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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

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Contents

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Foreword

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

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

International Standard ISO 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.*

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(NaOH) = 0,1 mol/l.

5.8 Screened methyl orange indicator solution, ρ = 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 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 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.