;

ISO/R 652, *Enclosed-scale calorimeter thermometers*;

ISO/R . . . *, *Solid stem adjustable range thermometers*;

ISO/R . . . *, *Enclosed-scale adjustable range thermometers*.

A viewer with about $\times 5$ magnification is needed for reading the temperature to the required accuracy.

A mechanical vibrator to tap the thermometer for a period of about 10 seconds before reading the temperature is desirable to prevent sticking of the mercury column; if this is not available, the thermometer should be tapped manually, for example with a pencil.

* At present at the stage of draft proposal.

5.6 Crucible, of silica, nickel-chromium or platinum.

For coal, it should be about 25 mm in diameter, flat based and not more than 20 mm deep. Silica crucibles should be about 1.5 mm thick and metal crucibles about 0.5 mm thick. A shallow crucible of nickel-chromium foil about 0.25 mm thick is recommended when testing high ash coals, in order to reduce any error from incomplete combustion.

For coke, the nickel-chromium crucible, as described for use with coal, should be lined with a paste of fused aluminosilicate cement (see clause 4.3). After drying at 50 to 60 °C, the excess cement is scraped off to leave a smooth lining about 1.5 mm thick; the crucible is then incinerated at 1000 °C for 2 hours. Before use, 0.3 g of alumina (see clause 4.4) is spread over the base of the lined crucible and compacted with the flat end of a metal rod.

For benzoic acid, either of the crucibles specified for coal is suitable. If smears of unburned carbon occur, a smaller nickel-chromium crucible, for example 0.25 mm thick, 15 mm in diameter and 7 mm deep, may be used.

5.7 Ignition circuit. The electrical supply should be 6 to 12 V alternating current from a step-down transformer or direct current from batteries. It is desirable to include an ammeter or pilot light in the circuit to indicate when current is flowing.

The firing switch should be of the spring-loaded, normally open type.

CAUTION. — The firing switch should not be mounted on the calorimeter.

5.8 Ancillary pressure equipment

5.8.1 Pressure regulator to control the filling of the bomb with oxygen.

5.8.2 Pressure gauge (0 to 50 bar) to indicate the pressure in the bomb.

5.8.3 Relief valve or bursting disk operating at 35 bar installed in the filling line, to prevent overfilling the bomb.

WARNING. — Equipment for high pressure oxygen must be kept free from oil and grease. Do not test or calibrate the pressure gauge with hydrocarbon fluid.

5.9 Timer, fitted in a convenient place, indicating minutes and seconds. It may usefully incorporate a device giving audible signals lasting 10 seconds starting at 1 minute intervals.

6. SAMPLE

The coal or coke used for the determination of calorific value should be the analysis sample ground to pass a sieve of 200 μm aperture. The sample should be exposed in a thin layer for the minimum time necessary for the moisture content to reach approximate equilibrium with the laboratory atmosphere.

The sample should be mixed, preferably by mechanical means, immediately before the determination. Portions for duplicate determinations should be weighed out at the same time. The moisture content of the sample should be determined at the same time as the determination of calorific value, so that the appropriate correction can be made.

7. PROCEDURE

7.1 Adiabatic calorimeter

Weigh the crucible (see clause 5.6) to the nearest 0.1 mg and introduce into it sufficient of the sample to cause a temperature rise of 2 to 3 K (see Note 1, page 10). Weigh the crucible and contents to determine the mass of sample taken.

Connect a piece of firing wire tautly across the terminals of the bomb. Tie a known mass of cotton to the firing wire (see Note 2, page 10); arrange the ends of the cotton so that they touch the sample.