INTERNATIONAL STANDARD ISO 1928

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Solid mineral fuels – Determination of gross calorific value by the calorimeter bomb method, and calculation of net calorific value

Combustibles minéraux solides – Détermination du pouvoir calorifique supérieur selon la méthode à la bombe calorimétrique, et calcul du pouvoir calorifique inférieur

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FOREWORD

ISO (the International Organization for Standardization) is a worldwide federation of national standards institutes (ISO member bodies). The work of developing International Standards is carried out through ISO technical committees. Every member body interested in a subject for which a technical committee has been set up has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work.

Draft International Standards adopted by the technical committees are circulated to the member bodies for approval before their acceptance as International Standards by the ISO Council.

Prior to 1972, the results of the work of the technical committees were published as ISO Recommendations; these documents are in the process of being transformed into International Standards. As part of this process, Technical Committee ISO/TC 27, *Solid mineral fuels*, has reviewed ISO Recommendation R 1928-1971 and found it technically suitable for transformation. International Standard ISO 1928 therefore replaces ISO Recommendation R 1928-1971, to which it is technically identical.

ISO Recommendation R 1928 had been approved by the member bodies of the following countries :

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

The member bodies of the following countries had expressed disapproval of the Recommendation on technical grounds :

Germany
Poland*

The member body of the following country disapproved the transformation of the Recommendation into an International Standard :

Czechoslovakia

* Subsequently, this member body approved the Recommendation.

Printed in Switzerland

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Annexes

Solid mineral fuels — Determination of gross calorific value by the calorimeter bomb method, and calculation of net calorific value

1 SCOPE AND FIELD OF APPLICATION

This International Standard specifies a method for 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 REFERENCES

ISO 331, *Coal — Determination of moisture in the analysis sample — Direct gravimetric method.*

ISO 348, *Hard coal — Determination of moisture in the analysis sample — Direct volumetric method.*

ISO 609, *Coal and coke — Determination of carbon and hydrogen — High temperature combustion method.*

ISO 625, *Coal and coke — Determination of carbon and hydrogen — Liebig method.*

ISO 687, *Coke — Determination of moisture in the analysis sample.*

ISO 1170, *Coal and coke — Calculation of analyses to different bases.*

3 UNITS

3.1 Unit of heat : The joule (J).

$1\ \mathrm{J} = 1$ newton metre (N·m)

$= 1 \times 10^7$ ergs

$= 0{,}238\ 846$ International Table calories ($\mathrm{cal}_{\mathrm{IT}}$)

($1\ \mathrm{cal}_{\mathrm{IT}} = 4{,}186\ 8\ \mathrm{J}$)

3.2 Unit of temperature : The kelvin (K).

A temperature interval of 1 K is equal to a temperature interval of 1 °C.

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)].

4 DEFINITIONS

For the purpose of this International Standard, the following definitions apply.

4.1 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.

4.2 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, nitrogen, water vapour and ash, all at 25 °C.

4.3 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.

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

5 PRINCIPLE

5.1 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.

5.2 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.

6 REAGENTS

6.1 Oxygen, at a pressure capable of filling the bomb to 3 MPa* and free from combustible matter (oxygen made by the electrolytic process may contain up to 4 % of hydrogen and is therefore unsuitable).

6.2 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.

6.3 Paste, of fused aluminosilicate cement passing a 63 μm test sieve and suitable for use up to a temperature of 1 400 °C, mixed with water.

6.4 Aluminium oxide, fused, of analytical reagent quality, passing a 180 μm test sieve and retained on a 106 μm test sieve.

6.5 Standard volumetric solutions

6.5.1 Barium hydroxide, 0,1 N solution.

6.5.2 Sodium carbonate, 0,1 N solution.

6.5.3 Sodium hydroxide, 0,1 N solution.

6.5.4 Hydrochloric acid, 0,1 N solution.

6.6 Coloured indicators

6.6.1 Screened methyl orange indicator, 1 g/l solution.

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.

6.6.2 Phenolphthalein, 10 g/l solution.

Dissolve 2,5 g of phenolphthalein in 250 ml of 95 % (*V/V*) ethanol.

6.7 Benzoic acid of thermochemical standard certified by a national testing authority.

The benzoic acid shall be used in the condition as certified. Drying or any treatment other than pelleting shall not be carried out.

The heat of combustion of the benzoic acid listed in the certificate for the conditions of use shall be adopted in calculating the effective heat capacity of the colorimeter.

7 APPARATUS

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

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

7.2 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.

7.3 Stirrer, driven at a constant speed. The stirrer shaft shall 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 shall be above this cover.

NOTE — For isothermal and static bomb calorimeters, the rate of stirring shall ensure that the length of the chief period (see 9.2) in determinations of effective heat capacity using benzoic acid (see annex A) does not exceed 10 min.

7.4 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 shall 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 shall not exceed* 0,000 5 K/min.

The isothermal water jacket shall be provided with a means of keeping its temperature constant to ± 0,1 K.

The static water jacket shall 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 min, whichever is the greater, with a cooling constant *d* of 0,002 0 (see 10.2), the rise in temperature of the water in the jacket shall be less than 0,16 K; with a cooling constant *d* of 0,003 0, the rise in temperature shall be less than 0,11 K.

NOTE — For an insulated metal jacket, this can be ensured by making the capacity at least 12,5 l, contained in a wide annular jacket.

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* 1 MPa = 1 MN/m^2

7.5 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 shall 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.

The following types of thermometer are suitable :

a) resistance thermometers composed of a platinum resistance, resistance bridge and galvanometer;

b) mercury-in-glass thermometers which conform to ISO 651, ISO 652, ISO/R 1770 or ISO/R 1771.

A viewer with about X 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 s before reading the temperature is desirable to prevent sticking of the mercury column; if this is not available, the thermometer shall be tapped manually, for example with a pencil.

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

For coal, it shall be about 25 mm in diameter, flat based and not more than 20 mm deep. Silica crucibles shall 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, shall be lined with a paste of fused alumino-silicate cement (see 6.3). After drying at 50 to 60 °C, the excess cement shall scraped off to leave a smooth lining about 1,5 mm thick; the crucible shall then be incinerated at 1 000 °C for 2 h. Before use, 0,3 g of aluminium oxide (see 6.4) shall be 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 small nickel-chromium crucible, for example 0,25 mm thick, 15 mm in diameter and 7 mm deep, may be used.

7.7 Ignition circuit.

The electrical supply shall 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 shall be of the spring-loaded, normally open type.

CAUTION – The firing switch shall not be mounted on the calorimeter.

7.8 Ancillary pressure equipment

7.8.1 Pressure regulator, to control the filling of the bomb with oxygen.

7.8.2 Pressure gauge (0 to 5 MPa) to indicate the pressure in the bomb.

7.8.3 Relief valve or **bursting disk** operating at 3,5 MPa installed in the filling line, to prevent overfilling the bomb.

CAUTION – Equipment for high pressure oxygen shall be kept free from oil and grease. Do not test or calibrate the pressure gauge with hydrocarbon fluid.

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

8 SAMPLE

The coal or coke used for the determination of calorific value shall be the analysis sample ground to pass a test sieve of 200 μm aperture. The sample shall 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 shall be mixed, preferably by mechanical means, immediately before the determination. Portions for duplicate determinations shall be weighed out at the same time. The moisture content of the sample shall be determined at the same time as the determination of calorific value, so that the appropriate correction can be made.

9 PROCEDURE

9.1 Adiabatic calorimeter

Weigh the crucible (7.6) 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 after 9.2). 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 after 9.2); arrange the ends of the cotton so that they touch the sample.

Put 5 ml of distilled water in the bomb. Assemble the bomb and charge it slowly with oxygen to a pressure of 3 MPa without displacing the original air. If the bomb is inadvertently charged with oxygen above 3,3 MPa, discard the test and begin again.

Put sufficient water in the calorimeter vessel to cover the flat upper surface of the bomb cap. This quantity of water shall be the same, to within 1 g, as that used in determining the mean effective heat capacity of the calorimeter (see annex A). Transfer the calorimeter vessel to the water jacekt; lower the bomb into calorimeter vessel and check that the bomb is gas-tight. If gas escapes from the bomb, discontinue the test, eliminate the cause of leakage and begin again.

Assemble and start up the apparatus. Use a constant rate of stirring such that the length of the predetermined interval (see annex A, clause A.4) does not exceed 10 min. Select the setting of the bridge circuit that will result in the minimum drift in the temperature of the calorimeter vessel at the final temperature.

After 10 min, tap the thermometer lightly and read it to 0,001 K (the "firing temperature", t_o). Fire the charge; hold the switch closed only long enough to ignite the fuse.

CAUTION – Do not extend any part of the body over the calorimeter during firing, nor for 20 s thereafter.

After the predetermined interval, established when the effective heat capacity of the system is determined (see annex A), tap the thermometer again and read it to 0,001 K (the "final temperature", t_n). The observer shall take care to avoid parallax errors when using the magnifying viewer to read mercury-in-glass thermometers.

Remove the bomb from the calorimeter vessel, release the pressure and dismantle the bomb. Examine the bomb interior and discard the test if unburned sample or a sooty deposit is visible.

When certain unreactive cokes are tested, the residue in the bomb frequently contains detectable unburned sample. A correction to be applied for such persistently incomplete combustion may be calculated from the amount of unburned carbon, which may be estimated by the procedure described in note 3 after 9.2.

Wash the contents of the bomb into a beaker with distilled water. Wash the underside of the bomb cap and the outside of the crucible with distilled water; add the washings to the beaker. Dilute to approximately 100 ml and boil to expel carbon dioxide. While still hot, titrate with the barium hydroxide solution (6.5.1) using the phenolphthalein solution (6.6.2) as indicator. Add 20 ml of the sodium carbonate solution (6.5.2), filter the warm solution and wash the precipitate with distilled water. When cold, titrate the filtrate with the hydrochloric acid solution (6.5.4), using the screened methyl orange solution (6.6.1) as indicator, ignoring the phenolphthalein colour change. (These titrations may be omitted if the sulphur content of the coal and the nitric acid correction are known – see note 4 after 9.2.)

9.2 Isothermal and static calorimeters

Weigh the crucible (see 7.6) 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). 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); arrange the ends of the cotton so that they touch the sample.

Put 5 ml of distilled water in the bomb. Assemble the bomb and charge it slowly with oxygen to a pressure of 3 MPa without displacing the original air. If the bomb is inadvertently charged with oxygen above 3,3 MPa, discard the test and begin again.

Put sufficient water in the calorimeter vessel to cover the flat upper surface of the bomb cap. This quantity of water shall be the same, to within 1 g, as that used in determining the mean effective heat capacity. The initial temperature of the water shall be such that, at the end of the chief period, the temperature will not exceed that of the water in the jacket by more than 0,5 K. Transfer the calorimeter vessel to the water jacket; lower the bomb into the calorimeter vessel and check that the bomb is gas-tight. If gas escapes from the bomb, discard the test, eliminate the cause of leakage and begin again.

Assemble the apparatus. Start the stirrer and keep in operation at a constant rate throughout the determination. Stir for at least 10 min before starting to read the temperature (see note 5). Read the temperature to 0,001 K and continue to do so at intervals of 1 min for a period of 5 min. Tap the thermometer lightly for 10 s before each reading; take care to avoid parallax errors when using magnifying viewer to read mercury-in-glass thermometers. Fire the charge immediately after reading the last temperature in the preliminary period (see a) below); hold the switch closed only long enough to ignite the fuse.

CAUTION – Do not extend any part of the body over the calorimeter during firing, nor for 20 s thereafter.

Read the thermometer as follows :

a) *Preliminary period.* If the average deviation of the values of the rate of change of temperature during this period of 5 min exceeds 0,001 K/min (see note 6) continue to read the thermometer at 1 min intervals until the average deviation is less than 0,001 K/min for a period of 5 min.

The last temperature of the *preliminary period* is the initial temperature of the *chief period* (t_o).

b) *Chief period.* During the first few minutes of the chief period it will not be possible to read the thermometer to 0,001 K but resume readings to this precision as soon as possible and continue them to the end of the test. The chief period does not necessarily end with the attainment of maximum temperature; the end is assessed as the point at which the *after-period* begins.

c) *After-period.* The after-period begins at the point when, for a subsequent 5 min period, the average deviation of the individual values of change of temperature per minute is not more than 0,001 K (see note 6).

Remove the bomb from the calorimeter vessel, release the pressure and dismantle the bomb. Examine the bomb interior and discontinue the test if unburned sample or a sooty deposit is visible.

When certain unreactive cokes are tested, the residue in the bomb frequently contains detectable unburned sample. A correction to be applied for such persistently incomplete combustion may be calculated from the amount of unburned carbon, which may be estimated by the procedure described in note 3.

Wash the contents of the bomb into a beaker with distilled water. Wash the underside of the bomb cap and the outside of the crucible with distilled water; add the washings to the beaker. Dilute to approximately 100 ml and boil to expel carbon dioxide. While still hot, titrate with the barium hydroxide solution (6.5.1) using the phenolphthalein solution (6.6.2) as indicator. Add 20 ml of the sodium carbonate solution (6.5.2), filter the warm solution and wash the precipitate with distilled water. When cold, titrate the filtrate with the hydrochloric acid solution (6.5.4), using the screened methyl orange solution (6.6.1) as indicator, ignoring the phenolphthalein colour change. (These titrations may be omitted if the sulphur content of the coal and the nitric acid correction are known — see note 4.)

NOTES

1 Normally 1 g of coal ia an appropriate test portion. For high ash coals, the use of 0,75 g of the sample and the shallow crucible of nickel-chromium foil (see 7.6) should reduce the possibility of incomplete combustion.

2 For convenience, a measured length of cotton of known mass per unit length may be used; the length used in each determination of calorific value should be the same as was used in the determination of the effective heat capacity of the system.

3 The unburned carbon in the crucible may be estimated as follows. Transfer the contents of the crucible (not the lining) to a silica or porcelain dish and dry for 1 h at 320 °C. Cool, weigh the dish and its contents to the nearest 0,1 mg, heat at 815 °C for 1 h, cool and reweigh to determine the loss in mass. The loss is taken to be unburned carbon. Alternatively, the unburned carbon may be determined by one of the methods specified is ISO 609 or ISO 625. Should more than 6 mg of unburned carbon be found, the correction will be invalid and the determination of calorific value should be repeated.

4 For any given bomb, under constant conditions of heat release, the quantity of nitric acid formed, and therefore the consequent correction, is relatively constant; for hard coals in general, a typical value would be 33 J and for anthracite 25 J. After the value has been firmly established it may be applied in subsequent tests as an alternative to its determination. The determination of the sulphuric acid correction may then be shortened as follows :

> Titrate the warm (not boiling) bomb washings with the 0,1 N sodium hydroxide solution (6.5.3), using the screened methyl orange solution (6.6.1) as indicator, to determine the total acidity. Deduct from this titre (in millilitres) 0,7 times the nitric acid correction, in joules, to obtain the volume of 0,1 N sulphuric acid solution present.

If the sulphur content of the sample and the appropriate nitric acid correction are both known, the titration of the acids in the bomb washings is unnecessary. The sulphuric acid correction is equal to 9,5 J per milligram of sulphur in the mass of coal used for determination of calorific value.

5 If the Regnault-Pfaundler cooling correction (see 10.2) is to be calculated, the procedure specified should be adopted; if an alternative formula, which is equivalent and acceptable, is to be used, some of the temperature readings may not be required and the procedure should be modified accordingly.

6 A convenient method of checking that the average deviation of the rate of change of temperature during the preliminary period and the after-period is within the specified limit is to list the five differences as units without the decimal place, code them by subtracting the smallest and arrange the coded differences in descending sequence. If the sequence is listed in the following table, the average deviation is within the specified limit.

Table of acceptable difference sequences

Coded difference	Average deviation $\times 10^3$	Coded difference	Average deviation $\times 10^3$
10000	0,32	22210	0,72
11000	0,48	22220	0,64
11100	0,48	30000	0,96
11110	0,32	31000	0,96
20000	0,64	31100	0,80
21000	0,72	31110	0,72
21100	0,64	32110	0,88
21110	0,40	32210	0,88
22000	0,96	32220	0,72
22100	0,80	33220	0,80
22110	0,64	33320	0,96
22200	0,96	33330	0,96

Example :

Time min	Temperature °C	Difference (units)	Coded difference
0	24,157		
		7	2
1	24,164		
		5	0
2	24,169		
		8	3
3	24,177		
		8	3
4	24,185		
		7	2
5	24,192		

The sequence 33220 is acceptable.

10 CORRECTIONS

The following corrections shall be made to the experimental observations :

10.1 Thermometer corrections

If a mercury-in-glass thermometer is used, the corrections prescribed in the certificate issued with the thermometer shall be applied to the observed firing temperature, t_o, and to the final temperature, t_n.

10.2 Cooling correction

The heat loss to the water jacket is negligible in an adiabatic calorimeter such as is specified and a cooling correction is not necessary.

The heat lost to the water jacket of an isothermal or static calorimeter may be compensated by an addition to the temperature rise. This correcting addition may be calculated by the Regnault-Pfaundler formula or by any formula which is equivalent to it and which is accepted as such by a national standardizing body.

Regnault-Pfaundler formula

Cooling correction

$$= nv' + \frac{v'' - v'}{t'' - t'} \left[\sum_{i=1}^{i=n-1} t_i + \tfrac{1}{2}(t_o + t_n) - nt' \right]$$

+λ

$$= nv' + dZ$$

where

n is the number of minutes in the chief period;

v' is the rate of fall of temperature per minute in the preliminary period (if the temperature is rising, v' is negative, i.e. it should be added);

v'' is the rate of fall of temperature per minute in the after-period;

t' is the average temperature during the preliminary period;

t'' is the average temperature during the after-period;

t_o is the firing temperature;

$t_1, t_2, t_3 \ldots t_n$ are the successive temperatures recorded during the chief period, t_n being the first temperature after which the rate of change is constant within the defined limits;

$\sum_{i=1}^{i=n-1} t_i$ is the sum of $t_1, t_2, t_3 \ldots t_{n-1}$;

$d = \frac{v'' - v'}{t'' - t'}$ is the "cooling constant", in reciprocal minutes, of the calorimeter, which must be determined for each set of conditions;

Z represents the expression in square brackets.

10.3 Heat of ignition

The heat release from the cotton and firing wire shall be subtracted from the total heat released. The heat release from the cotton shall be calculated from its mass (dried at 100 °C) and the calorific value of cellulose (17 500 J/g). The heat release from the firing wire shall be calculated from the mass of a piece of wire equal in length to the distance between the poles of the bomb, allowing 1 400 J/g for nickel-chromium wire or 420 J/g for platinum wire.

10.4 Correction for heat of formation of acids

The heat gain due to the formation of sulphuric acid and nitric acid shall be subtracted from the total heat released. These corrections amount to 15,1 J/ml of 0,1 N sulphuric acid and 6,0 J/ml of 0,1 N nitric acid present in the bomb washings (see note 4 after 9.2).

If

V_1 is the volume, in millilitres, of the standard volumetric hydrochloric acid solution (6.5.4) used, and

V_2 is the volume, in millilitres, of the standard volumetric barium hydroxide solution (6.5.1) used,

then the sulphuric acid correction, in joules,

$$= 15{,}1\,(V_1 \underset{\lambda}{-} V_2 - 20)$$

and the nitric acid correction, in joules,

$$= 6{,}0\,(20 - V_1)$$

The sum of these two may be calculated directly from the formula

$$\text{total correction (joules)} = 9{,}1\,V_1 + 15{,}1\,V_2 - 181{,}7$$

10.5 Correction for unburned carbon (coke only)

Take the loss in mass on ignition of the residue from the coke crucible to be unburned carbon. Its heat equivalent, on the basis of 1 mg = 33,5 J, shall be added to the determined heat release.

11 EXPRESSION OF RESULTS

Compute the gross calorific value at constant volume from the observations by substituting in the equation

$$Q_{gr,v} = \frac{(\Delta\theta)C_{(5)} - e_1 - e_2 - e_3 - e_4}{m_f}$$

where

$Q_{gr,v}$ is the gross calorific value at constant volume of the coal as analysed, in joules per gram;

$\Delta\theta$ is the corrected temperature rise [this is calculated from the observed firing temperature (t_o), corrected for thermometer error, and the observed final temperature (t_n), corrected for thermometer error, plus the cooling correction calculated for isothermal and static calorimeters];

$C_{(5)}$ is the mean of five determinations of effective heat capacity of the calorimeter, in joules per kelvin (see annex A);

e_1 is the correction for heat of combustion of the cotton, in joules;

e_2 is the correction for heat of combustion of the firing wire, in joules;

e_3 is the correction for heat of formation of sulphuric acid, in joules;

e_4 is the correction for heat of formation of nitric acid, in joules;

m_f is the mass, in grams, of the sample of fuel.

Examples to illustrate the method of calculating the results of a calorific determination are given in annex B.

The result (preferably the mean of duplicate determinations, see clause 12) shall be reported to the nearest multiple of 20 J/g.

12 PRECISION OF THE METHOD

Calorific value, gross, at constant volume	Maximum acceptable differences between results obtained on the analysis samples (calculated to the same moisture content)	
	Repeatability	**Reproducibility**
	120 J/g	300 J/g

NOTE — A moisture content determination shall be carried out simultaneously by one of the methods specified in ISO 331, ISO 348 or ISO 687.

12.1 Repeatability

The results of duplicate determinations carried out at different times in the same laboratory by the same operator with the same apparatus on the same analysis sample should not differ by more than the above value.

12.2 Reproducibility

The means of the results of duplicate determinations carried out in each of two laboratories, on representative portions taken from the same sample at the last stage of sample preparation, should not differ by more than the above valve.

12.3 Calculation to other bases

For the calculation of results to other bases, see ISO 1170.

13 CALCULATION OF NET CALORIFIC VALUE

13.1 General

The result of the preceding determination is the gross calorific value of the fuel at constant volume. From this, the net calorific value at constant volume and the net calorific value at constant pressure may be calculated by the formulae given below.

The formulae take account of any change in the moisture basis that may be required. For calculation to other bases, see ISO 1170.

The derivations of the formulae are given in annex C; the constants have been rounded off to yield a suitable precision.

13.2 Net calorific value at constant volume

$$Q_{net,v,m} = \left(Q_{gr,v} - 206\,[H]\right) \times \frac{100 - M_T}{100 - M} - 23\,M_T$$

where

$Q_{net,v,m}$ is the net calorific value at constant volume, in joules per gram, of the fuel with moisture content M_T;

$Q_{gr,v}$ is the gross calorific value at constant volume, in joules per gram, of the analysis sample of the fuel;

[H] is the percentage of hydrogen in the analysis sample (this includes the hydrogen present in the water of hydration of the mineral matter as well as that in the coal substance);

M_T is the percentage moisture content for which the calculation is required. On the dry basis, $M_T = 0$; on the air-dried basis, $M_T = M$; on the as-fired basis, M_T is the percentage of total moisture;

M is the percentage of moisture in the analysis sample.

13.3 Net calorific value at constant pressure

$$Q_{net,p,m} = \left(Q_{gr,v} - 212\,[H] - 0{,}8\,[O]\right) \times \frac{100 - M_T}{100 - M} - 24{,}5\,M_T$$

where

$Q_{net,p,m}$ is the net calorific value at constant pressure, in joules per gram, of the fuel with moisture content M_T;

[O] is the percentage of oxygen in the analysis sample. It may be derived by subtracting from 100 the sum of the percentages of moisture, ash, carbon, hydrogen, nitrogen and sulphur;

$Q_{gr,v}$, [H], M_T and M are as defined in 13.2.

NOTE — A value for nitrogen typical of the fuel may be used; any error will be negligible.

ANNEX A

DETERMINATION OF THE EFFECTIVE HEAT CAPACITY OF THE CALORIMETER

A.1 PRINCIPLE

A known mass of benzoic acid of certified calorific value is burned in oxygen in the bomb calorimeter. To the heat of combustion of the benzoic acid are added the heats of combustion of the cotton and the firing wire and the heat of formation of nitric acid.

At least five complete determinations of effective heat capacity are carried out. Provided that their range does not exceed 55 J/K, the mean of these five, $C_{(5)}$, is taken for calculation of the calorific value of the fuel (see 11.1).

A.2 PROCEDURE

Proceed as specified in clause 9 for the determination of calorific value. If necessary, use the small metal crucible specified in 7.6.

When determining the effective heat capacity of an adiabatic calorimeter, read the temperature at 1 min intervals over a period of 10 min, commencing 5 min after firing the charge (see clause A.4).

Dilute the bomb washings to approximately 50 ml with distilled water. Titrate the nitric acid directly with the sodium hydroxide solution (6.5.3) or the sodium carbonate solution (6.5.2), using the screened methyl orange solution (6.6.1) as indicator.

A.3 CALCULATION OF A SINGLE COMPLETE DETERMINATION

The effective heat capacity C of the system is given, in joules per kelvin, by the formula :

$$C = \frac{m_b\,(Q^b_{gr,v}) + e_1 + e_2 + e_4}{\Delta\theta}$$

where

m_b is the mass, in grams, of the benzoic acid (6.7);

$Q^b_{gr,v}$ is the certified gross calorific value at constant volume, in joules per gram, of the benzoic acid (6.7);

$\Delta\theta$, e_1, e_2 and e_4 are as defined in clause 11.

NOTE – e_4 = 6,0 times the volume, in millilitres, of the sodium hydroxide solution or the sodium carbonate solution used in titrating the bomb washings.

A.4 PREDETERMINED INTERVAL (Adiabatic calorimeters)

The period between the firing of the charge and the reading of the final temperature is the predetermined interval. It is calculated from the temperature readings taken at intervals of 1 min in each determination of effective heat capacity.

From the recorded observations of each determination, note the shortest time in minutes from the firing of the charge to reaching the second of three consecutive readings which do not differ by more than 0,001 K. Calculate, to the nearest whole minute, the mean of the five values to obtain the length of the predetermined interval; this should not exceed 10 min.

Use the predetermined interval for all determinations of calorific value until a new value is established. It shall be re-established when commissioning a new calorimeter and checked after changing any component.

A.5 RE-DETERMINATION OF THE MEAN EFFECTIVE HEAT CAPACITY

When any part of the system is changed, the mean effective heat capacity shall be re-determined. It shall also be re-determined at intervals of not longer than 6 months.

Where a change to the system is not involved, the re-determined mean shall be within 20 J/K of that previously determined. If the difference is greater than 20 J/K, experimental procedures shall be examined and carefully checked.

ANNEX B

EXAMPLES TO ILLUSTRATE A METHOD OF CALCULATING RESULTS

B.1 ADIABATIC CALORIMETER

Mass of coal = 0,999 2 g
Volume V_1 of hydrochloric acid solution (6.5.4) used = 13,0 ml
Volume V_2 of barium hydroxide solution (6.5.1) used = 10,9 ml
Final temperature observed (t_n) = 25,416 °C
thermometer correction = + 0,011 K
Firing temperature observed (t_o) = 22,793 °C
thermometer correction = + 0,017 K
Temperature rise ($t_n - t_o$) corrected for thermometer inaccuracies = 2,617 K
Mean effective heat capacity = 10 370 K
Heat liberated (2,617 × 10 370) = 27 138 J

Subtract :

Sulphuric acid correction = 15,1 (13,0 + 10,9 − 20) = 59
Nitric acid correction = 6,0 (20 − 13,0) = 42
Correction for cotton and firing wire = 84
Correction for unburned carbon = Nil

= 185 J

Heat from 0,999 2 g of coal = 26 953 J

Gross calorific value at constant volume = 26 975 J/g

= **26,98 GJ/t**

B.2 ISOTHERMAL CALORIMETER

Temperature of water jacket = 25 °C
Mean effective heat capacity = 10 370 J/K

Mass of coal = 0,999 2 g
Volume V_1 of hydrochloric acid solution (6.5.4) used = 13,0 ml
Volume V_2 of barium hydroxide solution (6.5.1) used = 10,9 ml

Observed temperature readings :

Time	Temperature	Time	Temperature	Time	Temperature
min	°C	min	°C	min	°C
0	22,771	6	23,990	13	25,407 (t_n)
1	22,775	7	25,000	14	25,405
2	22,780	8	25,295	15	25,403
3	22,785	9	25,373	16	25,400
4	22,789	10	25,400	17	25,398
5	22,793 (t_o)	11	25,407	18	25,396
		12	25,408		

Cooling correction (Regnault-Pfaundler formula) :

$\nu' = -0{,}004\,4$
$t' = 22{,}782$

$$d = \frac{0{,}006\,6}{2{,}620}$$

$= 0{,}002\,52$

$n = 8$

$$\sum_{i=1}^{i=n-1} t_i = 175{,}873$$

$\nu'' = 0{,}002\,2$
$t'' = 25{,}402$

$\frac{1}{2}(t_0 + t_n) = 24{,}100$

$-nt' = -182{,}256$

therefore $Z = 17{,}717$

$dZ = 0{,}044\,6$

$n\nu' = -0{,}035\,2$

Cooling correction $= dZ + n\nu' = 0{,}009$ K

Final temperature observed (t_n) $= 25{,}407$
thermometer correction $= +0{,}011$

Firing temperature observed (t_0) $= 22{,}793$
thermometer correction $= +0{,}017$

Temperature rise ($t_n - t_0$) corrected for thermometer inaccuracies = 2,608 K

Cooling correction = + 0,009 K

Corrected temperature rise = 2,617 K

Heat liberated (2,617 × 10 370) = 27 138 J

Subtract :

Sulphuric acid correction = 15,1 (13,0 + 10,9 − 20) = 59

Nitric acid correction = 6,0 (20 − 13,0) = 42

Correction for cotton and firing wire = 84

Correction for unburned carbon = Nil

= 185 J

Heat from 0,999 2 g of coal = 26 953

Gross calorific value at constant volume = 26 975 J/g

= 26,98 GJ/t

B.3 A SINGLE DETERMINATION OF EFFECTIVE HEAT CAPACITY

Mass of benzoic acid (6.7) taken = 1,183 3 g
Volume of sodium hydroxide solution (6.5.3) used = 7,0 ml
Temperature rise (see note) = 3,036 K
Final calorimeter temperature = 25,5 °C
Gross calorific value of the benzoic acid at 25,5 °C = 26 467 J/g
Heat liberated from the benzoic acid (1,183 3 × 26 467) = 31 318 J

Add :

Nitric acid correction = 7,0 × 6,0 = 42
Correction for cotton and firing wire = 84

= 126 J

Total heat release = 31 444 J

$$\text{Effective heat capacity} = \frac{31\,444}{3{,}036} = \mathbf{10\,357\ J/K}$$

NOTE — The temperature rise in this example is the difference between the firing and final thermometer readings, t_o and t_n, corrected for thermometer inaccuracies; for isothermal or static calorimeters it will also include the cooling correction.

ANNEX C

ADDITIONAL CALCULATIONS

C.1 CALCULATION OF THE NET CALORIFIC VALUE AT CONSTANT VOLUME

If fuel were burned at constant volume and the resulting water remained in the vapour state at 25 °C, the heat release would be equal to the gross calorific value of the fuel at constant volume less the latent heat of vaporization at 25 °C and constant volume of the water present in the fuel and that formed by its combustion.

The latent heat of vaporization of water at constant volume is less than the latent heat of evaporation at constant pressure (the figure normally quoted) by the heat equivalent to the work done on the atmosphere due to expansion when the vaporization is carried out at constant pressure.

The latent heat of vaporization at 25 °C and constant pressure of the water present in the analysis sample and formed from the hydrogen in it is given, in joules per mole, by the formula

$$0{,}01\,L\left(\frac{[\mathrm{H}]}{2{,}016\,0}+\frac{M}{18{,}015\,4}\right)$$

where

L is the latent heat of vaporization of water at 25 °C and constant pressure (44,0 kJ/mol);

[H] and M are as defined in 13.2.

The work done against the atmosphere when this water is expanded at constant pressure to vapour at 25 °C is given, in joules per mole, by the formula

$$0{,}01\,RT\left(\frac{[\mathrm{H}]}{2{,}016\,0}+\frac{M}{18{,}015\,4}\right)$$

where

R is the universal gas constant [8,315 J/(mol·K)];

T is the standard thermochemical reference temperature (298,15 K).

Hence

$$\begin{aligned} Q_{\mathrm{net,v}} &= Q_{\mathrm{gr,v}} - 0{,}01\,(L-RT)\left(\frac{[\mathrm{H}]}{2{,}016\,0}+\frac{M}{18{,}015\,4}\right) \\ &= Q_{\mathrm{gr,v}} - 205{,}96\,[\mathrm{H}] - 23{,}05\,M \end{aligned}$$

where $Q_{\mathrm{net,v}}$ is the net calorific value at constant volume, in joules per gram, of the analysis sample.

C.2 CALCULATION OF THE NET CALORIFIC VALUE AT CONSTANT PRESSURE

The formula for calculating the net calorific value at constant pressure may be derived from the gross calorific value at constant volume through the intermediate stage of the gross calorific value at constant pressure.

C.3 CALCULATION OF THE GROSS CALORIFIC VALUE AT CONSTANT PRESSURE FROM THE GROSS CALORIFIC VALUE AT CONSTANT VOLUME

If fuel were burned at constant pressure and the water formed condensed to the liquid state, there would be a contraction in the volume of the system due to the formation of water. This contraction is equal to the volume of gaseous oxygen required to burn the hydrogen, less the volume that would be occupied by the oxygen of the fuel substance in the gaseous state. Work is therefore done on the system by the atmosphere in filling this void in order to maintain constant pressure.

On the air-dried basis, the contraction is given, in moles per gram, by the formula

$$0{,}01\left(\frac{0{,}5\,\overline{\mathrm{H}}}{2{,}016\,0}-\frac{\overline{\mathrm{O}}}{31{,}998\,8}\right)$$

where

$\overline{\mathrm{H}}$ is the percentage of hydrogen in the coal substance in the analysis sample;

$\overline{\mathrm{O}}$ is the percentage of oxygen in the coal substance in the analysis sample.

The work done by the atmosphere to maintain constant pressure is given, in joules per gram, by the formula

$$0{,}01\,RT\left(\frac{0{,}5\,\overline{\mathrm{H}}}{2{,}016\,0}-\frac{\overline{\mathrm{O}}}{31{,}998\,8}\right)$$

$$= 6{,}15\,\overline{\mathrm{H}} - 0{,}775\,\overline{\mathrm{O}}$$

In order to use $\overline{\mathrm{H}}$ and $\overline{\mathrm{O}}$ in the formula, either additional analysis has to be carried out or certain assumptions have to be made. However, the differences between $\overline{\mathrm{H}}$ and $\overline{\mathrm{O}}$, and [H] and [O] as defined in 13.2 and 13.3, are a function of the nature and quantity of the mineral matter present and can be shown to have only a small effect. For a coal containing 20 % of mineral matter, of which 10 % is water of hydration, the difference between $\overline{\mathrm{H}}$ and [H] would be about 0,2 %, and substituting [H] for $\overline{\mathrm{H}}$ in the formula would introduce an error of + 1,23 J/g. The difference between $\overline{\mathrm{O}}$ and [O] for the same coal might be about 3 %, and substituting [O] for $\overline{\mathrm{O}}$ in the formula would introduce an error of − 2,325 J/g. Thus, in this example, the combined error in substituting [H] for $\overline{\mathrm{H}}$ and [O] for $\overline{\mathrm{O}}$ is no more than 1,095 J/g. For coal generally, it is unlikely that errors from this source would ever exceed 4 J/g; hence, the formula may be written :

$$Q_{\mathrm{gr,p}} = Q_{\mathrm{gr,v}} + 6{,}15\,[\mathrm{H}] - 0{,}775\,[\mathrm{O}]$$

where $Q_{\mathrm{gr,p}}$ is the gross calorific value at constant pressure, in joules per gram, of the analysis sample.

C.4 CALCULATION OF THE NET CALORIFIC VALUE AT CONSTANT PRESSURE FROM THE GROSS CALORIFIC VALUE AT CONSTANT PRESSURE

The net calorific value at constant pressure is equal to the gross calorific value at constant pressure minus the latent heat of vaporization, at 25 °C and constant pressure, of the water present in the fuel and formed during its combustion.

On the air-dried basis this is given, in joules per gram, by the formula

$$0{,}01\,L\left(\frac{[\mathrm{H}]}{2{,}016\,0}+\frac{M}{18{,}015\,4}\right)$$

$$= 218{,}25\,[\mathrm{H}] + 24{,}42\,M$$

Hence

$$Q_{\mathrm{net,p}} = Q_{\mathrm{gr,p}} - 218{,}25\,[\mathrm{H}] - 24{,}42\,M$$

where $Q_{\mathrm{net,p}}$ is the net calorific value at constant pressure, in joules per gram, of the analysis sample.

C.5 CALCULATION OF THE NET CALORIFIC VALUE AT CONSTANT PRESSURE FROM THE GROSS CALORIFIC VALUE AT CONSTANT VOLUME

Substituting $Q_{\mathrm{gr,p}} = Q_{\mathrm{gr,v}} + 6{,}15\,[\mathrm{H}] - 0{,}775\,[\mathrm{O}]$

in $Q_{\mathrm{net,p}} = Q_{\mathrm{gr,p}} - 218{,}25\,[\mathrm{H}] - 24{,}42\,M$

gives $Q_{\mathrm{net,p}} = Q_{\mathrm{gr,v}} - 212{,}10\,[\mathrm{H}] - 0{,}775\,[\mathrm{O}] - 24{,}42\,M$