
**Coal and coke — Determination of
gross calorific value**

Charbon et coke — Détermination du pouvoir calorifique supérieur

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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.

The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2. www.iso.org/directives

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For an explanation on the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the WTO principles in the Technical Barriers to Trade (TBT) see the following URL: [Foreword — Supplementary information](#)

This document was prepared by Technical Committee ISO/TC 27, *Coal and coke*, Subcommittee SC 5, *Methods of analysis*.

This fourth edition cancels and replaces the third edition (ISO 1928:2009), which has been technically revised.

The main changes compared to the previous edition are as follows:

- change the document title within the scope of TC 27,
- editorially update symbols within formulae,
- update references,
- expand on some derivations,
- remove ambiguity around crucible masses, and
- specify the analysis sample.

Any feedback or questions on this document should be directed to the user's national standards body. A complete listing of these bodies can be found at www.iso.org/members.html.

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Coal and coke — Determination of gross calorific value

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

1 Scope

This document 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 combustion vessel 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; formulae are given for calculating both values.

General principles and procedures for the calibrations and the fuel tests are specified 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. [Annex F](#) provides guidance around safe use, maintenance and testing of the calorimeter combustion vessel.

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

2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements 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 13909-4, *Hard coal and coke — Mechanical sampling — Part 4: Coal — Preparation of test samples*

ISO 17247, *Coal and coke — Ultimate analysis*

ISO 18283, *Hard coal and coke — Manual sampling*

3 Terms, definitions and symbols

3.1 Terms and definitions

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

ISO and IEC maintain terminological databases for use in standardization at the following addresses:

- ISO Online browsing platform: available at <https://www.iso.org/obp>
- IEC Electropedia: available at <http://www.electropedia.org/>

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 combustion vessel under the conditions specified

Note 1 to entry: 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 combustion vessel reaction, and of solid ash, all at the reference temperature.

Note 2 to entry: Gross calorific value is expressed in units of joules/gram.

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 combustion vessel

Note 1 to entry: 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* (3.1.8)

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* (3.1.8)

3.1.5

adiabatic calorimeter

calorimeter that has a rapidly changing jacket temperature

Note 1 to entry: 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 1 to entry: 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**aneroid calorimeter**

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

Note 1 to entry: 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 to entry: See [8.7](#).

Note 2 to entry: 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 vessel

Note 1 to entry: 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

$c_{p, \text{aq}}$	specific heat capacity of water at constant pressure
$c_{p, \text{s}}$	specific heat capacity of the sample
$c_p dt$	heat capacity times the temperature change
$c_{p, \text{cr}}$	specific heat capacity of the crucible
ΔC	is the difference in heat capacity ($m_{\text{cr}} \times c_{p, \text{cr}}$) of the crucible used in the calibrations and that used in combustion of the fuel
$\frac{dq}{dT}$	heat flow into the calorimeter
$(dt/d\tau)_i$	the initial drift rate
G	specific rate constant, which is evaluated from the time-temperature measurements of the rating periods, the fore- and the after-period
g	drift rate ($dt/d\tau$) in the rating periods
g_f	final drift rate (drift rate in the after-period)
g_i	initial drift rate (drift rate in the fore-period)
k	is the Newton's law cooling constant

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l_{wire}	length of ignition wire (fuse)
L	is the latent heat of vaporization of water at 25 °C and constant pressure (43 988 J/mol)
L_s	is 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
M	moisture in the analysis sample
m_{aq}	mass of combustion vessel water
M_T	total moisture mass fraction of the fuel for which the calculation is required
m_{ba}	mass of benzoic acid
m_{cr}	mass of crucible
m_s	mass of sample
m_{fuse}	mass of wire (fuse)
m_1	mass of fuel sample burned
m_2	mass of combustion aid
p_0	initial pressure of oxygen
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 combustion vessel to gaseous sulfur dioxide
$q_{p,gr,d}$	gross calorific value at constant pressure of the dry (moisture-free) fuel
$q_{p,net,M}$	net calorific value at constant pressure for air-dried fuel with moisture mass fraction
$q_{p,net,d}$	net calorific value at constant pressure of the dry (moisture-free) fuel
q_{p,net,M_T}	net calorific value at constant pressure of the fuel with moisture mass fraction 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 mass fraction M_T
$q_{V,net}$	net calorific value at constant volume
$q_{V,net,d}$	net calorific value at constant volume of the dry (moisture-free) fuel
$q_{V,net,M}$	net calorific value at constant volume for air-dried fuel with moisture mass fraction

q_{V,net,M_T}	net calorific value at constant volume of the fuel with moisture mass fraction M_T
$q_{V,2}$	gross calorific value at constant volume of a combustion aid
R	the universal gas constant, equal to 8,315 J/mol K
T	the reference temperature for calorific value, i.e. 298,15 K (25 °C)
Δn_g	contraction in volume of the gaseous phase for the combustion reaction, expressed in terms of moles per gram of sample, on an air-dried basis
t	calorimeter temperature
t_1	the correction of 1 applied after the ignition of the sample
Δm_{cr}	heat capacity from the mass of the crucible
Δt_{ex}	heat-leak correction, which is the contribution from the heat exchange
t_f	final temperature of the main period (equal to the reference temperature)
τ_a	time, a minutes after the end of the main period
$t_{f+\tau_a}$	temperature, a minutes after the end of the main period
$t_f - t_i$	observed temperature rise
Δt	observed temperature rise
t_i	initial temperature of the main period (at the time of firing the charge)
t_j	thermostat (jacket) temperature
$t_j - t$	thermal head
t_k	successive temperature readings, taken at 1 min intervals during the main period
t_m	the integrated mean temperature
t_0	is equal to t_i and is the temperature at the beginning of the main period
t_n	is the temperature reading, taken during the main period, at the n th one-minute interval, $t_n (= t_f)$ being the reading taken at the end
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_∞	is the temperature that the calorimeter eventually attains if left running for an extended period of time, which is the asymptotic temperature of an isoperibol calorimeter (at "infinite" time)
t_{ref}	reference temperature
V_1	is the volume of the barium hydroxide solution used
V_2	is the volume, of the hydrochloric acid solution used
V_{aq}	volume of combustion vessel water, may be substituted, as appropriate, for m_{aq}

V_{cv}	Combustion vessel volume
W_1	The work done against the atmosphere when the water is expanded at constant pressure to vapour at 25 °C
W_2	Δn_g multiplied by RT to interpret the volume change in terms of the associated work done by the atmosphere to maintain constant pressure
w_H	hydrogen mass fraction of the sample less the hydrogen contained in the moisture mass fraction
$w_{H,d}$	hydrogen, 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, mass fraction of the moisture-free fuel
$w_{O,d}$	oxygen, mass fraction of the moisture-free fuel
w_V	the volatile-matter mass fraction of the sample with moisture mass fraction, M_T
w_A	the ash mass fraction of the sample with moisture mass fraction, M_T
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 ($t_f - t_i$)
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_0	effective heat capacity of hypothetical calorimeter with no crucible in the combustion vessel
$\varepsilon_{0,n}$	mean effective heat capacity of the calorimeter based on n determinations of ε_0
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 general analysis sample of the solid fuel is burned in high-pressure oxygen in a combustion vessel 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 combustion vessel 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 combustion vessel 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 mass fractions of the analysis sample. In principle, the calculation of the net calorific value at constant pressure also requires information about the oxygen and nitrogen mass fractions of the sample.

5 Reagents

5.1 Oxygen, at a pressure high enough to fill the combustion vessel 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 can 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 $^{\circ}\text{C}$, 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 disk, an ash-free, silica-fibre.

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

5.4.1 Barium hydroxide solution, $c[\text{Ba}(\text{OH})_2] = 0,05 \text{ mol/l}$, prepared by dissolving 18 g of barium hydroxide, $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$, 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, $c(\text{Na}_2\text{CO}_3) = 0,05 \text{ mol/l}$, 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, $c(\text{NaOH}) = 0,1 \text{ mol/l}$, 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, $c(\text{HCl}) = 0,1 \text{ mol/l}$, prepared from a standard concentrated volumetric solution, as directed by the manufacturer.

Alternatively, prepare by diluting 9 ml of hydrochloric acid ($\rho = 1,18 \text{ g/ml}$) 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.

5.4.7 Water, deionised, distilled or water of equivalent purity, with a specific conductivity not higher than 0,2 mS/m at 25 °C.

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

Benzoic acid is the sole substance recommended for calibration of an oxygen-combustion vessel 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 vessel, 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 vessel 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 document as long as the basic requirements are met with respect to calibration conditions, comparability between calibration and fuel tests, ratio of sample mass to combustion vessel volume, oxygen pressure, combustion vessel 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](#).

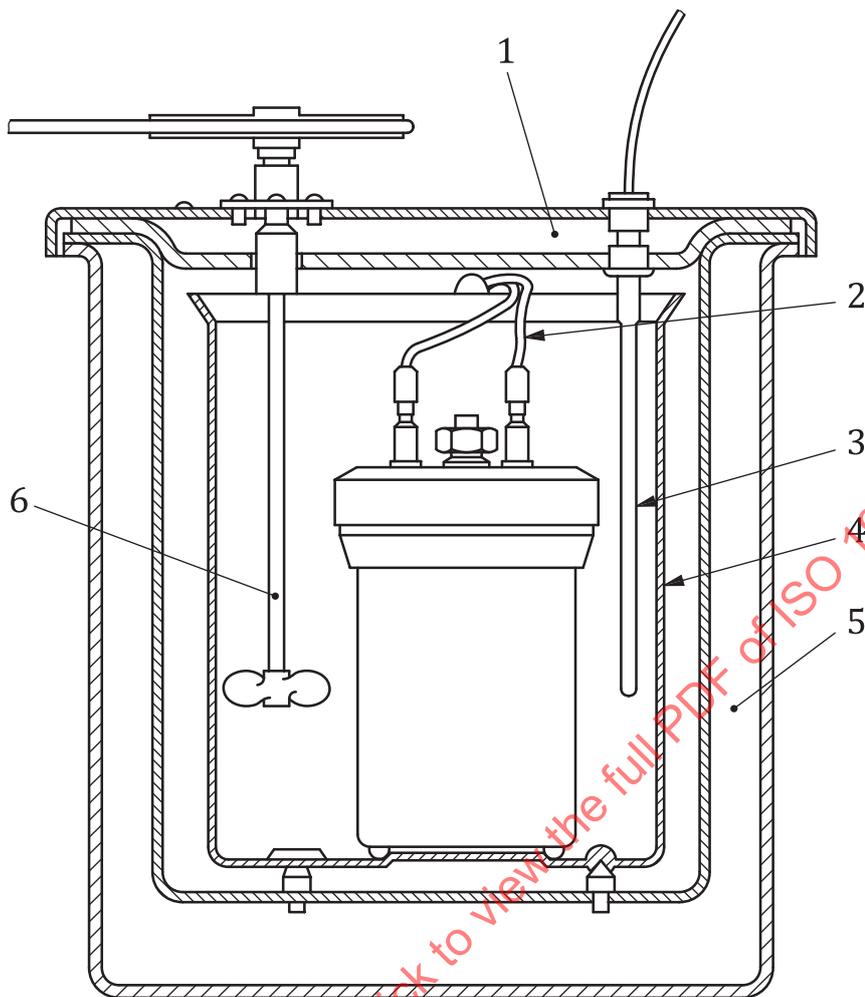
Equipment, adequate for determinations of calorific value in accordance with this document, is specified below.

6.2 Calorimeter with thermostat.

6.2.1 Combustion vessel, 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 combustion vessel is from 250 ml to 350 ml.

WARNING — Combustion vessel 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 combustion vessel shall be observed. When more than one combustion vessel of the same design is used, it is imperative to use each combustion vessel 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-vessel 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 combustion vessel 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 $\pm 0,1$ 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 shall 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, supplied by the instrument manufacturer.

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 disk for coke, anthracite, high-ash coal and other less reactive fuels. A crucible of nickel-chromium foil about 0,25 mm thick is recommended when testing high-ash coals, in order to reduce any error from incomplete combustion.

For coke, the nickel-chromium crucible, as described for use with coal, should be lined with a commercially produced ash-free, silica-fibre disk. The mass of the silica-fibre disk is not included as part of the sample mass. Alternatively, line the crucible 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 other substances with a high moisture mass fraction, such as bio-oils, the ashless silica-fibre disk is placed on top of the sample in the crucible. This helps to absorb the moisture, and easy burning occurs without misfires.

For benzoic acid, either of the crucibles specified for coal is suitable. However, the crucible type used for calibration, should also be used for the test sample, as any significant change in crucible mass will impact on the calibration of the instrument i.e. heat capacity. If smears of unburned carbon occur, a small, 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 combustion vessel with oxygen.

6.4.2 **Pressure gauge** (e.g. 0 MPa to 5 MPa), to indicate the pressure in the combustion vessel 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 combustion vessel.

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**, capable of 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**, capable of 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 test 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 the calorific value shall be the general analysis sample ground to pass a test sieve with an aperture of 212 μm and shall be prepared in accordance with ISO 13909-4 and ISO 18283. 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. Either the moisture mass fraction shall 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 mass fraction of the analysis sample shall be carried out in accordance with one of the methods specified in ISO 687, ISO 11722 or ISO 5068-2.

NOTE Coal samples from organic float-and-sink testing can contain halogen compounds, which can affect the determination of gross calorific value due to the heat of formation of acids. It is necessary to take care to remove as much of the traces of these residues as is practicable before the determination is carried out.

8 Calorimetric procedure

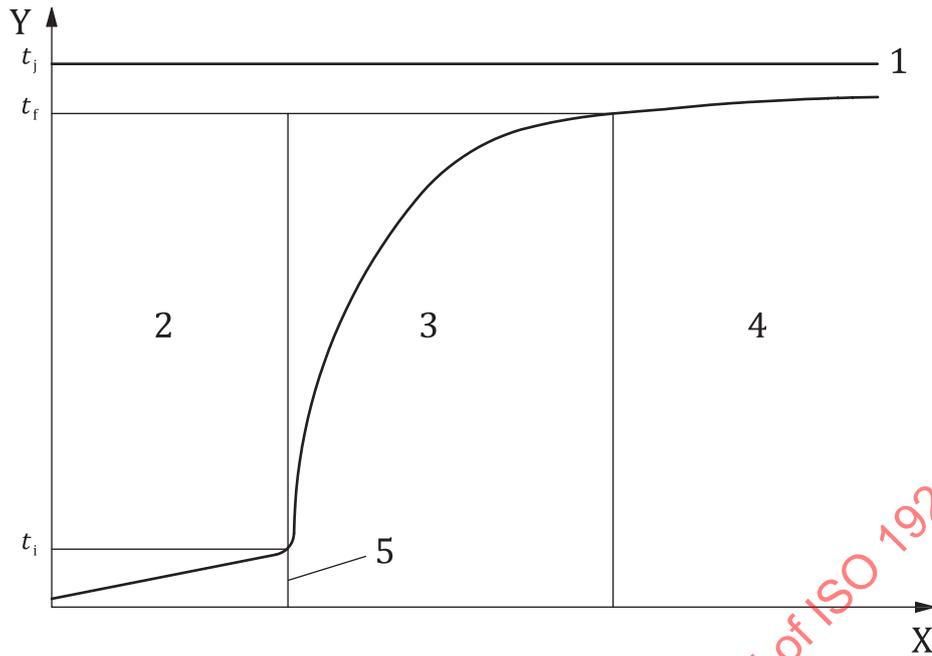
8.1 General

The calorimetric determination consists of two separate tests: 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 tests 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 test consists of carrying out quantitatively a combustion reaction (in high-pressure oxygen in the combustion vessel) to defined products of combustion and of measuring the change in temperature caused by the total combustion process.

The temperature measurements required for the evaluation of the corrected temperature rise, θ , are made during a fore-period, a main (equals the reaction") period and an after-period, as outlined in [Figure 2](#). For the adiabatic-type calorimeter, the fore- and after-periods, in principle, should 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. It is then necessary for the fore- and after-periods to be longer; see [Annex B](#).

The power of stirring shall be maintained constant throughout a test that 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.



Key

- | | | | |
|---|--------------------|-------|--|
| X | time | 4 | after period |
| Y | temperature | 5 | ignition |
| 1 | jacket temperature | t_i | initial temperature of the main period |
| 2 | fore period | t_j | is the jacket temperature |
| 3 | main period | t_f | final temperature of the main period
(equal to the reference temperature) |

Figure 2 — Time-temperature curve — Isoperibol calorimeter

During combustion, the combustion vessel head becomes appreciably hotter than other parts of the combustion vessel, and it is important to have enough well stirred water above it to maintain a reasonably small temperature gradient 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, complete 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 *n*-dodecane or paraffin oil, for example, 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. The amount used should not exceed an amount that contributes half the total energy in a test. The optimum proportion of sample to auxiliary material depends on the properties of the fuel, and it is necessary that it be determined experimentally.

For coals having ash values exceeding approximately 35 %, there is a possibility of incomplete combustion, and a sufficient, known mass of auxiliary material should be added to ensure a temperature rise similar to that obtained in benzoic acid calibrations.

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

8.2 Preparing the combustion vessel for measurement

8.2.1 General procedure

Weigh the sample in the crucible, with an accuracy of 0,01 % of the mass of sample 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 to that for weighing the sample, or keep its mass constant, within specified limits, for all tests; see 9.4 and 9.6.1.

Fasten the ignition wire tautly between the electrodes in the combustion vessel. Check the resistance of the ignition circuit of the combustion vessel; for most combustion vessels, it should not exceed 5 Ω to 10 Ω , measured between the outside connectors of the combustion vessel head, or between the connector for the insulated electrode and the combustion vessel 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 combustion vessel is symmetrical with respect to the surrounding combustion vessel wall.

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 samples in pellet form, the loop shall be 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 combustion vessel will be increased by a small amount only.

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

WARNING — Do not reach over the combustion vessel during charging.

The combustion vessel 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 less than 0,5 g in all tests; 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 combustion vessel in the calorimeter can after the can (containing the correct amount of water) has been placed into the thermostat.

Alternatively, the system may be operated on a constant total-calorimeter-mass basis; see 9.6.2. The combustion vessel is then mounted in the calorimeter can before this is weighed with the water. The total mass of the calorimeter can, with the assembled combustion vessel and the calorimeter water, shall then be at least within 0,5 g in all tests.

The assembled calorimeter shall contain enough water to thoroughly cover the flat, upper surface of the combustion vessel head and cap.

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

Check the combustion vessel 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 combustion vessel, discard the test, eliminate the cause of leakage and begin again. Apart from being a hazard, leaks 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 a 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 vessel is kept at its normal low value, the electrical energy required to initiate the reaction is so small that it is not necessary to measure and account for it separately.

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

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

8.5.1 At the end of the after-period, when all the required temperature readings have been completed, remove the combustion vessel from the calorimeter, release the pressure at a moderate rate and dismantle the combustion vessel. Examine the interior of the combustion vessel, 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 Another symptom of incomplete combustion is the presence of carbon monoxide in the combustion vessel gas. Slow release of the gas through a suitable detector tube reveals any presence of carbon monoxide and indicates the volume concentration level. 0,1 ml/l of carbon monoxide in the combustion gas from a 300 ml combustion vessel corresponds to an error of about 10 J.

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

In the case of calibration tests, 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.

8.5.2 If the sulfur mass fraction of the fuel and the nitric acid correction are known, analysis of the final combustion vessel liquid may be omitted; see 10.1. When the “sulfur” and/or nitric acid corrections are based on the actual amounts formed in the combustion vessel process, the combustion vessel washings from fuel combustions are analysed by the procedure described in 8.5.3 or by an equivalent method.

8.5.3 Dilute the combined combustion vessel 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 water. When the filtrate has cooled to ambient temperature, titrate it 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

8.6.1 Observed temperature rise, $t_f - t_i$

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

8.6.2 Isoperibol and static-jacket calorimeters

8.6.2.1 In addition to the rise in temperature caused by the processes in the combustion vessel, 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, as shown in Formula (1).

$$t_f - t_i = \theta + \Delta t_{\text{ex}} \quad (1)$$

Hence, the corrected temperature rise, θ , is given by rearranging Formula (1) as given in Formula (2):

$$\theta = t_f - t_i - \Delta t_{\text{ex}} \quad (2)$$

There are various ways of evaluating the term Δt_{ex} . The most common procedures used are the Regnault-Pfaundler and the Dickinson extrapolation methods; see 8.6.2.2 and 8.6.2.3, respectively.

NOTE 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 formulae for Δt_{ex} are summarized in Formulae (3) and (4).

8.6.2.2 The Regnault-Pfaundler method (see B.5.2) is based on Formula (3):

$$\Delta t_{\text{ex}} = (\tau_f - \tau_i) \times g_f + \frac{g_i - g_f}{t_{\text{mf}} - t_{\text{mi}}} \times \left[n \times t_{\text{mf}} - \frac{(t_i + t_f)}{2} - \sum_{k=1}^{n-1} t_k \right] \quad (3)$$

where

- g_i is the drift rate, expressed in kelvins per minute, in the fore- (initial rating) period;
- g_f is the drift rate, expressed in kelvins per minute, in the after- (final rating) period;
- t_{mi} is the mean temperature, expressed in degrees Celsius, in the fore-period;
- t_{mf} is the mean temperature, expressed in degrees Celsius, in the after-period;
- t_i is the temperature, expressed in degrees Celsius, at the beginning of the main period (the time for ignition), equivalent to t_0 ;
- t_f is the temperature, expressed in degrees Celsius, at the end of the main period, equivalent to t_n ;
- t_k are the successive temperature readings, expressed in degrees Celsius, taken at 1 min intervals during the main period (t_1 being the temperature 1 min after the beginning of the main period and $t_n = t_f$);
- t_n is the temperature reading, expressed in degrees Celsius, taken during the main period, at the n th one-minute interval, $t_n (= t_f)$ being the reading taken at the end;
- τ_i is the time, expressed in minutes, at the beginning of the main period (time of ignition);
- τ_f is the time, expressed in minutes, at the end of the main period;
- n is the number of 1 min intervals in the main period.

Alternatively, temperature may be expressed in some arbitrary unit throughout; see [9.6.1](#).

8.6.2.3 The Dickinson extrapolation method (see [B.5.3](#)) is based on [Formula \(4\)](#):

$$\Delta t_{ex} = g_i (\tau_x - \tau_i) + g_f (\tau_f - \tau_x) \tag{4}$$

where

- τ_x is the time, expressed in minutes, where the change in temperature, $(t_x - t_i)$, is 0,6 times the observed temperature rise, $(t_f - t_i)$;
- g_i and g_f are the drift rates, expressed in kelvins per minute, at τ_i and τ_f , respectively; they are calculated as for the Regnault-Pfaundler method.

8.6.3 Adiabatic calorimeters

In adiabatic systems, heat exchange is, by definition, negligible. It is, however, common practice to compensate for the stirring power by an offset in temperature in the adiabatic control system; see [Annex A](#). The corrected temperature rise, θ , is given by [Formula \(5\)](#).

$$\theta = (t_f - t_i) \tag{5}$$

Stirring power is otherwise manifested as a constant drift in temperature throughout the test and is easily corrected, but can prolong the total period of temperature observations.

Detailed instructions for the numerical evaluation of the corrected temperature rise, θ , for adiabatic calorimeters are given in [Annex A](#).

8.6.4 Thermometer corrections

When a mercury-in-glass thermometer is used, the corrections specified in the certificate issued with the thermometer shall be applied to the observed initial temperature, t_i , and the final temperature, t_f .

8.7 Reference temperature

The temperature at the end of the main period, the final temperature, t_f , is the reference temperature of the individual test.

9 Calibration

9.1 Principle

Combustion of certified benzoic acid under specified conditions to gaseous carbon dioxide and liquid water serves to make a change in temperature of the calorimeter of one unit interpretable in defined units of energy. The classical type of combustion calorimeter can be maintained unchanged over extended periods of time in terms of mass (heat capacity), geometry and heat exchange surfaces. This allows carrying out the calibration of the instrument as a separate series of measurements, establishing the effective heat capacity, i.e. the calibration constant, ε , of the calorimeter.

This calibration constant, ε , should not change significantly over time, provided minor repairs or other changes in the system are correctly accounted for. Some of the fully automated calorimetric instruments are, however, physically less well defined and, therefore, require more frequent calibrations: for some systems, even daily.

Systematic errors can arise, for example, from evaporation of calorimeter water, from uncontrolled heat exchange along various paths and/or imperfections, and lag in an adiabatic temperature control system during the reaction period. Cancellation of this type of error depends largely on the similarity between the calibration tests and the combustion of the fuel samples with respect to time-temperature profile and total change in temperature of the calorimeter. Systematic variation in the mass of benzoic acid used in the calibration tests is an expedient way of establishing the requirements for "similarity" for a particular calorimetric system; see [9.3](#).

9.2 Calibrant

9.2.1 Certification conditions

The certificate value for the energy of combustion of benzoic acid refers to a process where the mass, expressed in grams, of the sample and the initial water, respectively, is equal to three times the volume of the combustion vessel, expressed in litres (3 g/l), the initial pressure of oxygen is 3,0 MPa and the reference temperature is 25 °C. The products of combustion are defined as gaseous carbon dioxide, liquid water and an equilibrium amount of carbon dioxide dissolved in the aqueous phase. Any nitric acid formed is corrected for by the energy for the process, where the acid is decomposed to form liquid water and gaseous nitrogen and oxygen. When calibrations are performed under different conditions, the certificate reference value shall be adjusted. A numerical expression to correct for such deviations is given in the reference certificate for benzoic acid.

9.2.2 Calibration conditions

The calibration conditions determine the overall calorimetric conditions for the subsequent fuel determinations. For combustion vessels with an internal volume of about 300 ml, 1 g of calibrant and 1 ml of water initially in the combustion vessel are normally used. For combustion vessels with a

volume nearer to 200 ml, 0,6 g of benzoic acid is preferable; the amount of water should then be reduced accordingly.

NOTE 1 The correction terms (per gram of benzoic acid) for deviations from certificate conditions, quoted from a typical benzoic acid certificate, are for an initial pressure of 5 J/MPa, a mass-of-sample-to-combustion vessel volume ratio of 1,1 J/g/l, an initial mass-of-water-to-combustion vessel-volume ratio of 0,8 J/g/l, and a reference temperature for the test of $-1,2$ J/K.

NOTE 2 As long as the initial pressure of oxygen and the reference temperature are kept within $(3,0 \pm 0,3)$ MPa and (25 ± 2) °C, respectively, the departure from certification conditions caused by pressure and/or temperature deviations is within ± 3 J/g and it is not necessary to account for it.

NOTE 3 If larger ratios of water to calibrant, e.g. 5 ml/g, are used, this is usually the most significant deviation from the certification conditions. For a 300 ml combustion vessel, this causes an increase in the certified value of 11 J/g. If 1,0 g of benzoic acid and 5,0 ml of water are used in a 200 ml combustion vessel, the certified value increases by 20 J/g. The change is caused mostly by an increase in the fraction of carbon dioxide dissolved in the combustion vessel liquid.

NOTE 4 When the total heat capacity of the calorimeter is small, for example in aneroid systems, it can be necessary to reduce the sample mass in order to limit the total change in temperature; see [Annex C](#).

9.3 Valid working range of the effective heat capacity

It ought to be possible to vary the amount of calibrant at least ± 25 % without getting a significant trend in the values obtained for the effective heat capacity. If this is not the case, the working limits for a constant value of ϵ shall be defined in terms of total temperature rise measured. All subsequent measurements of calorific value shall be kept within these limits.

A plot of the values of the effective heat capacity, ϵ , as a function of the mass of calibrant used reveals whether there is a significant trend in the effective heat capacity for a particular calorimeter. In this test, the calibrant mass should be varied from 0,7 g to 1,3 g, or an equivalent relative amount, and a minimum of eight tests should be performed. It is not necessary to vary the initial amount of water in the combustion vessel.

A convenient way of checking a system already calibrated by combustion of, for example, 1,0 g samples is to use the benzoic acid as an unknown. The mean values from triplicate runs on 0,7 g and 1,3 g sample masses, respectively, are compared with the certificate values. This normally suffices to ascertain whether the effective heat capacity is constant for the range of heat produced. Deviations are generally expected to be in the direction of "low" calorific values for larger sample masses, equivalent to obtaining ϵ values on the high side when derived from large samples. Using benzoic acid as a test substance is particularly useful in checking the performance of highly automated systems.

The required range for a verified (validated) value of ϵ depends on the total variation in calorific value of the fuels normally analysed. A moderate trend in ϵ , e.g. $\pm 0,3$ % for a ± 30 % variation in the observed temperature rise, may be compensated for by expressing the effective heat capacity, ϵ , as a function of $(t_f - t_i)$ over some defined range. Similarly, if a non-linearized temperature sensor is used, ϵ may be expressed as a (linear) function of $(t_f - t_i)$, provided stringent criteria are also established for how much t_i or t_f is allowed to vary.

Deviation of ϵ from a constant value, as discussed here, is caused by the physical design of the calorimeter and/or shortcomings in the temperature control of the instrument. For a particular set-up, examination of the applicable range of ϵ from a given set of calibration conditions should be carried out when the instrument is new or has been subjected to major repair or moved to a different location, and when the temperature control system has been modified. It is necessary to check some adiabatic systems on a more regular basis; see [Annex A](#). Some automated calorimeters require calibration with a specified variation in sample mass; see [Annex C](#).

9.4 Ancillary contributions

In addition to the energy from the combustion of benzoic acid, there are contributions from the combustion of the fuse(s) and the formation of nitric acid (from "air" nitrogen in the gaseous phase).

The contribution from a fuse is derived from the amount involved and the appropriate energy of combustion. It is necessary to take into account any unreacted fuse wire, i.e. by subtracting it from the initial amount.

The amount of nitric acid formed is determined on the final combustion vessel solution, for example, by acid-base titration; see 8.5.

In most systems, the contribution from the fuse(s) can be kept nearly the same in all tests (fuel and calibration) and can, consequently, be assigned a constant value. For a given combustion vessel configuration, the amount of nitric acid formed in calibration tests is approximately proportional to the amount of benzoic acid burned.

9.5 Calibration procedure

For the ordinary series of calibrations, five satisfactory combustions on benzoic acid shall be carried out. The sample shall be burned as pellets; see 5.5. The calorimetric procedure described in Clause 8 shall be followed. Recommendations concerning the sample mass and the initial amount of combustion vessel water are given in 9.2.2. It is advantageous to use the same crucible type for both benzoic acid combustions and the test sample as required in the item of 6.3. The initial temperature shall be chosen such that the reference temperature of the test (defined as t_f ; see 8.7) is within the chosen range for the reference temperature.

The design of the calibration test, in terms of oxygen pressure, amount of combustion vessel water, reference temperature, duration of the fore-, main, and after-periods, etc., defines the detailed procedure for subsequent fuel combustions.

When the effective heat capacity, ε , of a calorimeter cannot be regarded as constant over the required working range and it is necessary that it be expressed as a function of $(t_f - t_i)$ (see 9.3), the number of calibration tests shall be increased to eight or more. The mass of sample for the individual tests is chosen to yield values for the change in temperature over the entire intended working range, with a few replicate measurements around the end points, to define the slope of the ε versus $(t_f - t_i)$ relationship.

9.6 Calculation of effective heat capacity for the individual test

9.6.1 Constant mass-of-calorimeter-water basis

For systems where the quantity of water in the calorimeter vessel is kept the same in all tests, ε is calculated as shown in Formula (6):

$$\varepsilon = \frac{m_{ba} \times q_{V,ba} + Q_{fuse} + Q_{ign} + Q_N}{\theta} \quad (6)$$

where

m_{ba} is the mass, expressed in grams, of benzoic acid (5.5);

$q_{V,ba}$ is the certified gross calorific value, expressed in joules per gram, at constant volume for the benzoic acid; see 9.2.1;

Q_{fuse} is the contribution, expressed in joules, from combustion of the fuse;

Q_{ign} is the contribution, expressed in joules, from oxidation of the ignition wire;

Q_N is the contribution, expressed in joules, from formation of nitric acid from liquid water and gaseous nitrogen and oxygen (see 9.2.1);

θ is the corrected temperature rise, expressed in kelvins or in an arbitrary unit; see 3.1.10 and 8.6.

NOTE ε is normally expressed in joules per kelvin. When θ is expressed in arbitrary units, ε is, of course, expressed in joules per this arbitrary unit, e.g. joules per ohm.

The contribution from combustion of a cotton fuse is 17 500 J/g and from a nickel-chromium wire 6 000 J/g. Platinum wire melts and resolidifies and gives no net contribution.

When the sum $Q_{\text{fuse}} + Q_{\text{ign}}$ is nearly the same, within a few joules, in all tests, it can be assigned a constant value. It is not generally recommended to incorporate $Q_{\text{fuse}} + Q_{\text{ign}}$ into the value of ε unless it is, in itself, small and the variation in θ is less than $\pm 20\%$.

For the formation of nitric acid from liquid water and gaseous nitrogen and oxygen, the contribution is 60 J/mmol, for example, equivalent to 6,0 J/ml of sodium hydroxide [$c(\text{NaOH}) = 0,1 \text{ mol/l}$] used in titrating the combustion vessel solution; see 8.5.

9.6.2 Constant total-calorimeter-mass basis

When the system is operated such that the calorimeter can with the assembled combustion vessel and the water always has the same total mass, the amount of water in the can varies slightly, depending chiefly on the mass of the crucible used. It is, then, convenient to define ε_0 as the effective heat capacity for the hypothetical calorimeter with no crucible in the combustion vessel, as given by [Formula \(7\)](#):

$$\varepsilon_0 = \varepsilon_* + m_{\text{cr}} \times c_{p,\text{aq}} \quad (7)$$

where

ε_* is the effective heat capacity of calorimeter on a “total-calorimeter-mass” basis and is equal to ε as defined in [9.6.1](#);

m_{cr} is the mass, expressed in grams, of the crucible used in the calibration test (see the Note below);

m_s mass of the sample

$c_{p,\text{aq}}$ is the specific heat capacity, in joules per gram-kelvin, of water when the ε values are expressed in joules per kelvin; at 25 °C, the specific heat capacity of water is equal to 4,18 J/(g K).

When arbitrary “units of temperature” are used, the value of $c_{p,\text{aq}}$ shall be adjusted accordingly. It is necessary to know the relationship between kelvins and the unit utilized only to within $\pm 10\%$ for this purpose.

NOTE In [Formula \(7\)](#), the second term is a simplification of the expression given as [Formula \(8\)](#):

$$\varepsilon_0 = \varepsilon_* + m_{\text{cr}} \times (c_{p,\text{aq}} - c_{p,\text{cr}}) + m_s \times (c_{p,\text{aq}} - c_{p,s}) \quad (8)$$

where

$c_{p,\text{cr}}$ is the specific heat capacity of the crucible, in J/g.

$c_{p,s}$ is the specific heat capacity of the sample, in J/g.

The third term of [Formula \(8\)](#) may be incorporated into ε_0 , without loss in accuracy, as its value does not vary significantly between calibration and fuel tests. [Formula \(8\)](#) then reduces to [Formula \(9\)](#):

$$\varepsilon_0 = \varepsilon_* + m_{\text{cr}} \times (c_{p,\text{aq}} - c_{p,\text{cr}}) \quad (9)$$

In most cases, the second term in [Formula \(9\)](#) may be simplified to $m_{\text{cr}} \times c_{p,\text{aq}}$ as used in [Formula \(7\)](#). However, when a wide variety of crucibles are used, it can be necessary to account for the heat capacity of the crucible. For instance, if a 10 g platinum crucible is used for the calibration tests and a 10 g quartz

crucible is used for the fuel combustions, an error of 6 J/K is introduced if $c_{p, \text{aq}}$ is not taken into account, corresponding to 18 J for a 3 K temperature rise. In this case [Formula \(9\)](#) should be used.

The specific heat capacities for platinum, quartz and steel are 0,133 J/(g K), 0,74 J/(g K) and 0,45 J/(g K),

9.7 Precision of the mean value of the effective heat capacity

9.7.1 Constant value of ε

Calculate the arithmetic mean, ε_n , and the standard deviation from the results of the individual calibration tests of the effective heat capacity, ε (see [9.6.1](#)) or ε_0 (see [9.6.2](#)). The standard deviation, s , shall not exceed 0,20 %. All results from the current series of calibrations shall be included in the calculations; only tests with evidence of incomplete combustion may, and shall, be discarded.

Provided the precision requirement is met, the arithmetic mean, ε_n or $\varepsilon_{0,n}$, is regarded as the value for the effective heat capacity of the calorimeter.

If the precision requirement is not met, the cause for the unsatisfactory results shall be identified and corrected, and a new series of calibration tests shall be performed.

9.7.2 ε as a function of the observed temperature rise

When ε cannot be regarded as constant, list the individual values of ε (see [9.6.1](#)) or ε_0 (see [9.6.2](#)), together with the corresponding values for the observed temperature rise ($t_f - t_i$), for clarity denoted Δt . Fit the results to a straight line by linear regression with Δt as the independent variable. In addition, calculate the coefficients a and b for ε as given in [Formula \(10\)](#):

$$\hat{\varepsilon} = a + b \times \Delta t \quad (10)$$

The estimate of the variance, s^2 , about the line shall be calculated. For convenience, θ may be used instead of Δt .

The standard deviation, s , shall not exceed 0,20 %. Only results from tests with evidence of incomplete combustion may, and shall, be discarded from the calculations.

Provided the precision requirement is met, $\hat{\varepsilon}$, as defined in [Formula \(10\)](#), is regarded as the value for the effective heat capacity of the calorimeter for use in the calculation of the calorific values for the fuels. The valid working range in terms of the observed temperature rise shall be clearly specified.

If the precision requirement is not met, the cause for the unsatisfactory results shall be identified and corrected, and a new series of calibration tests shall be performed.

9.8 Redetermination of the effective heat capacity

When any significant part of the system is changed, the mean effective heat capacity shall be redetermined; see [9.3](#). The mean effective heat capacity shall also be redetermined at intervals of not longer than six months.

It is recommended, especially on a new system, to check the calibration regularly by performing a few monthly tests using benzoic acid as a test substance; see [9.3](#).

Where a change to the system is not involved, the new mean value of ε shall be within 0,25 % of the previous value. If the difference is greater than 0,25 %, the test procedures shall be examined and the cause of the problem identified and dealt with.

10 Gross calorific value

10.1 General

The calorimetric conditions for the fuel combustions shall be consistent with those of the calibration tests; see [9.2.2](#) and [9.5](#). With the calorimetric procedure under satisfactory control, ascertaining complete combustion of the fuel is the most important issue.

Fuels with a low mass fraction of volatiles, e.g. coke, tend to be difficult to burn completely in the combustion vessel and it can be necessary to burn them in poor thermal contact with the crucible support. An alternative strategy, particularly useful with coke, is to mix the fuel sample with a combustion aid, e.g. benzoic acid or a hydrocarbon oil of low volatility. Benzoic acid has the advantage of having a well established value for the energy of combustion; see [8.1](#) and [8.2.2](#).

The variation in the correction for nitric acid is often on the borderline of significance. When the nitrogen mass fraction is determined separately on the sample, the nitric acid correction may be assigned a constant per-gram-of-sample value. A similar strategy shall, then, be adopted for the calibration tests. As nitric acid formation largely depends on the combustion temperature and is enhanced by nitrogen in the sample, the nitric acid correction is normally different for fuel and benzoic acid combustions. The nitric acid correction can also vary significantly for different types of fuels.

When analysis of the combustion vessel washings for sulfuric and nitric acid is required, the procedure described in [8.5](#), or an equivalent one, like ion chromatography, can be used.

10.2 Coal combustions

Duplicate combustions shall be made. A representative sample shall be taken from the analysis sample (see [Clause 7](#)), which is used without further pretreatment. The amount shall be such that the observed temperature rise is within the range of the calibration tests. The calorimetric procedure described in [8.2](#) to [8.6](#) shall be followed, with the same calorimetric conditions as in the calibration test; see [9.2.2](#).

Usually 1 g of coal is the appropriate test portion. For high-ash coals, the use of, for example, 0,75 g of sample and a shallow, (foil) crucible usually facilitates complete combustion. The use of an ash-free, silica-fibre disk to line the crucible ([6.3](#)), or something equivalent, is recommended. If the observed temperature rise falls outside the valid range for ϵ , the calibration shall be confirmed for the extended range; see [9.3](#).

10.3 Coke combustions

The same general conditions as specified for coal (see [10.2](#)) apply for coke. The use of an ash-free, silica-fibre disk to line the crucible ([6.3](#)), or something equivalent, is recommended. The coke sample shall be distributed evenly in the crucible. Certain unreactive cokes can persistently leave residues that contain significant amounts of unburned sample or soot. Optimum conditions for clean combustions may be investigated by varying the amount of sample.

NOTE Lower sample mass and the addition of one or two drops of water to the sample after weighing can lead to the complete combustion of some cokes that are difficult to burn.

An alternative method is to use a combustion aid to promote complete combustion of the sample; see [8.2.2](#). The optimum proportion of combustion aid to coke sample depends on the properties of the particular coke and it is necessary to determine it experimentally.

The nitric-acid correction for coke is usually smaller than that for most coals. When an auxiliary material is used, the correction for nitric acid per test is normally larger than in combustions with coke alone.

10.4 Calculation of gross calorific value

10.4.1 General

The energy change for the total combustion vessel process is given by the effective heat capacity, ε , multiplied by the corrected temperature rise, θ . To derive the energy of combustion of the fuel sample, the energy contributions from all the ancillary reactions shall be subtracted from $\varepsilon \times \theta$; see 9.4. When a combustion aid is used, its contribution is usually the largest ancillary quantity and shall be accurately accounted for.

Moreover, sulfur in the sample quantitatively yields sulfuric acid in the combustion vessel, whereas the required state of sulfur for the calorific value of the fuel is gaseous sulfur dioxide; see 4.1. This is accounted for by a term representing the decomposition, at constant volume, of the aqueous sulfuric acid into gaseous sulfur dioxide and oxygen, plus liquid water.

The derived calorific value for the fuel is the gross calorific value at constant volume.

10.4.2 Constant mass-of-calorimeter-water basis

Calculate the gross calorific value, $q_{V,gr}$, expressed in joules per gram, at a constant volume of the fuel as analysed, from the individual test by substituting into [Formula \(11\)](#):

$$q_{V,gr} = \frac{\varepsilon_n \times \theta - Q_{fuse} - Q_{ign} - Q_N - m_2 \times q_{V,2} - Q_S}{m_1} \quad (11)$$

where

$q_{V,gr}$ is the gross calorific value;

ε_n is the mean value of the effective heat capacity based on n determination of ε , expressed in joules per kelvin, or, alternatively, in joules per some arbitrary unit (see 9.6.1, Note), of the calorimeter as determined in the calibrations; see 9.6.1;

Q_S is the correction, expressed in joules, for taking the sulfur from the aqueous sulfuric acid in the combustion vessel to gaseous sulfur dioxide;

m_1 is the mass, expressed in grams, of the fuel sample;

m_2 is the mass, expressed in grams, of the combustion aid, if relevant;

$q_{V,2}$ is the gross calorific value, expressed in joules per gram, at a constant volume of the combustion aid, if relevant;

θ , Q_{fuse} , Q_{ign} , and Q_N are defined in 9.6.1.

When no buoyancy correction is applied to m_2 , care shall be taken to ensure that $q_{V,2}$ is valid for “per gram weighed in air”.

The energy quantities required to calculate the contributions from fuse, ignition wire and the formation of nitric acid are given in 9.6.1. Specific heat capacities for water and some common crucible materials are given in 9.6.2.

To account for the reaction where sulfuric acid decomposes into liquid water plus gaseous sulfur dioxide and oxygen, the correction is 302 J/mmol, equivalent to 9,41 J/mg of sulfur, which in turn corresponds to a Q_S/m_1 value of 94,1 J/g of sample for 1 % of sulfur in the analysis sample.

When the analytical procedure described in 8.5 is used, the contributions from sulfuric and nitric acids are given by [Formulae \(12\)](#) and [\(13\)](#), respectively:

$$Q_S = 15,1 \times (V_1 + V_2 - 20,0) \quad (12)$$

$$Q_N = 6,0 \times (20,0 - V_2) \quad (13)$$

where

- V_1 is the volume, expressed in millilitres, of the barium hydroxide solution used [\(5.4.1\)](#);
- V_2 is the volume, expressed in millilitres, of the hydrochloric acid solution used [\(5.4.4\)](#);
- 15,1 is the equivalent energy of 0,1 N sulfuric acid (formed from gaseous sulfur dioxide in the combustion) that reacts with the barium hydroxide and hydrochloric acid titrants and the excess sodium carbonate, used in 8.5, expressed in Joules per millilitre;
- 20,0 is the volume of excess sodium carbonate used in 8.5, expressed in millilitres;
- 6,0 is the equivalent energy of 0,1 M nitric acid (formed from gaseous nitrogen oxides in the combustion) that reacts with the hydrochloric acid titrant and the excess sodium carbonate, used in 8.5, expressed in Joules per millilitre.

The certification-condition value may be used for benzoic acid utilized as a combustion aid, provided 1 ml of water is used initially in the combustion vessel. For larger amounts of water, it is recommended to adjust the per-gram value in accordance with the amount-of-water term in the certificate.

The mean value of duplicate determinations is regarded as the gross calorific value for the analysis sample of the fuel.

10.4.3 Constant total-calorimeter-mass basis

In this case, the mean value of the effective heat capacity, $\varepsilon_{0,n}$ is the one derived from the individual ε_0 results (see [9.6.2](#)) and represents the calorimeter without a crucible. The value of ε_* valid for the actual fuel test is given by [Formula \(14\)](#):

$$\varepsilon_* = \varepsilon_{0,n} - m_{cr} \times C_{p,aq} \quad (14)$$

where

- $\varepsilon_{0,n}$ is the mean effective heat capacity of the calorimeter based on n determinations of ε_0 ;
- the other symbols are defined in [9.6.2](#).

NOTE If the heat capacity of the crucible has been taken into account (see [9.6.2](#), Note) in computing ε_0 , ($c_{p,aq} - c_{p,cr}$) values shall be substituted for $c_{p,aq}$ in the calculations of ε_* .

ε_* replaces ε_n in [Formula \(11\)](#) for the calculation of the gross calorific value at constant volume for the fuel sample from an individual test. The mean value of duplicate determinations is regarded as the resulting value for the analysis sample of the fuel.

10.4.4 ε as a function of the observed temperature rise

When it is required that the effective heat capacity of the calorimeter is expressed as a function of the observed temperature rise (see [9.3](#) and [9.7.2](#)), ε_n in [Formula \(11\)](#) and $\varepsilon_{0,n}$ in [Formula \(14\)](#), respectively, shall be replaced by [Formula \(10\)](#) and θ may be used instead of Δt ; see [9.7.2](#).

The mean value of duplicate determinations is regarded as the resulting value for the analysis sample of the fuel.

10.5 Expression of results

As the moisture mass fraction of the actual analysis sample is of interest merely in connection with the calculation to other bases, it is recommended to calculate a value for the gross calorific value, $q_{V,gr,d}$, expressed in joules per gram, at constant volume for the dry (moisture-free) fuel, using [Formula \(15\)](#):

$$q_{V,gr,d} = q_{V,gr} \times \frac{100}{100 - M} \quad (15)$$

where

M is the moisture mass fraction in the analysis sample, expressed as a percent;

$q_{V,gr}$ is defined in [10.4.2](#);

100 is the conversion factor from dimensionless mass fraction to percent, in %.

The gross calorific value at constant volume, $q_{V,gr,m}$, of the fuel with moisture, M_T , required for any particular moisture basis is derived from [Formula \(16\)](#):

$$q_{V,gr,m} = q_{V,gr,d} \times (1 - 0,01 M_T) \quad (16)$$

where M_T is the total moisture mass fraction, expressed as a percent, for which the calorific value is required, normally for the fuel as sampled or as fired, and

$$(1 - 0,01 M_T) = \frac{100 - M_T}{100} \quad (17)$$

where

1 is a dimensionless fraction equivalent to 100 %;

0,01 is a conversion factor from percent to a dimensionless fraction, in %⁻¹.

The result shall be reported to the nearest multiple of 10 J/g with unambiguous statements concerning the reporting basis (states), i.e. constant volume, gross (liquid water) and moisture basis (e.g. dry or "as sampled").

NOTE 1 To convert $q_{V,gr,m}$ from joules per gram to calories per gram, the joules per gram value is divided by the factor 4,186 8 J/cal, with the result being reported to the nearest multiple of 1 cal/g.

NOTE 2 To convert $q_{V,gr,m}$ from joules per gram to British thermal units per pound, the joules per gram value is divided by the factor 2,326 J lb/(g Btu), with the result being reported to the nearest multiple of 10 Btu/lb.

10.6 Calculation to other bases

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

All calculations of calorific value to other bases shall be done in joules per gram, observing the correct reporting standard to the nearest multiple of 10 J/g, before converting to calories per gram or British thermal units per pound. Conversion factors and reporting standards in accordance with [10.5](#) apply.

11 Precision

11.1 Repeatability limit

The results of duplicate determinations, carried out in the same laboratory by the same operator with the same apparatus within a short interval of time on the same analysis sample, shall not differ by more than 120 J/g.

11.2 Reproducibility limit

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, shall not differ by more than 300 J/g.

12 Calculation of net calorific value

12.1 General

The main difference between the gross and net calorific values is related to the physical state of water in the reaction products (compare 3.1.1 and 3.1.3). The calorific value of the fuel most commonly used for practical purposes is the net calorific value at constant pressure for the fuel with some specified moisture mass fraction. This value may be derived from the gross calorific value at constant volume for the dry sample, provided that the total hydrogen mass fraction of the moisture-free sample can be determined experimentally or, for the particular fuel, reliably estimated. In addition, the oxygen and nitrogen mass fractions of the moisture-free sample “add” to the gaseous phase of the product system and should, in principle, be taken into account. For this purpose, the nitrogen may be included in the term for oxygen.

NOTE The net calorific value at constant volume (3.1.3) for the fuel at some specified moisture level is as easily calculated, once a measure of the hydrogen mass fraction is available. In this case, the oxygen and nitrogen mass fraction is of no consequence.

12.2 Calculations

12.2.1 Calculation of net calorific value at constant pressure

12.2.1.1 General

Net calorific value at constant pressure, reflecting actual combustion conditions, is the preferred basis for reporting net calorific value.

The net calorific value, q_{p,net,M_T} expressed in joules per gram, at constant pressure of the fuel with moisture M_T may be calculated as given in [Formula \(18\)](#), which takes account of any required change in moisture level:

$$q_{p,net,M_T} = \left\{ q_{V,gr,d} - 212,2w_{H,d} - 0,8[w_{O,d} + w_{N,d}] \right\} \times (1 - 0,01M_T) - 24,43M_T \quad (18)$$

where

- $q_{V,gr,d}$ is the gross calorific value at constant volume, expressed in joules per gram, of the moisture-free fuel; see 10.5;
- $w_{H,d}$ is the hydrogen mass fraction of the moisture-free fuel including the hydrogen from the water of hydration of the mineral matter as well as the hydrogen in the coal substance, in percent;
- $w_{O,d}$ is the oxygen mass fraction of the moisture-free fuel, in percent;
- $w_{N,d}$ is the nitrogen mass fraction of the moisture-free fuel, in percent;
- M_T is the total moisture mass fraction of the fuel for which the calculation is required, in percent. On the dry basis, $M_T = 0$; on the air-dried basis, $M_T = M$ (see 10.5); on the as-sampled or as-fired basis, M_T is the total moisture.

The three factors 212,2, 0,8, and 24,43 can be derived from the atomic mass of the relevant elements, the universal gas constant, the standard thermochemical reference temperature and the constant pressure heat of vaporization of water at 25 °C. See E.2 for details.

Hydrogen and nitrogen are determined as given in ISO 29541 or other suitable methods. Oxygen shall not be determined directly but as “oxygen by difference” in accordance with ISO 17247.

Nitrogen may also be calculated together with oxygen using ISO 17247, i.e. $[w_{O,d} + w_{N,d}]$ calculated by subtracting from 100 the mass fractions of ash, carbon, hydrogen and sulfur, in percent.

12.2.1.2 Example calculations

The calculations are carried out with the following values:

M_T	total moisture	8,9 %	as-received basis;
M	moisture in the analysis sample	2,5 %	air-dried basis;
$q_{V,gr,d}$	gross calorific value, at constant volume	27 233 J/g	dry basis;
$w_{H,d}$	hydrogen	4,19 %	dry basis;
$w_{O,d}$	oxygen	6,81 %	dry basis;
$w_{N,d}$	nitrogen	1,45 %	dry basis.

The net calorific value at constant pressure can be determined as follows:

a) on a dry basis:

$$\begin{aligned}
 q_{p,net,dry} &= [27\,233 - (212,2 \times 4,19) - 0,8(6,81 + 1,45)] \times [1 - (0,01 \times 0) - (24,43 \times 0)] \\
 &= [27\,233 - 889,118 - (0,8 \times 8,26)] \times 1 - 0 \\
 &= (27\,233 - 889,118 - 6,608) \times 1 \\
 &= 26\,337,274 \text{ J/g} && \text{report as } 26\,340 \text{ J/g} \\
 &= 26\,337,27 / 4,1868 = 6\,290,55 \text{ cal/g} && \text{report as } 6\,291 \text{ cal/g} \\
 &= 26\,337,27 / 2,326 = 11\,322,99 \text{ Btu/lb} && \text{report as } 11\,320 \text{ Btu/lb}
 \end{aligned}$$

b) on an as-received basis:

$$\begin{aligned}
 q_{p,net,M_T} &= [27\,233 - (212,2 \times 4,19) - 0,8(6,81 + 1,45)] \times [1 - (0,01 \times 8,9) - (24,43 \times 8,9)] \\
 &= [27\,233 - 889,118 - (0,8 \times 8,26)] \times (1 - 0,089) - (217,427) \\
 &= (27\,233 - 889,118 - 6,608) \times 0,911 - 217,427 \\
 &= 26\,337,274 \times 0,911 - 217,427 \\
 &= 23\,993,257 - 217,427 \\
 &= 23\,775,83 \text{ J/g} && \text{report as 23 780 J/g} \\
 &= 23\,775,83 / 4,1868 = 5\,678,76 \text{ cal/g} && \text{report as 5 679 cal/g} \\
 &= 23\,775,83 / 2,326 = 10\,221,77 \text{ Btu/lb} && \text{report as 10 220 Btu/lb}
 \end{aligned}$$

c) on an air-dried basis:

$$\begin{aligned}
 q_{p,net,M} &= [27\,233 - (212,2 \times 4,19) - 0,8(6,81 + 1,45)] \times [1 - (0,01 \times 2,5) - (24,43 \times 2,5)] \\
 &= [27\,233 - 889,118 - (0,8 \times 8,26)] \times (1 - 0,025) - (61,075) \\
 &= (27\,233 - 889,118 - 6,608) \times 0,975 - 61,075 \\
 &= 26\,337,274 \times 0,975 - 61,075 \\
 &= 25\,678,842 - 61,075 \\
 &= 25\,617,767 \text{ J/g} && \text{report as 25 620 J/g} \\
 &= 25\,617,767 / 4,1868 = 6\,118,70 \text{ cal/g} && \text{report as 6 119 cal/g} \\
 &= 25\,617,767 / 2,326 = 11\,013,66 \text{ Btu/lb} && \text{report as 11 010 Btu/lb}
 \end{aligned}$$

12.2.2 Calculation of net calorific value at constant volume

12.2.2.1 General

The net calorific value, q_{V,net,M_T} , expressed in joules per gram, at constant volume of the fuel with a moisture mass fraction of M_T , may be calculated as given in [Formula \(19\)](#):

$$q_{V,net,M_T} = [q_{V,gr,d} - 206w_{H,d}] \times (1 - 0,01 M_T) - 23,05 M_T \tag{19}$$

The symbols are defined in [12.2.1.1](#).

The two factors 206 and 23,05 can be derived from the atomic mass of the relevant elements, the universal gas constant, the standard thermochemical reference temperature and the constant pressure heat of vaporization of water at 25 °C. See [E.1.1](#) for details.

12.2.2.2 Example calculations

The calculations are carried out with the following values:

M_T	total moisture	8,9 %	as-received basis;
M	moisture in the analysis sample	2,5 %	air-dried basis;
$q_{V,gr,d}$	gross calorific value, at constant volume	27 233 J/g	dry basis;
$w_{H,d}$	hydrogen	4,19 %	dry basis.

Oxygen and nitrogen are not required in the calculation of net calorific value at constant volume.

The net calorific value at constant volume can be determined as follows:

a) on a dry basis:

$$\begin{aligned}
 q_{V,\text{net},d} &= [27\,233 - (206 \times 4,19)] \times [1 - (0,01 \times 0)] - (23,05 \times 0) \\
 &= (27\,233 - 863,14) \times 1 - 0 \\
 &= 26\,369,86 \text{ J/g} && \text{report as } 26\,370 \text{ J/g} \\
 &= 26\,369,86 / 4,1868 = 6\,298,33 \text{ cal/g} && \text{report as } 6\,298 \text{ cal/g} \\
 &= 26\,369,86 / 2,326 = 11\,337,00 \text{ Btu/lb} && \text{report as } 11\,340 \text{ Btu/lb}
 \end{aligned}$$

b) on an as-received basis:

$$\begin{aligned}
 q_{V,\text{net},M_T} &= [27\,233 - (206 \times 4,19)] \times [1 - (0,01 \times 8,9)] - (23,05 \times 8,9) \\
 &= (27\,233 - 863,14) \times (1 - 0,089) - 205,145 \\
 &= 26\,369,86 \times 0,911 - 205,145 \\
 &= 24\,022,942 - 205,145 \\
 &= 23\,817,797 \text{ J/g} \\
 &= 23\,817,80 \text{ J/g} && \text{report as } 23\,820 \text{ J/g} \\
 &= 23\,817,80 / 4,1868 = 5\,688,78 \text{ cal/g} && \text{report as } 5\,689 \text{ cal/g} \\
 &= 23\,817,80 / 2,326 = 10\,239,81 \text{ Btu/lb} && \text{report as } 10\,240 \text{ Btu/lb}
 \end{aligned}$$

c) on an air-dried basis:

$$\begin{aligned}
 q_{V,\text{net},M} &= [27\,233 - (206 \times 4,19)] \times [1 - (0,01 \times 2,5)] - (23,05 \times 2,5) \\
 &= (27\,233 - 863,14) \times (1 - 0,025) - 57,625 \\
 &= 26\,369,86 \times 0,975 - 57,625 \\
 &= 25\,710,614 - 57,625 \\
 &= 25\,652,989 \text{ J/g} && \text{report as } 25\,650 \text{ J/g} \\
 &= 25\,652,99 / 4,1868 = 6\,127,11 \text{ cal/g} && \text{report as } 6\,127 \text{ cal/g} \\
 &= 25\,652,99 / 2,326 = 11\,028,80 \text{ Btu/lb} && \text{report as } 11\,230 \text{ Btu/lb}
 \end{aligned}$$

13 Test report

The test report shall include the following information:

- identification of the sample tested;
- a reference to this document, i.e. ISO 1928:2020;
- results with reference to the reporting basis [state(s)] valid for the calorific value(s).

Annex A (informative)

Adiabatic calorimeters

A.1 Principle

In a truly adiabatic calorimeter, there is no heat exchange between the calorimeter and its surrounding thermostat (water jacket). Heat exchange takes place via common boundaries, the driving force being a net difference in temperature. Ideally, therefore, the whole of the outside surface of the calorimeter can, including the lid, should have a uniform temperature, which, during a test, is always matched by the uniform temperature of the inner wall of the thermostat well and lid that are facing the calorimeter. Without any difference in temperature, i.e. with zero thermal head, there is no net flow of heat between calorimeter and thermostat. However, there is still a slow rise in calorimeter temperature caused, mainly, by the stirring power, with additional positive or negative contributions from thermometer probe self-heating and from conduction of heat along the stirrer shaft, ignition leads, thermometers, etc. For convenience, “adiabatic” calorimeters are often operated with a small negative thermal head to balance, i.e. offset, this upward drift in temperature.

A.2 Sources of error for the real calorimeter

Truly adiabatic conditions are difficult to achieve in practice, in particular during the rapid part of the rise in calorimeter temperature upon ignition of the sample. The design of the thermostat and the way it is operated determine how effectively it responds to the change in calorimeter temperature and, hence, also the extent of uncontrolled heat exchange.

When the calorimeter itself has no lid, its upper heat exchange properties are largely determined by the surface of the calorimeter water together with the surface of, for example, combustion vessel parts extending above the water. With such an “open”, calorimeter, there is always some uncontrolled evaporation of calorimeter water during the main period, accompanied by a corresponding “heat loss”. The magnitude of this error is mainly a function of how much the thermostat lid lags behind in temperature during the main period.

Unless special precautions have been taken in its design and mounting, a calorimeter lid is usually in poor thermal contact with the calorimeter itself. The calorimeter lid, then, lags behind in temperature and may, for instance, be responsible for uncontrolled heat leakage from the thermostat. The calorimeter lid may also prolong the time required for the calorimeter to reach thermal equilibrium or steady-state. On the other hand, a lid prevents a net heat loss from evaporation of calorimeter water since this condenses on the inside of the lid, restoring the evaporation energy to the calorimeter. In fact, the condensing water assists the thermal equilibration of the lid with the rest of the calorimeter.

To minimize heat exchange caused by temporary temperature differences that cannot be prevented entirely, it is important to keep the outside surface of the calorimeter, and the “inside” of the thermostat, clean (polished) and dry. Generally, errors and insufficiencies that differ or vary between calibration and fuel tests are the ones that, in the end, affect the accuracy of the final results.

A.3 Adiabatic conditions

A.3.1 Thermostat

When the thermostat is heated by passing an electrical current directly through the thermostat water, care shall be taken to keep the salt concentration (usually Na_2CO_3) at the specified level in order to maintain the heating power about the same in all tests. A diminishing salt concentration can

significantly hamper the heating rate, eventually leading to difficulties in achieving adiabatic conditions during the combustion of the sample.

Inadequate adiabatic control during the first half of the main period is easily overlooked. Irrespective of the mode of heating the thermostat, checks should be made at regular intervals (weekly) to ascertain, for example, that the time it takes for the thermostat to catch up with the rapidly rising calorimeter temperature during combustion does not gradually increase.

A.3.2 Adiabatic control

The controls for achieving adiabatic conditions shall be adjusted as specified in the instrument manual. In particular, select that setting of the bridge circuit that results in zero or minimum drift in calorimeter temperature at the final temperature of the tests; see [A.5](#).

NOTE Non-linear sensors are often used in the temperature control circuits. Unless the two sensors are perfectly matched, it is not possible to obtain zero drift in temperature over the whole of the selected working range. Neither is it, then, possible to achieve zero thermal head over the whole range with one bridge setting. Imperfectly matched sensors also put restrictions on the acceptable variation in the final temperature of the tests.

In a well behaved calorimeter, the adiabatic control settings usually require little or no short-term adjustment. This behaviour shall, however, be verified by regularly checking the drift rate at the final temperature, for example by following the temperature over a 5 min to 10 min period in excess of the normal duration of the test. A drift rate of 0,001 K/min or more at the final temperature shall be eliminated by adjustment of the control settings, or corrected for; see [6.2.4](#) and [A.5](#).

A.4 Initial steady state and length of the main period

The equilibration period serves to let the various components of the assembled calorimeter reach a uniform temperature. Simultaneously, the adiabatic controls work to bring the thermostat to its working temperature close to that of the calorimeter. Let a few minutes pass after the controls have indicated that the temperature of the thermostat and of the calorimeter are about the same before taking readings of the calorimeter temperature at 1 min intervals.

When three consecutive readings yield the same value, within 0,001 K or better, or when they all change by the same (limited) amount (constant drift rate), the charge may be fired.

NOTE The expected duration of the combined equilibration and fore-period for most adiabatic systems is on the order of 8 min to 10 min. However, subjecting any part of the calorimeter to substantially deviating temperatures in between tests can significantly prolong the time for thermal equilibration of the calorimeter.

Depending on the type of sample, the combustion in the combustion vessel takes from about 10 s to 25 s. The time required for the total amount of heat released to become uniformly distributed, i.e. for all parts of the calorimeter to attain a uniform temperature, is primarily a function of stirring pattern and stirrer efficiency. The main period shall cover this temperature equalization time but there is no merit in making it longer than necessary.

The length of the main period is determined in a series of calibration tests where readings of temperature are taken at 1 min intervals from the time of firing the charge in each test. From these observations, note the length of time, expressed in minutes, between the time of firing and the second of three consecutive readings that do not differ by more than 0,001 K. The largest of these specific times from five calibration tests defines the length of the main period. This time shall not exceed 10 min, nor shall the time periods evaluated from the individual tests differ by more than 2 min.

When normal operation involves a slight drift of the final temperature of the test, the requirement of "constant temperature" changes to one of constant drift rate to within 0,001 K/min for three consecutive 1 min intervals.

A.5 Correction for drift at the final calorimeter temperature

When the adiabatic controls are set to give zero drift at the final temperature, the corrected temperature rise, θ , is equal to $(t_f - t_i)$ (see 8.6.3) where t_i is the calorimeter temperature at the time of firing the charge and t_f is the temperature at the end of the main period.

It is not necessary in the calculations to account for a limited drift in temperature prior to ignition of the sample. Significant drift at the end of and beyond the main period shall, however, be taken into account. A small limited constant drift may be regarded as a constant contribution throughout most of the main period. A reasonable approach is to make a correction commencing 1 min after ignition of the sample. The drift rate should, in principle, be determined for the individual run. But insofar as the final drift rate has been established as constant over extended periods of time for a defined range of final temperature, the correction may be based on such a fixed rate.

NOTE 1 A drift rate of 0,001 K/min unaccounted for can, with a main period of about 10 min, result in an error in θ of approximately 0,01 K. For ϵ values of about 10 kJ/K, the resulting error in the calorific value of the fuel is on the order of 100 J/g. If exactly the same error from the same source is made in the calibrations and in all fuel tests, it is, of course, of no consequence for the final result, at least as long as the variation in θ stays within about $\pm 30\%$.

The final drift rate, g_f , expressed in kelvins per minute, shall be determined over a time period that is at least half of what the drift correction is supposed to cover. For a main period of 9 min, this gives a drift rating period of 5 min.

NOTE 2 When the total temperature change of the calorimeter is expressed in units other than temperature (see 9.6.1), g_f is the corresponding per-minute value of that unit.

The corrected temperature rise, θ , corrected for drift at the final temperature, is calculated from [Formula \(A.1\)](#):

$$\theta = t_f - t_i - g_f \times (\Delta\tau - t_1) \quad (\text{A.1})$$

where

$\Delta\tau$ is the length of the main period, expressed in minutes;

t_1 is the correction of 1 applied after the ignition of the sample, expressed in min;

g_f is calculated from [Formula \(A.2\)](#):

$$g_f = \frac{t_{f+\tau_a} - t_f}{\tau_a} \quad (\text{A.2})$$

where

$t_{f+\tau_a}$ temperature, a minutes after the end of the main period;

τ_a time in a min after the end of the main period;

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

Another way of evaluating g_f is as the slope of a linear regression fitting of time-temperature readings at 1 min intervals from the end of the main period onwards (See [B.5](#)).

A.6 Strategy for checking on bias

For adiabatic combustion calorimeters, the main source for systematic error in the measurement is related to difficulties in maintaining adiabatic conditions during the rapid part of the temperature change in the calorimeter. This is manifested as an upward trend in the values obtained for the effective

heat capacity with increasing sample mass. Fast-burning samples, such as paraffin oil, usually aggravate this problem and this type of heat-leak error might not cancel between calibration and fuel tests.

In most calorimeters, a check on temperature lag in the thermostat as a function of sample mass and type is readily made. The change in thermostat temperature upon ignition of the sample is measured for about 3 min and plotted as a function of time together with time-temperature values for the calorimeter. For adiabatic calorimeters, readings of calorimeter temperature are, in fact, not required during the first part of the main period other than for diagnostic purposes. For the check on thermostat lag, they are required at a frequency sufficient to outline the features of the time-temperature curve.

No particular calibration of the thermostat thermometer is required, but it shall have a response time comparable to that of the calorimeter thermometer. On the graph plot, the two temperature "scales" are simply made to coincide at the time for ignition of the sample. The two temperatures should, of course, be close at the upper end where the system is approaching thermal equilibrium. The area between the two curves is a measure of potential heat leak, and a significant increase of this area as a function of sample mass, i.e. of θ , or sample type for comparable values of θ , indicates that there is a risk of systematic error in the determinations of calorific value. Special care is, then, required in restricting the variation in heat evolved per test to a safe level and range.

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Annex B (informative)

Isoperibol and static-jacket calorimeters

B.1 Principle

The characteristic feature of isoperibol calorimeters is the isothermal jacket. The temperature of the surrounding thermostat is kept constant throughout the test by active control. The thermostat of a static-jacket calorimeter has a thermal capacity such that, even without active control, its temperature remains nearly constant during measurements. In both cases, there is a flow of heat between the calorimeter itself and the thermostat. Calorimeters surrounded by thermally insulating material behave largely as static-jacket calorimeters.

Heat exchange between calorimeter and thermostat takes place via common boundaries, the driving force being the thermal head. Ideally, the whole of the outside surface of the calorimeter can, including the lid, should have a uniform temperature equal to that measured by the temperature sensor in the calorimeter. The temperature of the inner wall of the thermostat well and lid facing the calorimeter should remain constant and uniform throughout the test.

To make it possible to evaluate and correct for the actual heat exchange, the calorimeter as a whole shall behave in conformity with Newton's law of cooling, i.e. the heat flow between calorimeter and thermostat shall be directly proportional to the actual temperature difference for a sufficiently large range of thermal head. For this calorimeter, the heat flow into the calorimeter, $\frac{dq}{dT}$, is expressed as shown in [Formula \(B.1\)](#):

$$\frac{dq}{dT} = k(t_j - t) \quad (\text{B.1})$$

where

- t_j is the jacket temperature;
- t is the calorimeter temperature;
- $(t_j - t)$ is the thermal head;
- k is the Newton's law cooling constant.

In the above formula, dq (the heat change) may be replaced by $c_p dt$ (heat capacity times the temperature change). As the effective heat capacity, ϵ , of the calorimeter can be regarded as constant over the temperature range of a test, [Formula \(B.1\)](#) then can be written in terms of $\frac{dt}{d\tau}$, the rate of temperature change (drift) in the calorimeter caused by the flow of heat, as shown in [Formula \(B.2\)](#)

$$\frac{dt}{d\tau} = G(t_j - t) + P_{st} \quad (\text{B.2})$$

where

- G is the specific-rate constant;
- P_{st} is the power of stirring.

The requirement that the power of stirring be constant throughout a test (see 8.1) allows the expression of $\frac{dt}{d\tau}$, as shown in [Formula \(B.3\)](#)

$$\frac{dt}{d\tau} = G(t_{\infty} - t) \quad (\text{B.3})$$

where

t_{∞} is the temperature that the calorimeter eventually attains if left running for an extended period of time, which is the asymptotic temperature of an isoperibol calorimeter (at “infinite” time);

G specific rate constant, which is evaluated from the time-temperature measurements of the rating periods, the fore- and the after-period; see [Figure 2](#).

The heat leak correction, which is the contribution from heat exchange, Δt_{ex} , to the total observed temperature rise in the main period is obtained by integration as shown in [Formula \(B.4\)](#):

$$\begin{aligned} \Delta t_{\text{ex}} &= \int_{\tau_i}^{\tau_f} (dt/d\tau) d\tau \\ &= \int_{\tau_i}^{\tau_f} G(t_{\infty} - t) d\tau \end{aligned} \quad (\text{B.4})$$

using the pairs of time-temperature readings (t, τ) of the main period.

B.2 Sources of error for the real calorimeter

Making the isothermal jacket of an isoperibol calorimeter behave as required in terms of constant and uniform temperature presents no real problem, provided that the thermostat fluid is circulated through the thermostat lid at a reasonable rate.

In a static-jacket calorimeter, the thermostat temperature changes slightly during a test, with a somewhat different profile when the calorimeter temperature rises upon firing the charge. The thermal capacity of the thermostat shall be such that for a specific-rate (cooling) constant, G , of $0,002 \text{ 0 min}^{-1}$, the rise in temperature of the jacket water is less than $0,16 \text{ K}$ from the time of firing the charge to the end of the after-period; for a specific-rate constant of $0,003 \text{ 0 min}^{-1}$, it shall be less than $0,11 \text{ K}$. The drift in temperature of the thermostat is proportional to the thermal head.

A calorimeter lid in poor thermal contact with the main part of the calorimeter lags behind when the temperature changes rapidly in the main period and can give rise to an unpredictable heat exchange with the thermostat. A calorimeter lid can also prolong the time required for the calorimeter to reach thermal equilibrium or steady state. On the other hand, a lid prevents a net heat loss from evaporation of calorimeter water since the vapour condenses on the inside of the lid, restoring the evaporation energy to the calorimeter. In fact, the condensing water assists the thermal equilibration of the lid with the rest of the calorimeter. The choice of thermostat temperature affects the evaporation losses when the calorimeter has no lid.

Variations in heat-exchange properties are minimized by keeping the outside surface of the calorimeter and the “inside” of the thermostat clean (polished) and dry. The specific rate constant, G , then should not vary by more than $\pm 3 \%$ from one test to the other. Larger deviations can be indicative, for example, of a stirrer malfunction. It should be emphasized that the errors that really affect the accuracy of the final results are those that differ or vary between calibration and fuel tests.

B.3 Choice of jacket temperature

It is good calorimetric practice to run the thermostat of an isoperibol calorimeter at a temperature that is 0,2 K to 0,4 K higher than the final temperature of the calorimeter. In this way, the calorimeter is the colder part throughout the test, hence minimizing evaporation losses. This is particularly important when the calorimeter has no lid.

The same argument applies to static-jacket calorimeters.

B.4 Rating periods

B.4.1 Initial steady state and fore-period

A few minutes should be allowed to let the various components of the assembled calorimeter reach a uniform temperature after turning the stirrer on and before readings of temperature are taken at 1 min intervals. The initial rating period, the fore-period in principle, begins as soon as the calorimeter reaches a steady state in terms of temperature drift rate. For successive 1 min intervals, the temperature increments should, then, not differ by more than 0,002 K/min or the average difference should not exceed 0,001 K/min. A fore-period of 5 min (6 readings; 5 increments) should suffice to establish the value of $(dt/d\tau)_i = g$, the initial drift rate. For an increase in temperature, g_i has a positive value (>0).

NOTE The calorimeter temperature, as a function of time as a whole, is an exponential trending asymptotically to t_∞ . However, during rating periods of 10 min or less, the curvature is negligible except in cases of a large thermal head, in excess of 5 K, in combination with a large value for the specific-rate constant, greater than $0,005 \text{ min}^{-1}$.

The charge is fired directly upon taking the last reading of temperature in the fore-period; see 8.4.

B.4.2 After-period and length of the main period

The final rating period (the after-period) begins when all parts of the calorimeter have attained a uniform temperature after combustion of the sample, i.e. when the calorimeter has reached a new steady state in terms of temperature drift rate. The time required for the total amount of heat released to become uniformly distributed is primarily a function of stirring pattern and stirrer efficiency. The duration of the main period shall be chosen so that temperature equalization is assured, but there is no merit in making the main period longer than necessary.

The main period begins at the last reading of temperature in the fore-period and ends with the beginning of the after-period. The latter is determined by a series of calibration tests and is taken as the time when, for a subsequent 5 min period, the average deviation of the individual 1 min temperature increments is not more than 0,001 K/min. The mean of the length of time for the main period determined from five calibration tests, rounded to the nearest minute, defines the length of the main period. The main period shall not exceed 10 min nor shall the time intervals evaluated from the individual tests differ by more than 2 min.

The length of the main period shall be the same in the calibration and in the fuel tests. When θ is meant to vary over a wide range, it is advisable to determine the length of the main period at the larger values of θ .

The duration of the after-period should be 5 min to 7 min in order to establish the final drift rate, g_f , well enough for the calculation of the correction for heat exchange Δt_{ex} . For an increase in temperature with time, g_f has a positive value (>0).

B.5 Calculation of the corrected temperature rise, θ

B.5.1 General

The observed temperature rise, $(t_f - t_i)$, is the sum of θ , the change in temperature caused by the processes in the combustion vessel, and Δt_{ex} , the contribution from heat exchange with the surrounding

thermostat (including the contribution from stirring power). The time-temperature readings taken during the fore-, main and after-periods contain the information required for the evaluation of Δt_{ex} and, hence, θ is calculated from [Formula \(B.5\)](#):

$$\theta = t_f - t_i - \Delta t_{\text{ex}} \quad (\text{B.5})$$

The drift rates, in the fore- (initial rating) period, g_i and in the after- (final rating) period, g_f , expressed in kelvins per minute, are calculated as given in [Formulae \(B.6\)](#) and [\(B.7\)](#), respectively:

$$g_i = \left(\frac{dt}{d\tau} \right)_i \quad (\text{B.6})$$

$$= G(t_\infty - t_{\text{mi}})$$

$$g_f = \left(\frac{dt}{d\tau} \right)_f \quad (\text{B.7})$$

$$= G(t_\infty - t_{\text{mf}})$$

where

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

t_{mi} is the mean temperature in the fore-period, expressed in degrees Celsius.

The values calculated in [Formulae \(B.6\)](#) and [\(B.7\)](#) are utilized in the calculation of the specific-rate constant, G , as given in [Formula \(B.8\)](#):

$$G = \frac{g_i}{t_{\text{mf}}} - \frac{g_f}{t_{\text{mi}}} \quad (\text{B.8})$$

Temperature may be expressed in some arbitrary unit throughout. (See [9.6.1](#).)

g_i and g_f are preferably evaluated as the slope of a linear least-squares fitting of the time-temperature values of the fore- and after-periods, respectively. Alternatively, they are taken as the mean values of the 1 min temperature increments in the rating periods.

B.5.2 Regnault-Pfaundler method

For time-temperature readings in the main period all taken at equal time intervals, e.g. 1 min, Δt_{ex} may be expressed as shown in [Formula \(B.9\)](#):

$$\Delta t_{\text{ex}} = G \int_{\tau_i}^{\tau_f} (t_\infty - t) d\tau \quad (\text{B.9})$$

$$= [g_f + G(t_{\text{mf}} - t_m)] \times (\tau_f - \tau_i)$$

where t_m , the integrated mean temperature, is calculated from [Formula \(B.10\)](#):

$$t_m = \frac{1}{n} \left[\frac{t_0 + t_n}{2} \right] + \sum_{k=1}^{n-1} t_k \quad (\text{B.10})$$

where

t_0 is equal to t_i and is the temperature at the beginning of the main period;

$t_1, t_2, \dots, t_k, \dots, t_n$ are the successive temperature readings taken during the main period, $t_n (= t_f)$ being the reading taken at the end;

τ_i and τ_f are the times at the beginning and end of the main period, respectively.

B.5.3 Dickinson extrapolation method

In the Dickinson extrapolation method, the objective is to find the Dickinson extrapolation time, τ_x , that satisfies [Formula \(B.11\)](#):

$$g_i (\tau_x - \tau_i) + g_f (\tau_f - \tau_x) = G \int_{\tau_i}^{\tau_f} (t_\infty - t) d\tau = \Delta t_{ex} \quad (B.11)$$

This objective is accomplished when the hatched areas “a” and “b” in [Figure B.1](#) are of equal size. The corrected temperature rise, θ , becomes as calculated in [Formula \(B.12\)](#)

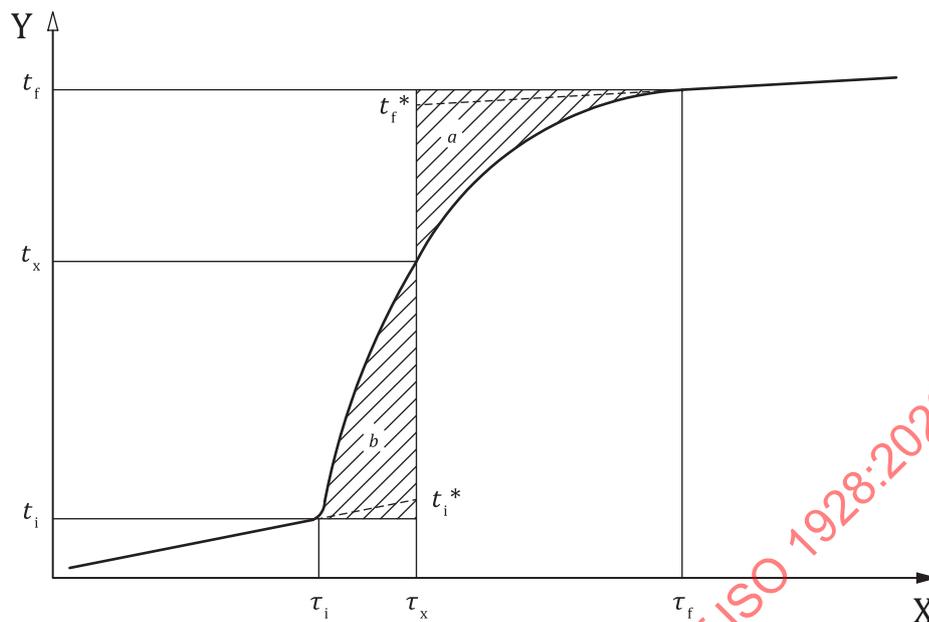
$$\theta = t_f - t_i - g_i (\tau_x - \tau_i) - g_f (\tau_f - \tau_x) = t_f^* - t_i^* \quad (B.12)$$

where

g_i and g_f represent, in principle, the drift rates at t_i and t_f , respectively;

t_f^* and t_i^* are the temperatures as shown in [Figure B.1](#).

For a combustion reaction, the time-temperature curve is close to being an exponential, which means that τ_x is the time associated with the temperature where the change in temperature ($\tau_x - \tau_i$) is 0,6 times the total (observed) temperature rise ($t_f - t_i$). The quantity ($\tau_x - \tau_i$) varies with the kinetic behaviour of the combustion reaction of the type of sample studied.

**Key**X time, τ Y temperature, t a, b hatched area, see [B.5.3](#) t_f final temperature of the main period (equal to the reference temperature) t_i initial temperature of the main period τ_x temperature at the time, τ_x **Figure B.1 — Dickinson extrapolation**

Annex C (informative)

Automated calorimeters

C.1 Calorimeter instrumentation

Among the various types of fully automated combustion vessel calorimeters there are instruments that fulfill all the basic requirements regarding a physically well defined calorimeter, as well as instruments whose thermal behaviour requires that they be described empirically. The former type of instrument usually demands less in terms of comparability, for example in the amount of heat released in calibrations and in fuel tests, respectively, in order to yield reliable results. Also, the effective heat capacity, ϵ , of a well defined calorimeter as a rule remains constant over long periods of time.

There is no particular reason to assume that instruments with a less well defined calorimeter cannot produce calorific values with the required accuracy, provided that the repeatability is within some set limits and the user is aware of, and adheres to, restrictions in the choice of operating conditions. Normally, a calorimeter of this kind requires more frequent calibrations, in some cases every day that it is used.

Aneroid calorimeters (see 6.1) are convenient for automated operation, as they require no apportioning of calorimeter water, thereby also eliminating evaporation errors. They are usually operated as adiabatic or quasi-adiabatic systems but can equally well be of the isoperibol type. Characteristically, they have a small heat capacity, leading to large changes in calorimeter temperature, thus facilitating the measurement of θ with a relatively high resolution. Conversely, large values of θ tend to increase the risk of introducing systematic error in aneroid systems, aggravated by difficulties in achieving uniform calorimeter surface temperature during combustion of the sample. A countermeasure is to limit the sample mass, bearing in mind that, for smaller samples, particular attention shall be given to their being representative.

In certain cases, well defined, stable calorimetric systems allow operation in dynamic mode, i.e. it is possible, within a few minutes into the main period, to predict the final outcome of the test in terms of θ , without a significant loss in accuracy of the results. The laboratory shall demonstrate they can meet the precision of this document using either dynamic or equilibrium mode.

C.2 Calibration

The effective heat capacity, ϵ , shall, in principle, be determined as specified in [Clause 9](#) with particular reference to [9.2](#), [9.4](#), and [9.5](#).

The instrument manufacturer may specify combustion vessel conditions (ratio of sample mass to combustion vessel volume, initial combustion vessel water, oxygen pressure) that deviate significantly from those defined in [9.2.1](#). When these combustion vessel conditions cause a change in the energy of combustion of the calibrant (benzoic acid) larger than ± 5 J/g (see [9.2.2](#)), it is possible to adjust any preset value for benzoic acid, i.e. to input the correct value for the calculations of ϵ .

Recommendations to exclude the initial amount of water in the combustion vessel should be disregarded; see [4.1](#). The amount, however, may be kept quite small but should be the same in all tests.

The reference temperature of the tests, equal to the final temperature, t_f , of the main period, should be kept the same, within ± 1 K, in all tests. If necessary, it may be chosen arbitrarily within ± 10 K from

25 °C without seriously affecting the numerical values of the determinations of calorific value; see [3.1.8](#). A deviation in excess of ± 5 K from 25 °C should be quoted with the test result.

NOTE Ancillary quantities given in [9.6.1](#), [9.6.2](#), and [10.4.2](#) refer, in principle, to states and reactions at 25 °C.

Some instruments call for calibration using samples differing by about a factor of 2 in mass. Correctly implemented, this offers considerable flexibility for subsequent fuel measurements. Establishing a valid working range for the effective heat capacity, ϵ , is always required; see [9.3](#). When the range is narrow in terms of the amount of heat released, special attention shall be given to performing all tests within these limits.

For instruments that require frequent calibration, the manufacturer may provide benzoic acid pellets of appropriate mass with an assigned value for the energy of combustion. As a rule, these pellets do not qualify as the calibrant (see [5.5](#) and [9.2](#)) but are convenient for everyday use. An alternative is to check the calibration by making a series of measurements on a pelletized sample of certified benzoic acid at regular intervals and whenever a new batch of the manufacturer's sample is used. The mean value from a series of five combustions, with the sample mass about the same throughout, shall not differ by more than 50 J/g from the certified value, recalculated when applicable, to the actual combustion vessel conditions.

Some instruments require preconditioning by combustion of a few samples before yielding stable results. Almost any benzoic acid (pelletized) or combustion aid (see [8.1](#)) may be used for this purpose. The results from these conditioning runs should be disregarded.

Combustion of certified reference materials of coal or certified benzoic acid as an "unknown" (see [9.3](#)) are generally the most convenient way of checking the performance of a calorimeter.

C.3 Precision requirements for calibrations

The values of ϵ for the individual calibration tests should be printed or displayed so that they can be manually recorded (in joules per kelvin or in arbitrary units, together with θ in these units). Generally, the precision requirements for ϵ , as given in [9.7](#), apply.

Some systems compensate for significant drift by using the mean of the previous mean value and the value for ϵ from the latest calibration test as the measure for the effective heat capacity. In such a case, the individual values of ϵ for a series of calibration tests cannot be used to evaluate the precision characteristics of the measurements. Instead, a series of individual measurements using certified benzoic acid as the sample shall be performed over a period of 1 day or, at the most, 2 days. For a series of five benzoic acid combustions, the standard deviation shall not exceed 0,20 %. The mean value shall not differ by more than ± 50 J/g from the certificate value; see [C.2](#).

C.4 Comparability of calibration and fuel tests

The conditions specified in [10.1](#) to [10.3](#) apply, including arguments about whether it is necessary to take into account thermal contributions from combustion of the fuse and/or side reactions, such as the formation of nitric acid; see [9.6.1](#).)

In the computational procedures of automated instruments, there are normally no provisions to allow specifically for the use of crucibles of widely different material and mass.

In aneroid systems or systems working on a constant mass-of-water basis, the error from disregarding a difference in heat capacity of individual crucibles is as given in [Formula \(C.1\)](#):

$$(\theta \times \Delta C) / m_1 \quad (C.1)$$

where

ΔC is the difference in heat capacity ($m_{cr} \times c_{p,cr}$) of the crucible used in the calibrations and that used in combustion of the fuel;

m_1 is the mass of fuel sample burned.

For calorimeters working on a constant total-calorimeter-mass basis, the error is estimated by [Formula \(C.2\)](#); see [9.6.2](#):

$$\left[\theta \times \Delta m_{cr} \times c_{p,cr} \right] / m_1 \quad (C.2)$$

where:

$c_{p,cr}$ specific heat capacity of the crucible, in J/g;

Δm_{cr} heat capacity from the mass of the crucible, in g.

Getting clean combustions is the first priority. Optimizing the overall conditions to achieve it is usually worthwhile.

C.5 Documentation and print-out

The evaluation of the gross calorific value at constant volume of the fuel as analysed, $q_{V,gr}$ for the analysis sample shall, in principle, be in accordance with [10.4](#). The value shall be given in joules per gram or another convenient unit.

The printed or otherwise recorded information on the individual test shall allow the user to verify the calculations starting from values of θ , ε , mass of sample, fuse and any combustion aid. The formulae used should be given in the manual itself or in an annex. Ancillary quantities used in the calculations shall be unambiguously identifiable, and it shall be possible to make the necessary alterations in the program required by changes in procedure, including a change in the numerical value used for the energy of combustion of the calibrant in calibration tests. Corrections applied for ignition energy, side reactions, etc. shall be clearly stated.

The reference temperature of the test shall be identified to the nearest 0,2 K.

C.6 Precision requirements for fuel tests

The precision requirements in terms of repeatability limit of the results of duplicate measurements are stated in [Clause 11](#).

Annex D (informative)

Checklists for the design of combustion tests and their procedures

D.1 Overview

This annex contains checklists intended as aids in setting up and carrying out a complete determination of a calorific value, including calibration of the instrument, using a specified type of calorimeter. Formulae identical to those given in the main text are repeated here for clarity.

The general experimental conditions that are common to the use of all types of combustion vessel calorimeters are defined in [D.2](#). [D.3](#) contains information pertinent to the use of adiabatic calorimeters, [D.4](#) applies to isoperibol calorimeters and [D.5](#) deals with the highly automated combustion vessel-calorimetric systems. Static-jacket calorimeters may be treated as isoperibol systems.

The basic calorimetric procedure is described in [Clause 8](#). The calibration procedures are described in [9.5](#) and [9.6](#). The experimental and computational procedures for the fuel combustions are specified in [10.2](#) to [10.4](#). Additional information required for the particular type of calorimeter is given as follows:

- for adiabatic calorimeters: [Annex A](#) and [D.3](#);
- for isoperibol or static-jacket calorimeters: [Annex B](#) and [D.4](#);
- for other types of calorimeters: [Annex C](#) and [D.5](#);

D.2 Choice of general parameters

D.2.1 Calibration conditions

The basis for the conditions of subsequent fuel tests are as follows; see [9.2.2](#) and [9.3](#) for general calibration requirements:

- Combustion vessel volume, V_{cv} , expressed in litres;
- mass of benzoic acid, m_{ba} , expressed in grams;
- mass of combustion vessel water, m_{aq} , expressed in grams; V_{aq} , volume of combustion vessel water, expressed in millilitres, may be substituted for m_{aq} ;
- initial pressure of oxygen, p_0 , expressed in megapascals;
- reference temperature, t_{ref} , expressed in degrees Celsius.

D.2.2 Calculation of the combustion vessel condition value of benzoic acid

This value is used in the calculations of the effective heat capacity of the calorimeter, ε . Consult the particular benzoic acid certificate; see also [9.6.1](#) and [9.6.2](#).

D.2.3 Certificate value of benzoic acid, expressed in joules per gram

NOTE See [9.2.1](#).

The certificate value of benzoic acid, $q_{V,ba}$, is calculated from the following values:

- (m_{ba}/V_{cv}) , expressed in grams per litre, equal to 3,0 g/l;
- (V_{aq}/V_{cv}) , expressed in millilitres per litre, equal to 3,0 ml/l;
- p_0 , expressed in megapascals, equal to 3,0 MPa;
- t_{ref} , expressed in degrees Celsius, equal to 25 °C; see [8.7](#);
- adjustment of certified value, expressed in joules per gram, in accordance with the equation in the certificate for benzoic acid.

This yields, $q_{V,ba}$, expressed in joules per gram.

D.2.4 Amount of calorimeter water

NOTE See [8.1](#) and the Note in [8.3](#); (not relevant for aneroid systems).

The amount of calorimeter water is determined either

- a) on a constant mass-of-calorimeter-water basis, i.e. the mass of calorimeter water, expressed in grams; see [8.3](#), [9.6.1](#), [10.4.2](#); or, alternatively
- b) on a constant total-calorimeter-mass basis, i.e. the mass of the (calorimeter plus water plus assembled combustion vessel), expressed in grams; see [8.3](#), [9.6.2](#), [10.4.3](#).

D.2.5 Additional parameters

It is necessary to consider the following additional parameters:

- length of ignition wire (fuse), l_{wire} , expressed in centimetres, or a constant Q_{ign} , expressed in joules; see [9.4](#), [9.6.1](#);
- mass of wire (fuse), m_{fuse} , expressed in grams, or a constant Q_{fuse} , expressed in joules; see [9.4](#), [9.6.1](#).

It is necessary to decide whether or not it is necessary to determine the correction, Q_N , for nitric acid by analysis for the individual test, or whether to assign a constant per-gram value (not necessarily the same for the calibrant as for the fuel tests) or per-test value; see [9.4](#), [10.1](#).

D.3 Adiabatic calorimeters

D.3.1 Determination of the corrected temperature rise, θ

For a determination of the corrected temperature rise, θ , it is necessary to make the necessary adjustments to achieve adiabatic conditions; see [A.3.1](#), [A.3.2](#).

Estimate the heat capacity of the system and, from the choice of sample mass, make a prediction of the expected temperature rise, Δt , in order to determine the starting temperature, $(t_{ref} - \Delta t)$.

Determine what the conditions are for an initial steady state; see [A.4](#).

Make a series of tests to determine the length of the main period; see [8.2](#) to [8.5](#), [9.5](#) and [A.4](#).

From the time-temperature measurements for a set of benzoic acid combustions (see [A.5](#)), calculate the corrected temperature rise, θ , for the individual tests as given in [Formula \(D.1\)](#).

$$\theta = t_f - t_i \quad (\text{D.1})$$

For a significant (but limited) drift at the end of the main period, θ is derived from [A.5](#) as shown in [Formula \(D.2\)](#)

$$\theta = t_f - t_i - g_f \times (\Delta\tau - 1) \quad (\text{D.2})$$

D.3.2 Evaluation of the effective heat capacity

Calculate the effective heat capacity, ε , for the individual tests.

For alternative [D.2.4 a](#)), the calculation of ε on the constant mass-of-calorimeter-water basis is given by [Formula \(D.3\)](#); see [9.6.1](#):

$$\varepsilon = \frac{m_{\text{ba}} \times q_{V,\text{ba}} + Q_{\text{fuse}} + Q_{\text{ign}} + Q_{\text{N}}}{\theta} \quad (\text{D.3})$$

For alternative [D.2.4 b](#)), the calculation of ε_0 on the constant total-calorimeter-mass basis is given by [Formula \(D.4\)](#); see [9.6.2](#).

$$\varepsilon_0 = \varepsilon + m_{\text{cr}} \times c_{p,\text{aq}} \quad (\text{D.4})$$

where

ε^* is the effective heat capacity of calorimeter on a “total-calorimeter-mass” basis and is equal to ε as defined above;

m_{cr} is the mass of the crucible used in the individual calibration test; see the Note in [9.6.2](#).

Calculate the mean value ε_n or $\varepsilon_{0,n}$ and make sure that the precision requirements are met; see [9.7](#).

The system is now calibrated and the main calorimetric parameters set for subsequent combustion measurements on fuel samples.

Ancillary quantities required in the calculations are given in [9.6.1](#).

D.3.3 Gross calorific value at constant volume

To calculate the gross calorific value at constant volume, $q_{V,\text{gr}}$, perform the fuel combustions in accordance with the instructions in [10.2](#) and [10.3](#). θ is calculated in the same way as for the calibrations.

For alternative [D.2.4 a](#)), a calorimeter operated on the constant mass-of-calorimeter-water basis, calculate the calorific value from [Formula \(D.5\)](#); see [10.4.2](#):

$$q_{V,\text{gr}} = \frac{\varepsilon_n \times \theta - Q_{\text{fuse}} - Q_{\text{ign}} - Q_{\text{N}} - m_2 \times q_{V,2}}{m_1} - \frac{Q_{\text{S}}}{m_1} \quad (\text{D.5})$$

For alternative [D.2.4 b](#)), a calorimeter operated on the constant total-calorimeter-mass basis, calculate the calorific value from [Formula \(D.6\)](#); see [10.4.3](#):

$$q_{V,\text{gr}} = \frac{\varepsilon^* \times \theta - Q_{\text{fuse}} - Q_{\text{ign}} - Q_{\text{N}} - m_2 \times q_{V,2}}{m_1} - \frac{Q_{\text{S}}}{m_1} \quad (\text{D.6})$$

where

ε_* is derived from the formula $\varepsilon_* = \varepsilon_{0,n} - m_{cr} \times c_{p,aq}$;

m_{cr} is the mass, expressed in grams, of the crucible in the individual test.

Always use the crucible best suited for the particular sample under investigation.

Ancillary quantities required in the calculations are given in [9.6.1](#) and [10.4.2](#).

D.4 Isoperibol calorimeters

D.4.1 Determination of the corrected temperature rise

D.4.1.1 General

For a determination of the corrected temperature rise, θ , it is necessary to set the jacket temperature to the value chosen for the tests; see [B.3](#).

Estimate the heat capacity of the system and, from the choice of sample mass, make a prediction of the expected temperature rise, Δt , in order to determine the starting temperature, $(t_{ref} - \Delta t)$.

Investigate what the conditions are for an initial steady state and decide on the length of the fore- or initial rating period; see [B.4.1](#).

Make a series of tests to determine the length of the main period; see [B.4.2](#), [8.2](#) to [8.5](#) and [9.5](#).

From the time-temperature measurements (τ_k, t_k) for a set of benzoic acid combustions, calculate the corrected temperature rise, θ , for the individual tests, utilizing either the Regnault-Pfaundler or the Dickinson method.

D.4.1.2 Regnault-Pfaundler method

NOTE See [B.5.1](#) and [B.5.2](#).

Determine the drift rates, g_i and g_f , and the mean temperatures, t_{mi} and t_{mf} , of the rating periods and calculate the specific-rate constant, G , according to [Formula \(B.8\)](#):

Then calculate t_m , the integrated mean temperature, and Δt_{ex} , the contribution from heat exchange, according to [Formulae \(D.7\)](#) and [\(D.8\)](#):

$$t_m = \frac{1}{n} \left[\frac{t_0 + t_n}{2} + \sum_{k=1}^{n-1} t_k \right] \quad (D.7)$$

$$\Delta t_{ex} = G \int_{\tau_i}^{\tau_f} (t_{\infty} - t) d\tau = [g_f + G(t_{mf} - t_m)] \times (\tau_f - \tau_i) \quad (D.8)$$

Finally, calculate θ from [Formula \(D.9\)](#):

$$\theta = t_f - t_i - \Delta t_{ex} \quad (D.9)$$

D.4.1.3 Dickinson extrapolation method

NOTE See [B.5.1](#) and [B.5.3](#).

Make a graph of the time-temperature (τ_k, t_k) values of the main period and determine the time for $t_i + 0,6 \times (t_f - t_i)$. This time is taken as τ_x . Determine the drift rates, g_i and g_f , i.e. the slopes of the rating periods, using [Formulae \(D.10\)](#) and [\(D.11\)](#):

$$g_i = (dt/d\tau)_i \quad (\text{D.10})$$

$$g_f = (dt/d\tau)_f \quad (\text{D.11})$$

Then calculate θ from [Formula \(D.12\)](#)

$$\theta = t_f - t_i - g_i (\tau_x - \tau_i) - g_f (\tau_f - \tau_x) \quad (\text{D.12})$$

NOTE The extrapolated time, τ_x , for the fuel tests is likely to differ from that for the calibrations.

D.4.2 Evaluation of the effective heat capacity

Calculate the effective heat capacity, ε , for the individual tests using the appropriate formula [alternative [D.2.4 a\)](#) or [D.2.4 b\)](#)] as given in [D.3.2](#).

Calculate the mean value, ε_n or $\varepsilon_{0,n}$, and make sure that the precision requirements are met (see [9.7](#)).

The system is now calibrated and the main calorimetric parameters set for subsequent combustion measurements on fuel samples.

D.4.3 Gross calorific value at constant volume

For the gross calorific value at constant volume, $q_{v,gr}$, perform the fuel combustions in accordance with the instructions in [10.2](#) and [10.3](#). θ is calculated in the same way as for the calibrations.

Calculate the calorific value using the appropriate formula [alternative [D.2.4 a\)](#) or [D.2.4 b\)](#)] as given in [D.3.3](#).

D.5 Automated combustion vessel calorimeters

Operate the calorimeter according to the instructions. The corrected temperature rise, θ , is usually derived automatically by the system.

Make sure that the correct value is used for the energy of combustion of the calibrant under the combustion vessel conditions utilized (see [D.2](#)) in the evaluation of the calibration constant.

Make sure that the precision requirements are met. If necessary, check the system by burning a certified reference material of coal or benzoic acid as an unknown. Any restrictions set by the manufacturer on the amount of sample burned shall be adhered to.

Define the valid working range for subsequent measurements.

Make a check on the calculations with respect to fuse wire and nitric acid corrections. Unless the correction for sulfuric acid to sulfur dioxide, Q_S/m_1 , is taken care of by the system, use the value given in [10.4.2](#).

Annex E (informative)

Examples to illustrate some of the calculations used in this document

E.1 Gross calorific value at constant volume

E.1.1 Isoperibol calorimeters

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 minus the latent heat of vaporization at 25 °C and constant volume of both the water present in the fuel and water 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, L_s , is given, in joules per gram, in [Formula \(E.1\)](#):

$$L_s = 0,01 \times L \times \left[\left(\frac{w_H}{2,0159} \right) + \left(\frac{M_T}{18,0153} \right) \right] \quad (\text{E.1})$$

where

0,01 is defined in [10.5](#);

L is the latent heat of vaporization of water at 25 °C and constant pressure (43 988 J/mol);

w_H and M_T are defined in [12.2](#);

2,015 9 is the relative molecular mass of hydrogen in the form of a gas (H_2), expressed in g/mol;

18,105 3 is the relative molecular mass of water, expressed in g/mol.

The work done against the atmosphere when this water is expanded at constant pressure to vapour at 25 °C, W_1 , is given, in joules per gram, in [Formula \(E.2\)](#):

$$W_1 = 0,01 \times RT \times [(w_H/2,0159) + (M_T/18,0153)] \quad (\text{E.2})$$

where

R is the universal gas constant (8,314 5 J/(mol/K));

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

Hence, q_{p,net,M_T} , the net calorific value at constant volume of the analysis sample, in joules per gram, is given in [Formula \(E.3\)](#):

$$q_{p,\text{net},M_T} = q_{V,\text{gr,d}} - 0,01 \times (L - RT) \times [(w_H/2,0159) + (M_T/18,0153)]$$