INTERNATIONAL STANDARD

**ISO
1928**

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

Combustibles minéraux solides — Détermination du pouvoir calorifique supérieur par la méthode de la bombe calorimétrique et calcul du pouvoir calorifique inférieur.

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Foreword

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International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 2.

The main task of technical committees is to prepare International Standards. Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights.

ISO 1928 was prepared by Technical Committee ISO/TC 27, *Solid mineral fuels*, Subcommittee SC 5, *Methods of analysis*.

This third edition cancels and replaces the second edition (ISO 1928:1995), which has been technically revised.

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

WARNING — Strict adherence to all of the provisions prescribed in this International Standard should ensure against explosive rupture of the bomb, or a blow-out, provided that the bomb is of proper design and construction and in good mechanical condition.

1   Scope

This International Standard specifies a method for the determination of the gross calorific value of a solid mineral fuel at constant volume and at the reference temperature of 25 °C in a bomb calorimeter calibrated by combustion of certified benzoic acid.

The result obtained is the gross calorific value of the analysis sample at constant volume with all the water of the combustion products as liquid water. 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 can also be used; equations are given for calculating both values.

General principles and procedures for the calibrations and the fuel tests are presented in the main text, whereas those pertaining to the use of a particular type of calorimetric instrument are described in Annexes A to C. Annex D contains checklists for performing calibration and fuel tests using specified types of calorimeters. Annex E gives examples illustrating some of the calculations.

NOTE   Descriptors: solid fuels, coal, coke, tests, determination, calorific value, rules of calculation, calorimetry.

2   Normative references

The following referenced documents are indispensable for the application of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 651, *Solid-stem calorimeter thermometers*

ISO 652, *Enclosed-scale calorimeter thermometers*

ISO 687, *Solid mineral fuels — Coke — Determination of moisture in the general analysis test sample*

ISO 1770, *Solid-stem general purpose thermometers*

ISO 1771, *Enclosed-scale general purpose thermometers*

ISO 5068-2, *Brown coals and lignites — Determination of moisture content — Part 2: Indirect gravimetric method for moisture in the analysis sample*

ISO 11722, *Solid mineral fuels — Hard coal — Determination of moisture in the general analysis test sample by drying in nitrogen*

ISO 17247, *Coal — Ultimate analysis*

3 Terms, definitions and symbols

3.1 Terms and definitions

For the purposes of this document, the following terms and definitions apply.

3.1.1
gross calorific value at constant volume
absolute value of the specific energy of combustion for unit mass of a solid fuel burned in oxygen in a calorimetric bomb under the conditions specified

NOTE 1   The products of combustion are assumed to consist of gaseous oxygen, nitrogen, carbon dioxide and sulfur dioxide, of liquid water (in equilibrium with its vapour) saturated with carbon dioxide under the conditions of the bomb reaction, and of solid ash, all at the reference temperature.

NOTE 2   Gross calorific value is expressed in units of joules.

3.1.2
gross calorific value at constant pressure
absolute value of the specific energy of combustion, for unit mass of a solid fuel burned in oxygen at constant pressure, instead of constant volume in a calorimetric bomb

NOTE   The hydrogen in the fuel, reacting with gaseous oxygen to give liquid water, causes a decrease in the volume of the system. When the fuel carbon reacts with gaseous oxygen, an equal volume of gaseous carbon dioxide is formed and, hence, no change in volume occurs in combustion of the carbon. The oxygen and nitrogen in the fuel both give rise to an increase in volume.

3.1.3
net calorific value at constant volume
absolute value of the specific energy of combustion, for unit mass of a solid fuel burned in oxygen under conditions of constant volume and such that all the water of the reaction products remains as water vapour (in a hypothetical state at 0,1 MPa), the other products being as for the gross calorific value, all at the reference temperature

3.1.4
net calorific value at constant pressure
absolute value of the specific heat (enthalpy) of combustion, for unit mass of the fuel burned in oxygen at constant pressure under such conditions that all the water of the reaction products remains as water vapour (at 0,1 MPa), the other products being as for the gross calorific value, all at the reference temperature

3.1.5
adiabatic calorimeter
calorimeter that has a rapidly changing jacket temperature

NOTE   The inner calorimeter chamber and the jacket exchange no energy because the water temperature in both is identical during the test. The water in the external jacket is heated or cooled to match the temperature change in the calorimeter proper.

3.1.6
isoperibol calorimeter
⟨isothermal type⟩ calorimeter that has a jacket of uniform and constant temperature

NOTE   These calorimeters have the inner chamber surrounded by a water jacket in which the temperature is maintained at ambient temperature. The outer jacket acts like a thermostat and the thermal conductivity of the interspace between the two chambers is kept as small as possible.

3.1.7
automated calorimeter
colorimeter system without fluid, where the calorimeter can, stirrer and water are replaced by a metal block and the combustion bomb itself constitutes the calorimeter

NOTE   Characteristically, these calorimeters have a small heat capacity, leading to large changes in temperature. Therefore, smaller masses of sample are used. A calorimeter of this kind requires more frequent calibrations.

3.1.8
reference temperature
international reference temperature for thermochemistry, 25 °C

NOTE 1   See 8.7.

NOTE 2   The temperature dependence of the calorific value of coal or coke is small, about 1 J/(g·K).

3.1.9
effective heat capacity of the calorimeter
amount of energy required to cause unit change in temperature of the calorimeter

3.1.10
corrected temperature rise
change in calorimeter temperature caused solely by the processes taking place within the combustion bomb

NOTE   The change in temperature can be expressed in terms of other units: resistance of a platinum or thermistor thermometer, frequency of a quartz crystal resonator, etc., provided that a functional relationship is established between this quantity and a change in temperature. The effective heat capacity of the calorimeter can be expressed in units of energy per such an arbitrary unit. Criteria for the required linearity and closeness in conditions between calibrations and fuel tests are given in 9.3.

3.2   Symbols

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$c_{p,aq}$	specific heat capacity of water
$c_{p,cr}$	specific heat capacity of the crucible
G	specific rate constant
g	drift rate ($dt/d\tau$) in the rating periods
g_f	drift rate in the after-period
g_i	drift rate in the fore-period
M	moisture in the analysis sample
M_T	total moisture content of the fuel for which the calculation is required
m_{ba}	mass of benzoic acid
m_{cr}	mass of crucible
m_1	mass of fuel sample
m_2	mass of combustion aid
P_{st}	power of stirring
Q_{fuse}	contribution from combustion of the fuse
Q_{ign}	contribution from oxidation of the ignition wire
Q_N	contribution from formation of nitric acid (from liquid water and gaseous nitrogen and oxygen)

Q_S correction for taking the sulfur from the aqueous sulfuric acid in the bomb to gaseous sulfur dioxide

$q_{p,gr,d}$ gross calorific value at constant pressure of the dry (moisture-free) fuel

$q_{p,net}$ net calorific value at constant pressure

$q_{p,net,d}$ net calorific value at constant pressure of the dry (moisture-free) fuel

$q_{p,net,m}$ net calorific value at constant pressure of the fuel with moisture content M_T

$q_{V,ba}$ certified gross calorific value at constant volume for benzoic acid

$q_{V,gr}$ gross calorific value at constant volume of the fuel as analysed

$q_{V,gr,d}$ gross calorific value at constant volume of the dry (moisture-free) fuel

$q_{V,gr,m}$ gross calorific value at constant volume of the fuel with moisture content M_T

$q_{V,net,m}$ net calorific value at constant volume of the fuel with moisture content M_T

$q_{V,2}$ gross calorific value at constant volume of a combustion aid

t calorimeter temperature

Δt_{ex} heat-leak correction

t_f final temperature of the main period (equal to the reference temperature)

t_{f+a} temperature, a min after the end of the main period

$t_f - t_i$ observed temperature rise

t_i initial temperature of the main period

t_j thermostat (jacket) temperature

$t_j - t$ thermal head

t_{mf} mean temperature in the after-period

t_{mi} mean temperature in the fore-period

t_x temperature at the time τ_x,

t_∞ asymptotic temperature of an isoperibol calorimeter (at "infinite" time)

$w_{H,d}$ hydrogen, percent mass fraction of the moisture-free fuel (includes the hydrogen from the water of hydration of the mineral matter as well as hydrogen in the coal substance)

$w_{N,d}$ nitrogen, percent mass fraction of the moisture-free fuel

$w_{O,d}$ oxygen, percent mass fraction of the moisture-free fuel

ε effective heat capacity of the calorimeter

$\hat{\varepsilon}$ best estimate (corresponds to "mean" value) of ε from linear regression of ε as a function of the observed temperature rise $(t_f - t_i)$

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ε_*	effective heat capacity of calorimeter on a "total-calorimeter-mass" basis
ε_n	mean effective heat capacity of the calorimeter based on n determinations of ε
ε_O	effective heat capacity of hypothetical calorimeter with no crucible in the bomb
$\varepsilon_{O,n}$	mean effective heat capacity of the calorimeter based on n determinations of ε_O
θ	corrected temperature rise
τ	time
$\Delta\tau$	length of the main period
τ_f	time at the end of the main period
τ_i	time at the beginning of the main period
τ_x	dickinson extrapolation time

4 Principle

4.1 Gross calorific value

A weighed portion of the analysis sample of the solid fuel is burned in high-pressure oxygen in a bomb calorimeter under specified conditions. The effective heat capacity of the calorimeter is determined in calibration tests by combustion of certified benzoic acid under similar conditions, accounted for in the certificate. The corrected temperature rise is established from observations of temperature before, during, and after the combustion reaction takes place. The duration and frequency of the temperature observations depend on the type of calorimeter used. Water is added to the bomb initially to give a saturated vapour phase prior to combustion, thereby allowing all the water formed from the hydrogen and moisture in the sample to be regarded as liquid water.

The gross calorific value is calculated from the corrected temperature rise and the effective heat capacity of the calorimeter, with allowances made for contributions from ignition energy, combustion of the fuse(s) and for thermal effects from side reactions such as the formation of nitric acid. Furthermore, a correction is applied to account for the difference in energy between the aqueous sulfuric acid formed in the bomb reaction and gaseous sulfur dioxide, i.e. the required reaction product of sulfur in the fuel.

4.2 Net calorific value

The net calorific value at constant volume and the net calorific value at constant pressure of the 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 information about the moisture and hydrogen contents of the analysis sample. In principle, the calculation of the net calorific value at constant pressure also requires information about the oxygen and nitrogen contents of the sample.

5 Reagents

5.1 Oxygen, at a pressure high enough to fill the bomb to 3 MPa, pure, with an assay of at least 99,5 % volume fraction, and free from combustible matter.

NOTE   Oxygen made by the electrolytic process may contain up to 4 % volume fraction of hydrogen.

5.2 Fuse

5.2.1 Ignition wire, of nickel-chromium 0,16 mm to 0,20 mm in diameter, platinum 0,05 mm to 0,10 mm in diameter, or another suitable conducting wire with well characterized thermal behaviour during combustion.

5.2.2 Cotton fuse, of white cellulose cotton, or equivalent, if required; see 8.2.1, fourth paragraph.

5.3 Crucible lining material, for use in aiding total combustion of coke, anthracite, high ash coal and other less reactive fuels.

5.3.1 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.

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

5.3.3 Silica fibre, an ash-free, silica-fibre disc.

5.4 Standard volumetric solutions and **indicators**, only for use when analysis of final bomb solutions is required.

5.4.1 Barium hydroxide solution, $c[Ba(OH)_2] = 0,05$ mol/l, prepared by dissolving 18 g of barium hydroxide, $Ba(OH)_2.8H_2O$, in about 1 l of hot water in a large flask.

Stopper the flask and allow the solution to stand for two days or until all the barium carbonate has completely settled out. Decant or siphon off the clear solution through a fine-grained (slow flowrate) filter paper into a storage bottle fitted with a soda-lime guard tube to prevent ingress of carbon dioxide. Standardize the solution against 0,1 mol/l hydrochloric acid solution (5.4.4) using phenolphthalein solution (5.4.6) as an indicator.

5.4.2 Sodium carbonate solution, $c(Na_2CO_3) = 0,05$ mol/l, prepared by dissolving 5,3 g of anhydrous sodium carbonate, Na_2CO_3, dried for 30 min at 260 °C to 270 °C, but not exceeding 270 °C, in water. Transfer the resulting solution quantitatively to a 1 l volumetric flask and make up to volume with water.

5.4.3 Sodium hydroxide solution, $c(NaOH) = 0,1$ mol/l, prepared from a standard concentrated volumetric solution as directed by the manufacturer.

Alternatively, prepare from anhydrous sodium hydroxide by dissolving 4,0 g of sodium hydroxide, NaOH, in water; transfer the resulting solution to a 1 l volumetric flask and make up to volume with water.

Standardize the resulting solution against 0,1 mol/l hydrochloric acid solution (5.4.4) using phenolphthalein solution (5.4.6) as an indicator.

5.4.4 Hydrochloric acid solution, $c(HCl) = 0,1$ mol/l, prepared from a standard concentrated volumetric solution, as directed by the manufacturer.

Alternatively, prepare by diluting 9 ml of hydrochloric acid ($\rho = 1,18$ g/ml) to 1 l with water. Standardize the resulting solution against anhydrous sodium carbonate or against sodium carbonate solution (5.4.2) using a screened indicator solution (5.4.5).

5.4.5 Methyl orange indicator, screened, 1 g/l solution.

Dissolve 0,25 g of methyl orange and 0,15 g of xylene cyanole FF in 50 ml of 95 % volume fraction ethanol and dilute to 250 ml with water.

5.4.6 Phenolphthalein, 10 g/l solution.

Dissolve 2,5 g of phenolphthalein in 250 ml of 95 % volume fraction ethanol or 2,5 g of the water-soluble salt of phenolphthalein in 250 ml of water.

5.5 Benzoic acid, of calorimetric-standard quality, certified by (or with certification unambiguously traceable to) a recognized standardizing authority.

Benzoic acid is the sole substance recommended for calibration of an oxygen-bomb calorimeter. For the purpose of checking the overall reliability of the calorimetric measurements, test substances, e.g. n-dodecane, are used. Test substances are used mainly to prove that certain characteristics of a sample, e.g. burning rate or chemical composition, do not introduce bias in the results. A test substance should have a certified purity and a well-established energy of combustion.

The benzoic acid is burned in the form of pellets. The benzoic acid is normally used without drying or any treatment other than pelletizing; consult the sample certificate. The benzoic acid does not absorb moisture from the atmosphere at a relative humidity below 90 %, but it is recommended that the benzoic acid be stored in a moisture-free environment (desiccator) until use.

The benzoic acid shall be used as close to certification conditions as is feasible; significant departures from these conditions shall be accounted for in accordance with the directions in the certificate. The energy of combustion of the benzoic acid, as defined by the certificate for the conditions utilized, shall be adopted in calculating the effective heat capacity of the calorimeter; see 9.2.

6 Apparatus

6.1 General

The **calorimeter** (see Figure 1), consists of the assembled combustion bomb, the calorimeter can (with or without a lid), the calorimeter stirrer, water, temperature sensor and leads with connectors inside the calorimeter can required for ignition of the sample or as part of temperature measurement or control circuits. During measurements, the calorimeter is enclosed in a thermostat. The manner in which the thermostat temperature is controlled defines the working principle of the instrument and, hence, the strategy for evaluating the corrected temperature rise.

In aneroid systems (systems without a fluid), the calorimeter can, stirrer and water are replaced by a metal block. The combustion bomb itself constitutes the calorimeter in some aneroid systems.

In combustion calorimetric instruments with a high degree of automation, especially in the evaluation of the results, the calorimeter is, in a few cases, not as well defined as the traditional, classical-type calorimeter. Using such an automated calorimeter is, however, within the scope of this International Standard as long as the basic requirements are met with respect to calibration conditions, comparability between calibration and fuel tests, ratio of sample mass to bomb volume, oxygen pressure, bomb liquid, reference temperature of the measurements and accuracy of the results. A printout of some specified parameters from the individual measurements is essential. Details are given in Annex C.

Equipment, adequate for determinations of calorific value in accordance with this International Standard, is specified below.

6.2 Calorimeter with thermostat

6.2.1 Combustion bomb, capable of withstanding safely the pressures developed during combustion; see Figure 1.

The design shall permit complete recovery of all liquid products. The material of construction shall resist corrosion by the acids produced in the combustion of coal and coke. A suitable internal volume of the bomb is from 250 ml to 350 ml.

WARNING — 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. Manufacturers' instructions and any local regulations regarding the safe handling and use of the bomb shall be observed. When more than one bomb of the same design is used, it is imperative to use each bomb as a complete unit. Colour coding is recommended. Swapping of parts can lead to a serious accident.
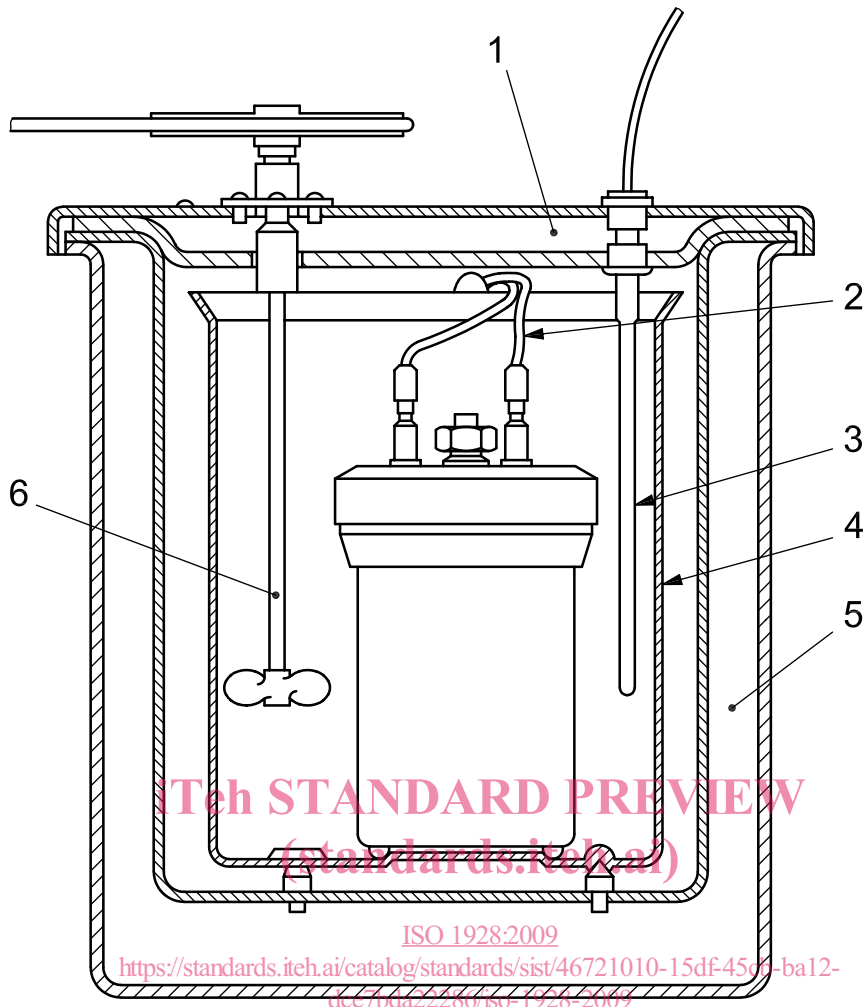
Key

1	thermostat lid	4	calorimeter can
2	ignition leads	5	thermostat
3	thermometer	6	stirrer

Figure 1 — Classical-type combustion-bomb calorimeter with thermostat

6.2.2   Calorimeter can, made of metal, highly polished on the outside and capable of holding an amount of water sufficient to completely cover the flat upper surface of the bomb while the water is being stirred.

A lid generally helps reduce evaporation of calorimeter water but, unless it is in good thermal contact with the can, it lags behind in temperature during combustion, giving rise to undefined heat exchange with the thermostat and a prolonged main period.

6.2.3   Stirrer, working at constant speed.

The stirrer shaft should have a low-heat-conduction and/or a low-mass section below the cover of the surrounding thermostat to minimize transmission of heat to or from the system. This is of particular importance when the stirrer shaft is in direct contact with the stirrer motor. When a lid is used for the calorimeter can, this section of the shaft should be above the lid.

The rate of stirring for a stirred-water-type calorimeter should be large enough to make sure that hot spots do not develop during the rapid part of the change in temperature of the calorimeter. A rate of stirring such that the length of the main period can be limited to 10 min or less is usually adequate; see Annexes A and B.

6.2.4   **Thermostat** (water jacket), completely surrounding the calorimeter, with an air gap of approximately 10 mm separating calorimeter and thermostat.

The mass of water of a thermostat intended for isothermal operation shall be sufficiently large to outbalance thermal disturbances from the outside. The temperature should be controlled to within ± 0,1 K or better throughout the test. A passive constant temperature ("static") thermostat shall have a heat capacity large enough to restrict the change in temperature of its water. Criteria for satisfactory behaviour of this type of water jacket are given in Annex B.

NOTE 1   For an insulated metal static jacket, satisfactory properties are usually ensured by making a wide annular jacket with a capacity for water of at least 12,5 l.

NOTE 2   Calorimeters surrounded by insulating material, creating a thermal barrier, are regarded as static-jacket calorimeters.

When the thermostat (water jacket) is required to follow closely the temperature of the calorimeter, it should be of low mass and preferably have immersion heaters. Energy shall be supplied at a rate sufficient to maintain the temperature of the water in the thermostat to within 0,1 K of that of the calorimeter water after the charge has been fired. When in a steady state at 25 °C, the calculated mean drift in temperature of the calorimeter shall not exceed 0,000 5 K/min; see A.3.2.

6.2.5   **Temperature-measuring instrument**, capable of indicating temperature with a resolution of at least 0,001 K so that temperature intervals of 2 K to 3 K can be determined with a resolution of 0,002 K or better.

The absolute temperature shall be known to the nearest 0,1 K at the reference temperature of the calorimetric measurements. The temperature-measuring device should be linear, or linearized, in its response to changes in temperature over the interval it is used.

As alternatives to the traditional mercury-in-glass thermometers, suitable temperature sensors are platinum-resistance thermometers, thermistors, quartz crystal resonators, etc., which, together with a suitable resistance bridge, null detector, frequency counter, or other electronic equipment, provide the required resolution. The short-term repeatability of this type of device shall be 0,001 K or better. Long-term drift shall not exceed the equivalent of 0,05 K for a period of six months. Sensors with linear response (in terms of temperature) are less likely to drift, causing bias in the calorimetric measurements, than are non-linear sensors.

For adiabatic systems, a suitable arrangement is as follows: Mercury-in-glass thermometers in accordance with ISO 651, ISO 652, ISO 1770 or ISO 1771 satisfy the measurement requirements. A viewer with magnification about 5x is needed for reading the temperature with the resolution required.

Also, a mechanical vibrator to tap the thermometer is suitable for preventing the mercury column from sticking; see 8.4. If this is not available, the thermometer can be tapped manually before reading the temperature.

6.2.6   **Ignition circuit**

The electrical supply shall be 6 V to 25 V alternating current from a step-down transformer or direct current. It is desirable to include a pilot light in the circuit to indicate when current is flowing.

Where the firing is done manually, the firing switch shall be of the spring-loaded, normally open type, located in such a manner that any undue risk to the operator is avoided; see warning in 8.4.

6.3   **Crucible**, of silica, nickel-chromium, platinum or similar unreactive material.

For coal, the crucible 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. The crucible should be lined with an ash-free, silica-fibre disc for coke, anthracite, high-ash coal and other less reactive fuels. A low-mass, 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.