INTERNATIONAL STANDARD

ISO 9831

First edition
1998-08-01

Animal feeding stuffs, animal products, and faeces or urine — Determination of gross calorific value — Bomb calorimeter method

Aliments des animaux, produits d'origine animale et excréments ou urines — Détermination de la valeur calorifique brute — Méthode à la bombe calorimétrique

Reference number
ISO 9831:1998(E)

Contents

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Printed in Switzerland

Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

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

International Standard ISO 9831 was prepared by Technical Committee ISO/TC 34, *Agricultural food products*, Subcommittee SC 10, *Animal feeding stuffs*.

Annexes A and B are an integral part of this International Standard. Annexes C to F are for information only.

Animal feeding stuffs, animal products, and faeces or urine — Determination of gross calorific value — Bomb calorimeter method

1 Scope

This International Standard specifies a method for the determination of the gross calorific value of animal feeding stuffs, animal products and faeces or urine at constant volume in an adiabatic, an isothermal, or a static bomb calorimeter.

The result obtained by this method is the gross calorific value of the test sample at constant volume, the water of the combustion products being condensed to liquid at the calorimeter temperature.

NOTE The international reference temperature for thermochemistry of 25 °C is used as the reference temperature for calorific value, although the temperature dependence of the calorific value of the materials to which this International Standard applies is small (about 1 $J \cdot g^{-1} \cdot K^{-1}$).

2 Normative references

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

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

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

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

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

ISO 1928:1995, *Solid mineral fuels — Determination of gross calorific value by the bomb calorimeter method, and calculation of net calorific value.*

ISO 3696:1987, *Water for analytical laboratory use — Specification and test methods.*

ISO 6496:—[1], *Animal feeding stuffs — Determination of moisture and volatile matter content.*

ISO 6498:—[2], *Animal feeding stuffs — Preparation of test samples.*

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[1] To be published. (Revision of ISO 6496:1983)

[2] To be published. (Revision of ISO 6498:1983)

3 Definitions

For the purposes of this International Standard, the definitions given in ISO 1928 apply.

4 Principle

Combustion of a weighed portion of the test sample in oxygen in a bomb calorimeter under standardized conditions. Calculation of the gross calorific value from the temperature rise of the water in the calorimeter vessel and the mean effective heat capacity of the calorimeter. Allowances are made for the heat released by the ignition fuse, for thermochemical corrections and, where appropriate, for heat losses from the calorimeter to the water jacket.

5 Reagents and materials

Use only reagents of recognized analytical grade.

5.1 Water, complying with at least grade 3 in accordance with ISO 3696.

5.2 Oxygen, at a pressure capable of filling the bomb to 3 MPa and free from combustible matter.

NOTE 1 Oxygen manufactured by an electrolytic process may contain up to 4 % of hydrogen and is therefore unsuitable.

NOTE 2 1 MPa = 1 MN/m^2.

5.3 Fuse, comprising the following.

5.3.1 Firing wire, nickel/chromium wire (0,16 mm to 0,20 mm in diameter), or platinum wire (0,06 mm to 0,10 mm in diameter).

5.3.2 Cotton thread, white cellulose.

5.3.3 Polyethylene strip, thin film of dimensions 30 mm by 5 mm.

5.4 Polyethylene bags, of dimensions 68 mm by 110 mm.

5.5 Polyethylene bags, of dimensions 50 mm by 55 mm, and mass approximately 170 mg.

5.6 Silica gel, chromatographic-grade powder.

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

5.8 Screened methyl orange indicator solution, $\rho = 1$ g/l.

Dissolve 0,25 g of methyl orange and 0,15 g of xylene cyanol FF in 50 ml of 95 % (V/V) ethanol and dilute to 250 ml with water.

5.9 Benzoic acid, thermochemical standard, certified by a national testing authority.

Drying or any treatment other than pelleting shall not be carried out.

The gross calorific value at constant volume of the benzoic acid, listed in the certificate for the conditions of use, shall be adopted in calculating the effective heat capacity of the calorimeter (see annex A).

6 Apparatus

Usual laboratory apparatus and, in particular, the following.

6.1 Bomb, capable of withstanding safely the pressure developed during combustion.

The design shall permit complete recovery of all liquid products.

The construction materials shall resist corrosion by the acids produced by the combustion.

CAUTION — Inspect bomb parts regularly for wear and corrosion. Pay particular attention to the condition of the threads of the main closure.

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

The vessel shall be provided with a console to centre the bomb in the vessel and to obtain water circulation below the bomb.

6.3 Stirrer, driven at a constant rotational speed.

The stirrer shaft shall contain a non-conducting section below the cover of the water jacket to minimize the transmission of heat to or from the system. If a cover is used for the calorimeter vessel, the non-conducting section shall be above this cover.

For isothermal and static bomb calorimeters, the rate of stirring shall ensure that the length of the main period (see 9.6) in determinations of effective heat capacity using benzoic acid (see annex A) does not exceed 10 min.

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

The adiabatic water jacket shall have either electrode or immersion heaters capable of supplying energy at a rate sufficient to maintain the temperature of the water in the jacket to within 0,1 °C of that of the calorimeter vessel after the charge has been fired. When in equilibrium at 25 °C, the temperature drift of the calorimeter vessel shall not exceed 0,000 5 °C/min.

NOTE 1 Special precautions are needed at high environmental temperatures.

The isothermal water jacket shall be provided with a means of maintaining it at a constant temperature to the nearest 0,1 °C.

The static water jacket shall have a thermal capacity great enough to restrict changes of temperature of the water in it. From the time of firing the charge to the end of the after-period or during a period of 15 min, whichever is the greater, with a cooling factor $d = 0{,}002\,0\ \text{min}^{-1}$ (see 10.3), the rise in temperature of the water in the jacket shall be less than 0,16 °C; with a cooling factor $d = 0{,}003\,0\ \text{min}^{-1}$, the rise in temperature shall be less than 0,11 °C.

NOTE 2 For an insulated metal jacket, this can be ensured by making the capacity at least 12,5 l, contained in a wide annular jacket.

6.5 Temperature-measuring instrument, capable of indicating temperatures which, when corrected, have an accuracy of 0,002 °C, so that temperature intervals of 2 °C to 3 °C can be determined with an accuracy of 0,004 °C.

It shall be calibrated against a known standard by a national testing authority, at intervals not larger than 0,5 °C over the range of use or, for mercury-in-glass thermometers, over the whole graduated scale.

The following types of thermometer are suitable:

a) resistance thermometers comprising a platinum resistance, resistance bridge and galvanometer;

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

A viewer with a magnification of about five times is required for reading the temperature to the required accuracy.

A mechanical vibrator is recommended to tap the thermometer for a period of about 10 s before reading the temperature, to prevent sticking of the mercury column. If this is not available, the thermometer shall be tapped manually, for example with a pencil.

6.6 Crucible, of silica, nickel/chromium or platinum.

The crucible shall be about 25 mm in diameter, flat-based and not more than 20 mm high. Silica crucibles shall be about 1,5 mm thick and metal crucibles about 0,5 mm thick.

For benzoic acid, either of the crucibles specified is suitable. If, after combustion, smears or unburned material occur on the crucible, a small nickel/chromium crucible (for example 0,25 mm thick, 15 mm in diameter and 7 mm high) may be used.

6.7 Ignition circuit.

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

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

6.8 Ancillary equipment, comprising the following.

6.8.1 Balance, capable of weighing at least 3 kg to the nearest 1 g.

6.8.2 Analytical balance, capable of weighing to the nearest 0,1 mg.

6.8.3 Briquette press.

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

6.8.5 Pressure gauge, range from 0 MPa to 5 MPa, to indicate the pressure in the bomb.

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

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

6.9 Timer, fitted in a convenient place, indicating minutes and seconds.

It may usefully incorporate a device giving audible signals lasting 10 s starting at 1-min intervals.

7 Sampling

Sampling is not part of the method specified in this International Standard. A recommended sampling method is given in ISO 6497 [4].

It is important that the laboratory receive a sample which is truly representative and has not been damaged or changed during transport or storage.

8 Preparation of test sample and test portion

Prepare the test sample in accordance with ISO 6498.

8.1 Air-dry samples

8.1.1 Grind the laboratory sample so that it passes completely through a sieve with 1 mm apertures.

Mix the sample, preferably by mechanical means, immediately before the determination. By use of the briquette press (6.8.3), press 0,5 g to 5 g of the test sample to form a pellet. The mass of the test portion depends on the calorific value and the effective heat capacity of the calorimeter. The mass of the test portion should be such that the temperature rise due to combustion is between 2 °C and 3 °C.

Adequate precautions shall be taken to prevent uptake or loss of moisture by the test sample during mixing and pelletizing, so that the moisture content of the test sample, recently determined as specified in 9.2, can be used in further calculations. If this is not possible, the sample shall be exposed in a thin layer for the minimum time necessary for the moisture content to reach approximate equilibrium with the atmosphere of the laboratory containing the bomb calorimeter.

8.1.2 For air-dry samples with a fat content exceeding 10 % (m/m), and for air-dry samples which cannot be pelleted easily, proceed as specified in B.1.

8.2 Liquid samples

Proceed as specified in B.2.

8.3 Samples of fresh materials

Proceed as specified in B.3.

9 Procedure

9.1 Determination of effective heat capacity of the calorimeter

If the effective heat capacity of the calorimeter is not known, or if the known value is questioned, and at intervals not exceeding 6 months, determine the effective heat capacity of the calorimeter as specified in annex A.

9.2 Determination of moisture content

For air-dry samples, determine the moisture content of the test sample in accordance with ISO 6496, at the same time as the determination of the calorific value.

9.3 Preparation of the bomb

Place the test portion (clause 8) in the form of a pellet (see 8.1.1) or contained in a polyethylene bag (see 8.1.2, 8.2 and 8.3), weighed to the nearest 0,1 mg, in the crucible (6.6) of the bomb.

NOTE 1 Normally 1 g of air-dry sample is an appropriate test portion (see also clause 8).

Connect a piece of firing wire (5.3.1) tautly across the terminals of the bomb. Tie a cotton thread (5.3.2) or a strip of polyethylene film (5.3.3), of known mass, to the firing wire. Arrange the ends of the cotton thread or polyethylene film so that they touch the sample.

NOTE 2 For convenience, a measured length of cotton thread of known mass per length may be used. The length used in each determination of calorific value should be the same as was used in the determination of the effective heat capacity of the calorimeter. The same applies to the polyethylene strip, if used.

Put 5 ml of water in the bomb (6.1). Assemble the bomb and charge it slowly with oxygen (5.2) to a pressure of 3 MPa without displacing the original air. If the bomb is inadvertently charged with oxygen above 3,3 MPa, discard the test and begin again.

9.4 Preparation of the calorimeter vessel

Put sufficient water in the calorimeter vessel (6.2) to cover the flat upper surface of the bomb cap. This quantity of water shall be the same, to within 1 g, as that used in the determination of the mean effective heat capacity of the calorimeter (9.1).

If an isothermal calorimeter or static calorimeter is used, the initial temperature of the water shall be such that, at the end of the main period [see 9.6 b)], the temperature does not exceed that of the water in the jacket by more than 0,5 °C.

Transfer the calorimeter vessel to the water jacket (6.4). Lower the bomb into the calorimeter vessel and check that the bomb is gas-tight. If gas escapes from the bomb, discard the test, eliminate the cause of leakage and begin again.

For an adiabatic calorimeter, proceed in accordance with 9.5.

For isothermal and static calorimeters, proceed in accordance with 9.6.

9.5 Procedure specific for an adiabatic calorimeter

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

After 10 min, tap the thermometer (see 6.5) lightly and read it to 0,001 °C. This is the firing temperature (t_0). Fire the charge, holding the switch closed only long enough to ignite the fuse.

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

After the predetermined interval, established in the determination (9.1) of the effective heat capacity of the calorimeter, tap the thermometer again and read it to 0,001 °C. This is the final temperature (t_n). The observer shall take care to avoid parallax errors when using the magnifying viewer (see 6.5) to read mercury-in-glass thermometers.

Proceed in accordance with 9.7.

9.6 Procedure specific for isothermal and static calorimeters

Assemble the apparatus. Start the stirrer and maintain in operation at a constant rate throughout the determination. Stir for at least 10 min before starting to read the temperature to 0,001 °C and continue to do so at intervals of 1 min for a period of 5 min.

Tap the thermometer (see 6.5) lightly for 10 s before each reading. Take care to avoid parallax errors when using the magnifying viewer (see 6.5) to read mercury-in-glass thermometers.

Fire the charge immediately after reading the last temperature in the preliminary period [see a) below]. Hold the switch closed only long enough to ignite the fuse.

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

Read the thermometer as follows.

a) **Preliminary period:** If the average deviation of the values of the rate of change of temperature during this period of 5 min exceeds 0,001 °C/min (see note 2), continue to read the thermometer at 1-min intervals until the average deviation is less than 0,001 °C/min for a period of 5 min. The last temperature of the preliminary period is the initial temperature (t_0) of the main period.

b) **Main period:** During the first few minutes of the main period, it will not be possible to read the thermometer to 0,001 °C, but resume readings to this precision as soon as possible and continue them to the end of the test. The main period does not necessarily end with the attainment of maximum temperature. The last temperature of the main period is the final temperature (t_n), which is the initial temperature of the after-period.

c) **After-period:** This period begins at the first temperature after which for a subsequent 5-min period, the average deviation of the individual values of the rate of change of temperature is not more than 0,001 °C/min (see note 2). This first temperature is the final temperature (t_n).

NOTE 1 If the Regnault-Pfaundler cooling correction (see 10.3) is to be calculated, the procedure specified should be adopted. If an alternative formula, which is equivalent and acceptable, is to be used, some of the temperature readings may not be required and the procedure should be modified accordingly.

NOTE 2 A convenient method of checking that the average deviation of the rate of change of temperature during the preliminary period and the after-period is within the specified limit is specified in annex C.

9.7 Assesment of the bomb contents

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

9.7.2 When certain samples are tested, the residue in the bomb may contain detectable unburned sample. A correction to be applied for such persistently incomplete combustion may be calculated from the amount of unburned carbon, which may be estimated by the procedure described in 9.7.3.

9.7.3 The mass of unburned carbon in the crucible may be estimated as follows.

Transfer the contents of the crucible (not the lining) to a silica or porcelain dish and dry for 1 h at 105 °C. Leave to cool, then weigh the dish and its contents to the nearest 0,1 mg. Heat at 550 °C for 1 h. Leave to cool and reweigh to determine the loss in mass. The loss is taken to be unburned carbon.

Alternatively, the unburned carbon may be determined by one of the methods specified in ISO 609 [1] or ISO 625 [2]. Should more than 6 mg of unburned carbon be determined, the correction will be invalid and the determination of gross calorific value should be repeated.

9.8 Determination of acidity

Wash the contents of the bomb into a beaker with water. Wash the underside of the bomb cap and the outside of the crucible with water. Add the washings to the beaker. Dilute to approximately 100 ml and boil to expel carbon dioxide.

While the mixture is still hot, titrate the warm (not boiling) bomb washings with sodium hydroxide solution (5.7) using the screened methyl orange solution (5.8) as indicator, to determine the total acidity.

10 Corrections

10.1 General

Apply the corrections given in 10.2 to 10.6 to the experimental observations.

10.2 Thermometer corrections

If a mercury-in-glass thermometer is used, apply the corrections specified in the certificate issued with the thermometer, to the observed firing temperature (t_0) and to the final temperature (t_n).

10.3 Cooling correction

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

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

Calculate the cooling correction according to Regnault-Pfaundler by the equation:

$$t_\mathrm{c} = (nv_\mathrm{p} + dZ)f$$

in which

$$d = \frac{v_\mathrm{a} - v_\mathrm{p}}{t_\mathrm{a} - t_\mathrm{p}}$$

$$Z = \left[\sum_{i=1}^{i=n-1} t_i + 0{,}5\left(t_{0\mathrm{o}} + t_{n\mathrm{o}}\right) - nt_\mathrm{p}\right]$$

where

t_c is the cooling correction, in degrees Celsius, according to Regnault-Pfaundler;

n is the number of minutes in the main period;

d is the cooling factor, in reciprocal minutes, of the calorimeter, which shall be determined for each set of conditions;

Z is a temperature term, in degrees Celsius;

f is a correction factor for units, in minutes (f = 1 min);

v_p is the rate of fall of temperature, in degrees Celsius per minute, in the preliminary period (if the temperature is rising, v_p is negative);

v_a is the rate of fall of temperature, in degrees Celsius per minute, in the after-period;

t_p is the average temperature (without thermometer correction), in degrees Celsius, during the preliminary period;

t_a is the average temperature (without thermometer correction), in degrees Celsius, during the after-period;

$t_{0\mathrm{o}}$ is the firing temperature (without thermometer correction), in degrees Celsius;

$t_1, t_2, ..., t_i, ..., t_n$ are the successive temperatures (without thermometer correction), in degrees Celsius, recorded during the main period;

$t_{n\mathrm{o}}$ is the final temperature (without thermometer correction), in degrees Celsius, (see 9.6 and note 2 in 9.6);

$\sum_{i=1}^{i=n-1} t_i$ is the sum of the temperatures $t_1, t_2, ..., t_i, ..., t_{n-1}$, in degrees Celsius.

NOTE The calculations may also be carried out with temperatures corrected for thermometer inaccuracies, provided that the thermometer correction is applied to each temperature.

10.4 Correction for heat of ignition

The heat release from the cotton thread and firing wire shall be subtracted from the total heat released.

Calculate the heat release (e_1) from the cotton thread from its mass (dried at 100 °C) and the calorific value of cellulose (17 500 J/g).

Calculate the heat release (e_2) from the firing wire from the mass of a piece of wire equal in length to the distance between the poles of the bomb, allowing 1 400 J/g for nickel/chromium wire or 420 J/g for platinum wire.

Determine the calorific value (e_1) of the polyethylene strip from the combustion of 0,5 g (approximately 10 sheets).

10.5 Correction for heat of formation of acids

The heat gain due to the formation of sulfuric acid and nitric acid shall be subtracted from the total heat released.

If V is the volume, in millilitres, of the sodium hydroxide solution (5.7) used in the titration in 9.8, the correction for heat (e_3) of formation of acids shall be 6,0 V.

10.6 Correction for incomplete combustion

Take as the value of the mass of unburned residue the loss in mass obtained after ignition of the residue contained in the crucible. Add its heat equivalent (e_4), calculated on the basis of a calorific value of 33 500 J/g, to the heat release determined.

10.7 Correction for polyethylene bag (if used)

Determine the calorific value (e_5) of polyethylene from the combustion of the polyethylene bags (5.4 or 5.5). Repeat the determination at least six times.

11 Expression of results

Calculate the gross calorific value at constant volume from the experimental values using the following equation:

$$Q = \frac{C\left(t_n - t_0 + t_c\right) - e_1 - e_2 - e_3 - e_4 - e_5}{m}$$

where

Q is the gross calorific value, in joules per gram, at constant volume of the test portion;

C is the effective heat capacity, in joules per degree Celsius, of the calorimeter, calculated as the mean of five determinations (see 9.1);

t_0 is the firing temperature, in degrees Celsius, corrected for the thermometer error;

t_n is the final temperature, in degrees Celsius, corrected for the thermometer error;

t_c is the cooling correction, in degrees Celsius, according to Regnault-Pfaundler for isothermal or static calorimeters (see 10.3);

e_1 is the correction for heat of combustion, in joules, of the cotton thread or the polyethylene strip (see 10.4);

e_2 is the correction for heat of combustion, in joules, of the firing wire (see 10.4);

e_3 is the correction for heat, in joules, of formation of sulfuric acid and nitric acid (see 10.5);

e_4 is the correction for incomplete combustion, in joules (see 10.6);

e_5 is the correction for heat of combustion, in joules, of the polyethylene bag (see 10.7), if used;

m is the mass, in grams, of the test portion.

Report the result to the nearest multiple of 10 J/g. The result should preferably be the mean of duplicate determinations (see clause 12).

Examples to illustrate the method of calculating the results of calorific determinations are given in annex D.

12 Precision

12.1 Interlaboratory tests

Details of interlaboratory tests on the precision of the method are given in annex E. The values derived from these tests may not be applicable to concentration ranges and matrices other than those given.

12.2 Repeatability

The absolute difference between two independent single test results, obtained using the same method on identical test material in the same laboratory by the same operator using the same equipment within a short interval of time, will in not more than 5 % of the cases exceed the value of r shown in table 1.

12.3 Reproducibility

The absolute difference between two single test results, obtained using the same method on identical test material in different laboratories by different operators using different equipment, will in not more than 5 % of the cases exceed the value of R shown in table 1.

Table 1 — Repeatability limit (r) and reproducibility limit (R)

Sample	Gross calorific value at constant volume J/g[1]	r J/g	R J/g
Hay	17 421	108	322
Wilted silage	17 467	115	292
Mixed feed	17 106	81	347
Pig faeces	18 311	49	316
Urine [2]	7 184	426	957
Milk powder [2]	17 770	333	697

1) Based on air-dry matter.

2) Outliers were not removed. The indicated values are for the sum of the test portion and the polyethylene bag.

13 Test report

The test report shall specify:

- all information necessary for the complete identification of the sample;
- the sampling method used, if known;
- the test method used, with reference to this International Standard;
- all operating details not specified in this International Standard, or regarded as optional, together with details of any incidents which may have influenced the test result(s);
- the test result(s) obtained; or
- if the repeatability has been checked, the final quoted result obtained.

Annex A
(normative)

Determination of the effective heat capacity of the calorimeter

A.1 Principle

Combustion of a known mass of benzoic acid of certified calorific value in oxygen in a bomb calorimeter. Calculation of the sum of the heat of combustion of the benzoic acid, the heats of combustion of the cotton thread and the firing wire and the heat of formation of nitric acid.

Carry out at least five complete determinations of effective heat capacity. Provided that their range does not exceed 55 J/°C, take the mean of the five test results for calculation of the calorific value of the test sample (see clause 11).

A.2 Procedure

Proceed as specified in 9.3 to 9.8 for the determination of calorific value. If necessary, use the small metal crucible specified in 6.6.

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

Dilute the bomb washings to approximately 50 ml with water. Titrate the nitric acid directly with the sodium hydroxide solution (5.7) using the screened methyl orange solution (5.8) as indicator.

A.3 Calculation of a single complete determination

Calculate the effective heat capacity of the calorimeter by the equation:

$$C = \frac{m_\mathrm{b}\, Q_\mathrm{b} + e_1 + e_2 + e_3}{t_n - t_0 + t_\mathrm{c}}$$

where

C is the effective heat capacity, in joules per degree Celsius, of the calorimeter;

m_b is the mass, in grams, of benzoic acid (5.9);

Q_b is the certified gross calorific value, in joules per gram, at constant volume of benzoic acid (5.9);

e_1 is the correction for heat of combustion, in joules, of the cotton thread or the polyethylene strip (see 10.4);

e_2 is the correction for heat of combustion, in joules, of the firing wire (see 10.4);

e_3 is the correction for heat, in joules, of formation of sulfuric acid and nitric acid (see 10.5);

t_0 is the firing temperature, in degrees Celsius, corrected for the thermometer error;

t_n is the final temperature, in degrees Celsius, corrected for the thermometer error;

t_c is the cooling correction, in degrees Celsius, according to Regnault-Pfaundler for isothermal or static calorimeters (see 10.3).

A.4 Predetermined interval (adiabatic calorimeter)

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

For each of the five determinations, note the shortest time, in minutes, from the firing of the charge to reaching the second of three consecutive readings which do not differ by more than 0,001 °C.

Calculate, to the nearest 1 min, the mean of the five values to obtain the length of time of the predetermined interval. This should not exceed 10 min.

Use the predetermined interval for all determinations of calorific value, until a new value is established (e.g. when commissioning a new calorimeter). The predetermined interval shall be checked after changing any component.

A.5 Re-determination of the mean effective heat capacity

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

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

Annex B
(normative)

Special procedures for preparation of the test sample

B.1 Air-dry samples

B.1.1 Air-dry samples with a fat content exceeding 100 g/kg

Samples with a high fat content are preferably pre-extracted (see ISO 6498) and the calorific value determined for both the sample and the collected fat.

Dissolve the collected fat in hexane. Take a sample, put it into a polyethylene bag (5.4) and then treat it like a liquid (see B.2).

Alternatively, mix 10 g to 20 g of the test sample thoroughly with sufficient fine silica gel powder (5.6), so that it is possible to prepare a pellet with the briquette press (6.8.3) without separation of fat or oil. Determine the mixing ratio to the nearest 0,001.

B.1.2 Air-dry samples which cannot easily be pelleted

Weigh, to the nearest 0,1 mg, the necessary number of polyethylene bags (5.4) of known calorific value.

Weigh the required mass of the test sample in a weighed polyethylene bag and wrap up the bag. The test portion and the bag shall undergo combustion together.

B.2 Liquid samples

Weigh, to the nearest 0,1 mg, the necessary number of polyethylene bags (5.5) of known calorific value.

Place a weighed bag in a small beaker with the aid of a rod fitting in the bag. Weigh the beaker with the bag. Fill the bag with the desired quantity of liquid. Weigh the beaker with the bag and its contents again.

Evaporate the liquid to dryness in a vacuum oven at room temperature, or freeze-dry the liquid.

After complete drying, fold the bag containing the liquid residue and fit it into the bomb in which the firing wire is attached so, that a curve of wire lies in the crucible.

If combustible compounds disappear during the drying process, analyse these compounds in the wet material as well as in the material after drying, so that appropriate corrections for loss of calorific value can be made.

B.2.1 Milk samples

Before taking a sample, heat to 40 °C milk samples which have been stored, and mix them thoroughly. The sample volume shall be approximately 5 ml.

B.2.2 Urine samples

Mix the urine thoroughly. Fill the polyethylene bag (5.5) in the beaker with about 25 ml of urine. Weigh the beaker with the bag and its contents again. On drying, carefully obtain a vacuum, since acidified urine may contain much dissolved carbon dioxide.

NOTE Urine is acidified with sulfuric acid, since it is necessary to preserve the daily urine sample. Before use, the urine is neutralized.

B.3 Samples of fresh materials

B.3.1 Samples of faeces

Mix fresh faeces thoroughly. Mince them in a disc cutter mixer or similar device.

Sample the faeces at random. Constitute fresh samples for analysis from at least 10 sub-samples.

Store the samples in closed glass containers in a refrigerator.

Weigh 2 g into a polyethylene bag (5.5) in a beaker for immediate analysis.

B.3.2 Samples of other fresh materials

In general, samples of fresh faeces and other fresh materials may be analysed as such, when their moisture content is less than 70 % (m/m).

Although samples of other fresh materials, like silages, may be analysed in this way, subsequent sample preparation may cause an observed loss of moisture.

Some samples cannot be cut finely enough, even after freezing in liquid nitrogen.

Annex C
(informative)

Method of checking that the average deviation of the rate of change of temperature is within the specified limit

When an isothermal or a static calorimeter is applied, the following method may conveniently be used to check that the average deviation of the rate of change of temperature during the preliminary period and the after-period is within the specified limit.

List the five differences obtained during the 5-min period as units without the decimal place. Code them by subtracting the smallest and arrange the resulting coded differences in descending sequence.

If the sequence is listed in table C.1, the average deviation is within the specified limit. Table C.2 gives an example. The sequence 33220 is acceptable.

Table C.1 — Acceptable difference sequences

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

Table C.2 — Example

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

Annex D
(informative)

Examples of calculating the results of calorific determinations

D.1 Determination of effective heat capacity

D.1.1 Measurement data

Gross calorific value of benzoic acid (5.9) at 25,5 °C	Q_b = 26 467 J/g
Mass of benzoic acid (5.9)	m_b = 1,183 3 g
Volume of sodium hydroxide solution (5.7) used	V = 7,0 ml
Temperature rise	$t_n - t_0 + t_c$ = 3,036 °C
Final calorimeter temperature	= 25,5 °C
Correction for cotton thread (e_1) and firing wire (e_2)	$(e_1 + e_2)$ = 84 J

NOTE For adiabatic calorimeters: t_c = 0 °C

D.1.2 Calculations

Correction for acids (e_3): e_3 = (6,0 J/ml) × 7,0 ml = 42 J.

Applying the equation of clause A.3, the effective heat capacity (C) of the calorimeter is calculated as follows.

$$C = \frac{m_b\, Q_b + (e_1 + e_2) + e_3}{t_n - t_0 + t_c}$$

$$C = \frac{1{,}183\,3\ \text{g} \times 26\,467\ \text{J/g} + 84\ \text{J} + 42\ \text{J}}{3{,}036\ {}^\circ\text{C}} = \frac{31\,318\ \text{J} + 126\ \text{J}}{3{,}036\ {}^\circ\text{C}}$$

$$C = \frac{31\,444\ \text{J}}{3{,}036\ {}^\circ\text{C}} = 10\,357\ \text{J/}{}^\circ\text{C}$$

This is the result of a single determination. As specified in annex A, the determination shall be carried out at least five times.

Provided that the range of the test results does not exceed 55 J/°C, their mean is used as the effective heat capacity of the calorimeter.

D.2 Determination with an adiabatic calorimeter

D.2.1 Measurement data

Effective heat capacity of the calorimeter	C = 10 370 J/°C
Mass of the test portion	m = 0,999 2 g
Volume of sodium hydroxide solution (5.7) used	V = 17,0 ml