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Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established 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. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

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.

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

This second edition cancels and replaces the first edition (ISO 1928:1976), which has been technically revised.

Annexes A, B and C form an integral part of this International Standard. Annexes D, E, F and G are for information only.

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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 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 may also be used; formulae are given for calculating both values.

General principles and procedures for the calibrations and the fuel experiments 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 experiments using specified types of calorimeters. Annex E gives examples to illustrate some of the calculations.

2 Normative references

The following standards contain provisions which, through reference in this text, constitute provisions of this International Standard. At the time of publication, the editions indicated were valid. All standards are subject to revision, and parties to agreements based on this International Standard are encouraged to investigate the possibility of applying the most recent editions of the standards indicated below. Members of IEC and ISO maintain registers of currently valid International Standards.

ISO 331:1983, *Coal — Determination of moisture in the analysis sample — Direct gravimetric method.*

ISO 651:1975, *Solid-stem calorimeter thermometers.*

ISO 652:1975, *Enclosed-scale calorimeter thermometers.*

ISO 687:1974, *Coke — Determination of moisture in the analysis sample.*

ISO 1170:1977, *Coal and coke — Calculation of analyses to different bases.*

ISO 1770:1981, *Solid-stem general purpose thermometers*.

ISO 1771:1981, *Enclosed-scale general purpose thermometers*.

3 Definitions

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

3.1 gross calorific value at constant volume: The absolute value of the specific energy of combustion, in joules, for unit mass of a solid fuel burned in oxygen in a calorimetric bomb under the conditions specified. 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.

3.2 net calorific value at constant volume: The absolute value of the specific energy of combustion, in joules, for unit mass of the 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.

3.3 net calorific value at constant pressure: The absolute value of the specific heat (enthalpy) of combustion, in joules, 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.

3.4 reference temperature: The international reference temperature for thermochemistry of 25 °C is adopted as the reference temperature for calorific values (see 8.7).

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

3.5 effective heat capacity of the calorimeter: The amount of energy required to cause unit change in temperature of the calorimeter.

3.6 corrected temperature rise: The change in calorimeter temperature caused solely by the processes taking place within the combustion bomb. It is the total observed temperature rise corrected for heat exchange, stirring power, etc. (8.6).

NOTE 2 The change in temperature may 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 may be expressed in units of energy per such an arbitrary unit. Criteria for the required linearity and closeness in conditions between calibrations and fuel experiments are given in 9.3.

A list of the symbols used and their definitions is given in annex F.

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 experiments 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 ther-

mal 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 % (V/V), and free from combustible matter.

NOTE 3 Oxygen made by the electrolytic process may contain up to 4 % (V/V) 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 note 8 to 8.2.1).

5.3 Crucible lining material, for coke only. [ISO 1928:1995](https://standards.iteh.ai/catalog/standards/sist/7182abc8-e40e-4799-b650-)

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.

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

5.4.1 Barium hydroxide solution, $c[\text{Ba}(\text{OH})_2] = 0,05 \text{ mol/l}$.

5.4.2 Sodium carbonate solution, $c(\text{Na}_2\text{CO}_3) = 0,05 \text{ mol/l}$.

5.4.3 Sodium hydroxide solution, $c(\text{NaOH}) = 0,1 \text{ mol/l}$.

5.4.4 Hydrochloric acid solution, $c(\text{HCl}) = 0,1 \text{ mol/l}$.

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

Dissolve 0,25 g of methyl orange and 0,15 g of xylene cyanole FF in 50 ml of 95 % (V/V) 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 % (V/V) ethanol.

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

NOTE 4 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 mainly used 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 shall have a certified purity and a well-established energy of combustion.

The benzoic acid is burned in the form of pellets. It is normally used without drying or any treatment other than pelletizing; consult the sample certificate. It does not absorb moisture from the atmosphere at relative humidities below 90 %.

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** (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 evaluation of 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 experiments, ratio of sample mass to bomb volume, oxygen pressure, bomb liquid, reference temperature of the measurements and repeatability of the results. A print-out 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. 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 would be 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. Swapping of parts may lead to a serious accident.

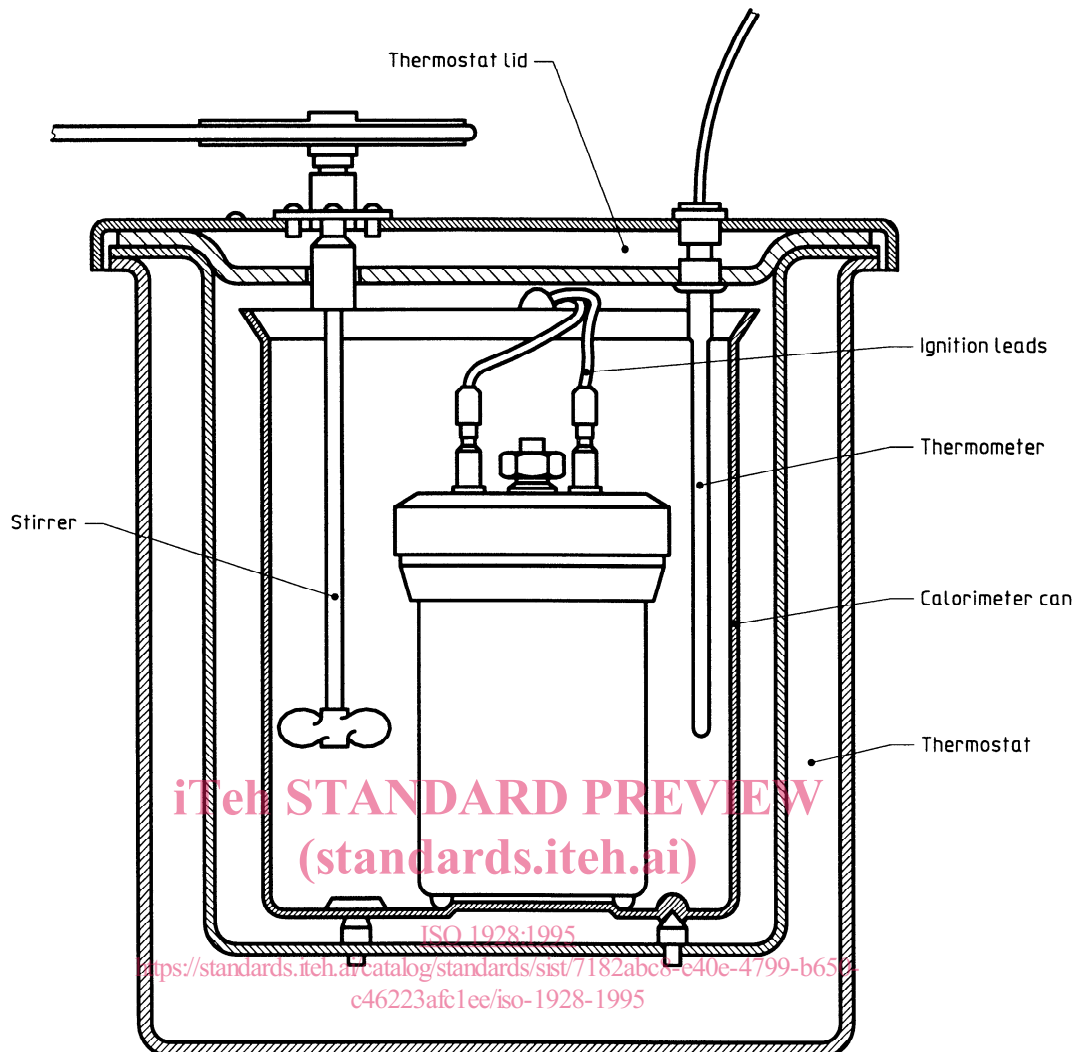


Figure 1 — Classical-type bomb combustion calorimeter with thermostat

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.

NOTE 5 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 $\pm 0,1$ K or better

throughout the experiment. 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.

NOTES

6 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.

7 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. For sensors with linear response (in terms of temperature), drift is less likely to cause bias in the calorimetric measurements than are non-linear sensors.

Mercury-in-glass thermometers which conform to ISO 651, ISO 652, ISO 1770 or ISO 1771 satisfy the requirements. A viewer with magnification about 5x is needed for reading the temperature with the resolution required.

A mechanical vibrator to tap the thermometer is suitable for preventing the mercury column from sticking (8.4). If this is not available, the thermometer shall be tapped manually before reading the temperature.

6.2.6 Ignition circuit

The electrical supply shall be 6 V to 12 V alternating current from a step-down transformer or direct current from batteries. 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. 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.

For coke, the nickel-chromium crucible, as described for use with coal, may be lined with a paste of fused aluminosilicate cement (5.3.1). After drying at 50 °C to 60 °C, the excess cement shall be 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 (5.3.2) 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 low-mass platinum or nickel-chromium crucible, for example 0,25 mm thick, 15 mm in diameter and 7 mm deep, may be used.

6.4 Ancillary pressure equipment

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

6.4.2 Pressure gauge (e.g. 0 MPa to 5 MPa), to indicate the pressure in the bomb with a resolution of 0,05 MPa.

6.4.3 Relief valve or bursting disk, operating at 3,5 MPa, and 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.

6.5 Timer, indicating minutes and seconds.

6.6 Balances

6.6.1 Balance for weighing the sample, fuse, etc., with a resolution of at least 0,1 mg; 0,01 mg is preferable and is recommended when the sample mass is of the order of 0,5 g or less (see 8.2.1).

6.6.2 Balance for weighing the calorimeter water, with a resolution of 0,5 g (unless water can be dispensed into the calorimeter by volume with the required accuracy, see 8.3).

6.7 Thermostat (optional), for equilibrating the calorimeter water before each experiment to a predetermined initial temperature, within about $\pm 0,3$ K.

7 Preparation of test sample

The coal and coke used for the determination of calorific value shall be the analysis sample ground to pass a test sieve with an aperture of 212 μm . In some circumstances, it has been shown that a maximum particle size of 250 μm is acceptable for low and medium rank coals.

The sample shall be well-mixed and in reasonable moisture equilibrium with the laboratory atmosphere. The moisture content shall either be determined on samples weighed within a few hours of the time that samples are weighed for the determination of calorific value, or the sample shall be kept in a small, effectively closed container until moisture analyses are performed, to allow appropriate corrections for moisture in the analysis sample.

Determination of the moisture content of the analysis sample shall be carried out by one of the methods specified in ISO 331 or ISO 687.

8 Calorimetric procedure

8.1 General

The calorimetric determination consists of two separate experiments, combustion of the calibrant (benzoic acid) and combustion of the fuel (coal or coke), both under specified conditions. The calorimetric procedure for the two types of experiment is essentially the same. In fact, the overall similarity is a requirement for proper cancellation of systematic errors caused, for example, by uncontrolled heat leaks not accounted for in the evaluation of the corrected temperature rise θ .

The experiment consists of carrying out quantitatively a combustion reaction (in high-pressure oxygen in the bomb) to defined products of combustion and of measuring the change in temperature caused by the total bomb process.

The temperature measurements required for the evaluation of the corrected temperature rise θ are made during a fore period, a main (= reaction) period, and an after period as outlined in figure 2. For the adiabatic type calorimeter, the fore and after periods need, in principle, be only as long as required to establish the initial (firing) and final temperatures, respectively (see annex A). For the isoperibol (isothermal jacket) and the static-jacket type

calorimeters, the fore and after periods serve to establish the heat exchange properties of the calorimeter required to allow proper correction for heat exchange between calorimeter and thermostat during the main period when combustion takes place. The fore and after periods then have to be longer; see annex B.

The power of stirring shall be maintained constant throughout an experiment which calls for a constant rate of stirring. An excessive rate of stirring results in an undesirable increase in the power of stirring with ensuing difficulties in keeping it constant. A wobbling stirrer is likely to cause significant short-term variations in stirring power.

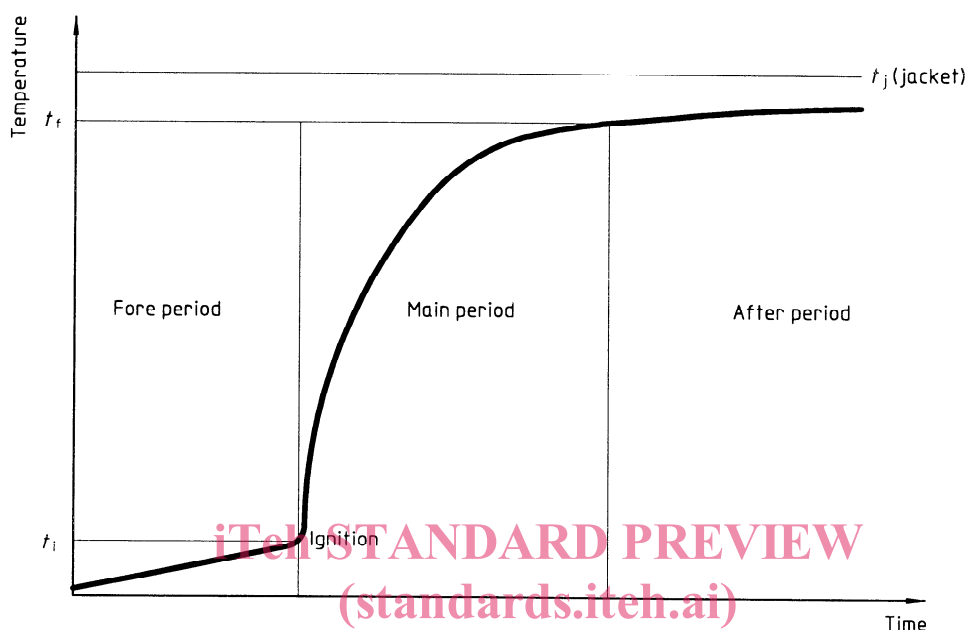


Figure 2 — Time-temperature curve (isoperibol calorimeter)

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During combustion, the bomb head will become appreciably hotter than other parts of the bomb, and it is important to have enough well-stirred water above it to maintain reasonably small temperature gradients in the calorimeter water during the rapid part of the rise in temperature. For aneroid systems, the particular design determines to what extent hot spots may develop (see annex C).

Certain less reactive fuels may persistently leave residues that contain significant amounts of unburned sample or soot. By mixing these samples with known amounts of an auxiliary material, clean combustions can in most instances be achieved. Wrapping samples in tissue or rice paper, in addition to providing a combustion aid, gives an opportunity to affect the configuration of the sample in the crucible at the moment of ignition.

The auxiliary material shall be chemically stable, have a low vapour pressure and a well-established energy of combustion; the energy should be known to within 0,10 % for the particular material used. Benzoic acid appears to be the ideal compound even though for example *n*-dodecane or paraffin oil, being liquids, are easier to distribute evenly. The amount used should be limited to the minimum amount required to achieve complete combustion of the sample. It should not exceed an amount that contributes half the total energy in an experiment. The optimum proportion of sample to auxiliary material depends on the properties of the fuel, and needs to be determined by experiment.

When the auxiliary material is a liquid, it may wet the sample more thoroughly if it is added to the crucible before the fuel sample.

8.2 Preparing the bomb for measurement

8.2.1 General procedure

Weigh the sample, in the crucible, with a resolution of 2 parts in 10^4 , or better. For 1 g samples (see 9.2 and 10.2) this means weighing to the nearest 0,1 mg. Weigh the combustible fuse and/or ignition wire either with a precision comparable with that for weighing the sample, or keep its mass constant, within specified limits, for all experiments (see 9.4 and 9.6.1).

Fasten the ignition wire tautly between the electrodes in the bomb. Check the resistance of the ignition circuit of the bomb; for most bombs it should not exceed 5 Ω to 10 Ω , measured between the outside connectors of the bomb head, or between the connector for the insulated electrode and the bomb head.

Tie, or attach firmly, the fuse to the ignition wire, place the crucible in its support and bring the fuse into contact with the sample. Make sure that the position of the crucible in the assembled bomb will be symmetrical with respect to the surrounding bomb wall.

NOTE 8 When the ignition wire is combustible as well as electrically conducting, an alternative procedure may be adopted. A longer piece of wire, enough to make an open loop, is connected to the electrodes. After mounting of the crucible, the loop is brought close to the sample, for pellets in contact with the sample. (In some cases the ignition process is better controlled when the wire is kept at a small distance above the sample.) Care should be taken to prevent any contact between ignition wire and crucible, in particular when a metal crucible is used since this would result in shorting the ignition circuit. A special fuse is superfluous under these conditions. The resistance of the ignition circuit of the bomb will be increased by a small amount only.

Add the prescribed amount of distilled water to the bomb, for example $(1,0 \pm 0,1)$ ml for 1 g of sample (see 9.2.2). Assemble the bomb and charge it slowly with oxygen to a pressure of $(3,0 \pm 0,2)$ MPa without displacing the original air. If the bomb is inadvertently charged with oxygen above 3,3 MPa, discard the test and begin again.

WARNING — Do not reach over the bomb during charging.

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The bomb is now ready for mounting in the calorimeter can.

8.2.2 Using a combustion aid

Use a low-mass crucible. Weigh the auxiliary material as accurately as possible so that its contribution can be correctly accounted for; this is particularly important when a hydrocarbon oil is used as its specific energy of combustion is considerably higher than that of the fuel.

When the auxiliary material is for instance rice paper or a liquid, it is weighed before the fuel sample. Weigh the benzoic acid last when it is used as the combustion aid. Mix the solid materials without removing any of the mixture (check by weighing). Compact the mixture by tapping the bottom of the crucible against a clean table. A flat, polished rod can be used for additional compression of the mixture.

8.3 Assembling the calorimeter

Bring the calorimeter water to within $\pm 0,3$ K of the selected initial temperature and fill the calorimeter can with the required amount. The quantity of water in the calorimeter can shall be the same to within 0,5 g or better, in all experiments (see 9.6.1). Make sure that the outer surface of the can is dry and clean before the latter is placed in the thermostat. Mount the bomb in the calorimeter can, after the can (containing the correct amount of water) has been placed in the thermostat.

Alternatively, the system may be operated on a constant total-calorimeter-mass basis (see 9.6.2). The bomb is then mounted in the calorimeter can before this is weighed with the water. The total mass of the calorimeter can, with the assembled bomb and the calorimeter water, shall then be within the 0,5 g or better limit in all experiments.

The assembled calorimeter shall contain enough water to **well** cover the flat upper surface of the bomb head and cap.

NOTE 9 Weighing the water to within 0,5 g applies when the effective heat capacity is in the order of 10 kJ/K.

Check the bomb for gas leaks as soon as its top becomes covered with water. If the gas valves are not fully submerged, check for leaks with a drop of water across the exposed opening. Connect the leads for the ignition circuit and mount the thermometer.

WARNING — If gas escapes from the bomb, discard the test, eliminate the cause of leakage and begin again. Apart from being a hazard, leaks will inevitably lead to erroneous results.

Cooling water, temperature controls, stirrers, etc. are turned on and adjusted, as outlined in the instrument manual. Make sure that the calorimeter stirrer works properly. A period of about 5 min is normally required for the assembled calorimeter to reach a steady state in the thermostat or jacket, irrespective of the type of calorimeter. The criteria for when steady state has been attained depend on the working principle of the calorimeter (see annexes A and B).

8.4 Combustion reaction and temperature measurements

Start taking temperature readings, to the nearest 0,001 K or better, as soon as the calorimeter has reached steady-state conditions. Readings at 1 min intervals normally suffice to establish the drift rate of the fore period or check the proper functioning of an adiabatic system. When a mercury-in-glass thermometer is used for the temperature measurements, tap the thermometer lightly for about 10 s before each reading and take care to avoid parallax errors.

At the end of the fore period, when the initial temperature t_i has been established, the combustion is initiated by firing the fuse. Hold the switch closed only for as long as it takes to ignite the fuse. Normally, the current is automatically interrupted as the conducting wire starts burning or partially melts. As long as the resistance of the ignition circuit of the combustion bomb is kept at its normal low value, the electrical energy required to initiate the reaction is so small that there is no need to measure and account for it separately.

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

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Continue taking temperature readings at 1 min intervals. The time corresponding to t_i marks the beginning of the main period. During the first few minutes after the charge has been fired, when the temperature is rising rapidly, readings to the nearest 0,02 K are adequate. Resume reading temperatures to the nearest 0,001 K or better as soon as is practicable, but no later than 5 min after the beginning of the main period. Criteria for the length of the fore, main and after periods, and hence the total number of temperature readings required, are given in annexes A and B.

8.5 Analysis of products of combustion

At the end of the after period, when all the required temperature readings have been completed, remove the bomb from the calorimeter, release the pressure at a moderate rate and dismantle the bomb. Examine the interior of the bomb, the crucible and any solid residue **carefully** for signs of incomplete combustion. **Discard the test if unburned sample or any soot deposit is visible.** Remove and measure any unreacted pieces of combustible ignition wire.

NOTE 10 Another symptom of incomplete combustion is the presence of carbon monoxide in the bomb gas. Slow release of the gas through a suitable detector tube reveals any presence of carbon monoxide and indicates the concentration level. 0,1 ml/l of carbon monoxide in the combustion gas from a 300 ml bomb corresponds to an error of about 10 J.

Wash the contents of the bomb into a beaker with distilled water. Make sure that the underside of the bomb head, the electrodes and the outside of the crucible are also washed.

In the case of calibration experiments, dilute the combined washings to about 50 ml and analyse for nitric acid, e.g. by titration with the sodium hydroxide solution (5.4.3) to a pH of about 5,5 or by using the screened methyl orange solution (5.4.5) as an indicator.

When the "sulfur" and/or nitric acid corrections are based on the actual amounts formed in the bomb process, the bomb washings from fuel combustions are analysed by the procedure described in the next paragraph or by an equivalent method. If the sulfur content of the fuel and the nitric acid correction are known, analysis of the final bomb liquid may be omitted (see 10.1).

Dilute the combined bomb washings to about 100 ml. Boil the washings to expel carbon dioxide and titrate the solution with barium hydroxide solution (5.4.1) while it is still hot using the phenolphthalein solution (5.4.6) as an indicator. Add 20,0 ml of the sodium carbonate solution (5.4.2), filter the warm solution and wash the precipitate with distilled water. When cold, titrate the filtrate with the hydrochloric acid solution (5.4.4), using the screened methyl orange solution (5.4.5) as an indicator, ignoring the phenolphthalein colour change.

8.6 Corrected temperature rise θ

8.6.1 Observed temperature rise

The temperature at the end of the main period t_f gives, together with the initial or firing temperature t_i , the **observed temperature rise** $t_f - t_i$.

8.6.2 Isoperibol and static-jacket calorimeters

In addition to the rise in temperature caused by the processes in the combustion bomb, the observed temperature rise contains contributions from heat exchange between calorimeter and thermostat and from stirring power. Allowance for heat exchange is made by the so-called heat-leak correction Δt_{ex} , which includes the contribution from stirring power.

$$\text{i.e. } t_f - t_i = \theta + \Delta t_{\text{ex}}$$

and hence

$$\theta = (t_f - t_i) - \Delta t_{\text{ex}}$$

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<https://standards.iteh.ai/catalog/standards/sist/7182abc8-e40e-4799-b650-c46223afc1ee/iso-1928-1995>

There are various ways of evaluating the term Δt_{ex} . The most common procedures used are the Regnault-Pfaundler and the Dickinson extrapolation methods.

NOTE 11 The Regnault-Pfaundler method automatically accounts for variations in the time-temperature relationship for different types of samples and is hence the more reliable of the two methods.

Detailed instructions for the numerical evaluation of Δt_{ex} and the corrected temperature rise θ for isoperibol and static-jacket calorimeters are given in annex B. The resulting equations for Δt_{ex} are summarized as follows:

Regnault-Pfaundler method (see B.5.2)

$$\Delta t_{\text{ex}} = (\tau_f - \tau_i) \times g_f + \frac{g_i - g_f}{t_{\text{mf}} - t_{\text{mi}}} \times \left[n \times t_{\text{mf}} - \frac{(t_i + t_f)}{2} - \sum_{k=1}^{k=n-1} t_k \right]$$

where

g_i is the drift rate in the fore (initial rating) period, in kelvins per minute;

g_f is the drift rate in the after (final rating) period, in kelvins per minute;

t_{mi} is the **mean** temperature in the fore period, in degrees Celsius;

t_{mf} is the **mean** temperature in the after period, in degrees Celsius;

t_i ($= t_0$) is the temperature at the beginning of the main period (the time for ignition), in degrees Celsius;

t_f ($= t_n$) is the temperature at the end of the main period, in degrees Celsius;