
**Methods of testing cement —
Determination of the heat of hydration —**

Part 2:

Semi-adiabatic method

*Méthodes d'essai des ciments — Détermination de la chaleur
d'hydratation —*

Partie 2: Méthode semi-adiabatique

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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.

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

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

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

ISO 29582-2 was prepared by Technical Committee ISO/TC 74, *Cement and lime*.

ISO 29582 consists of the following parts, under the general title *Methods of testing cement — Determination of the heat of hydration*:

- *Part 1: Solution method*
- *Part 2: Semi-adiabatic method*

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Methods of testing cement — Determination of the heat of hydration —

Part 2: Semi-adiabatic method

1 Scope

This part of ISO 29582 describes a method of measuring the heat of hydration of cements by means of semi-adiabatic calorimetry, also known as the Langavant method. The aim of the test is the continuous measurement of the heat of hydration of cement during the first few days. The heat of hydration is expressed in joules per gram of cement.

This part of ISO 29582 is applicable to all cements and hydraulic binders, whatever their chemical composition, with the exception of quick-setting cements.

NOTE 1 An alternative procedure, called the solution method, is described in ISO 29582-1. Either procedure can be used independently.

NOTE 2 It has been demonstrated that the best correlation between the two methods is obtained at 41 h for the semi-adiabatic method in this part of ISO 29582 compared with 7 d for the heat of solution method in ISO 29582-1.

2 Normative references

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

ISO 679¹⁾, *Cement — Test methods — Determination of strength*

EN 197-1, *Cement — Part 1: Composition, specifications and conformity criteria for common cements*

EN 573-3, *Aluminium and aluminium alloys — Chemical composition and form of wrought products — Part 3: Chemical composition and form of products*

3 Principle

The semi-adiabatic method consists of introducing a sample of freshly made mortar into a calorimeter in order to determine the quantity of heat emitted in accordance with the development of the temperature. At a given point in time, the heat of hydration of the cement contained in the sample is equal to the sum of the heat accumulated in the calorimeter and the heat lost into the ambient atmosphere throughout the period of the test.

1) To be published. (Revision of ISO 679:1989)

The temperature rise of the mortar is compared with the temperature of an inert sample in a reference calorimeter. The temperature rise depends mainly on the characteristics of the cement and is normally between 10 K and 50 K.

4 Apparatus

4.1 Calorimeter, consisting of an insulated flask sealed with an insulated stopper and encased in a rigid casing which acts as its support (see Figure 1).

The calorimeter shall have the following performance characteristics. The coefficient of total heat loss of the calorimeter shall not exceed $100 \text{ J}\cdot\text{h}^{-1}\cdot\text{K}^{-1}$ for a temperature rise of 20 K. This value, together with the thermal capacity, shall be determined in accordance with the calibration procedure given in A.3.1.

Recalibration is necessary

- at least every four years or after 200 tests;
- whenever deterioration occurs in the calorimeter or an insulating component.

In order not to impair the insulation of the calorimeter, the temperature of the mortar under test shall not exceed 75 °C.

Both the calorimeter used for the test and that for the reference (see 4.2) shall have the following construction and characteristics.

a) **Flask**, insulated (e.g. Dewar flask), made of silver-plated borosilicate glass, cylindrical in shape with a hemispherical bottom.

The internal dimensions shall be approximately 95 mm in diameter and 280 mm in depth and the external diameter, approximately 120 mm. A rubber disc of approximately 85 mm in diameter and 20 mm thick shall be placed at the bottom of the flask to act as support for the sample container and evenly distribute the load on the glass wall.

b) **Casing**, very rigid, having a sufficiently wide base to ensure good stability of the whole unit (e.g. made of duralumin, 3 mm thick).

The flask shall be separated from the lateral walls of the casing by an air space of approximately 5 mm and rest on a support 40 mm to 50 mm thick made of a material having low thermal conductivity (e.g. expanded polystyrene). The upper edge of the flask shall be protected by a rubber gasket above which, and in contact with it, shall be a ring not less than 5 mm thick, made of a low-thermal-conductivity material, fixed to the calorimeter casing. The ring shall serve to locate the flask in position and provide a bearing surface for the stopper so as to ensure the tightness of the locking device.

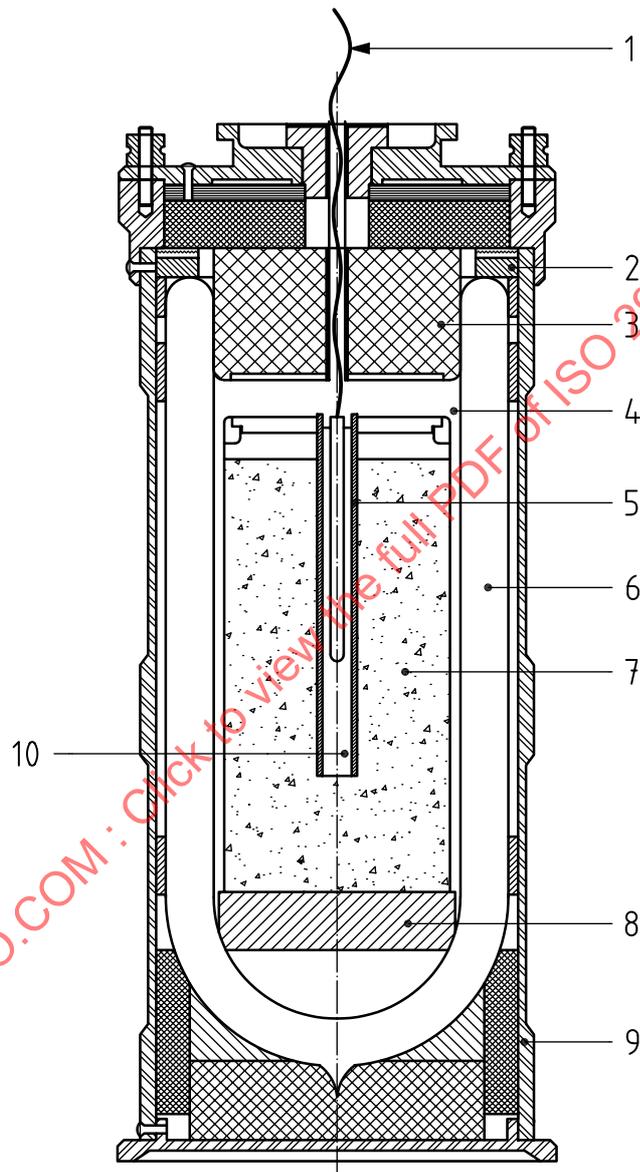
c) **Stopper**, insulating, made of the following three parts.

- The lower part, which is inserted into the flask and which serves to provide a maximum prevention of heat loss into the external atmosphere. It shall be cylindrical in shape, of diameter equal to the internal diameter of the flask, and approximately 50 mm thick. It shall be made of expanded polystyrene (class 20 kg/m³ approximately) or of another material of similar thermal characteristics. Its base can be protected by a layer of plastic (e.g. polymethyl methacrylate), approximately 2 mm thick.
- The central part, which serves to ensure the tightness of the calorimeter whilst contributing to the reduction of losses, shall consist of a foam rubber disc 120 mm in diameter.
- The upper part, which is intended to ensure the correct and consistent positioning of the stopper unit against the Dewar flask, shall consist of a rigid casing incorporating a snap locking device in such a way as to compress the foam rubber central part ensuring the tight fitting of the stopper.

4.2 Reference calorimeter, having the same construction and characteristics as the test calorimeter (4.1).

It shall contain a mortar box in which there is a sample of mortar mixed at least 12 months previously and which is considered to be inert.

Where an inert sample is not available, an aluminium cylinder of the same thermal capacity as the mortar box and mortar sample may be used.



Key

- | | | | |
|---|---------------------------------|----|---------------|
| 1 | platinum resistance thermometer | 6 | dewar flask |
| 2 | gasket | 7 | mortar sample |
| 3 | insulating stopper | 8 | rubber disc |
| 4 | mortar box | 9 | rigid casing |
| 5 | thermometer pocket | 10 | oil |

Figure 1 — Typical calorimeter

4.3 Thermometers, platinum resistance, for the reference calorimeter and each test calorimeter, having a minimum range of 19 °C to 75 °C. If the conductors of the electrical resistor are made of copper, they shall have a cross-sectional area not greater than 0,25 mm² in the part which passes through the stopper. If they are made of another metal, the total thermal resistance per centimetre of conductor shall be greater than 0,10 K·mW⁻¹ (thermal resistance equivalent to that of a copper conductor with a sectional area of 0,25 mm² and 1 cm long).

The thermal output of the thermometer shall not exceed 3 mW. Direct current supply, which constitutes a power input, shall be avoided if the thermal output exceeds 0,2 mW. It is advisable to ensure the accuracy of the overall temperature measuring and recording equipment.

The temperature of the test sample shall be measured to an accuracy of ± 0,3 °C.

Where the calorimeter is calibrated *in situ* with the conductors used for the tests of heat of hydration, the total cross-sectional area of the conductors will be a maximum of 0,80 mm² (four wires, 0,5 mm in diameter), but shall be such that the coefficient of heat loss of the calorimeter is less than 100 J·h⁻¹·K⁻¹ for a temperature rise of 20 K; see A.3.1.1.

The protective sheath of these conductors shall be made of a material having a low thermal conductivity.

4.4 Mortar box, consisting of a cylindrical container fitted with a cover, having a volume of approximately 800 cm³, designed to contain the sample of mortar under test.

The mortar box, discarded after each test, shall be impermeable to water vapour. This shall be checked in use by weighing the mortar box after each test (see 5.2.3). It shall be made of electrically counter-welded tin plate with a nominal thickness of 0,3 mm and shall have a diameter of approximately 80 mm and a height of approximately 165 mm. Its height shall be designed to provide an air space of approximately 10 mm between the top of the mortar box and the stopper.

The lid of the mortar box shall be fitted with a central thermometer pocket in the form of a cylindrical pipe, closed at its base. The internal diameter of the pocket shall be slightly greater than that of the thermometer. Its length shall be approximately 100 mm to 120 mm and enable it to extend to the centre of the test sample.

4.5 Temperature-recording apparatus, capable of recording the measurements taken by each thermometer.

4.6 Mortar mixing apparatus, conforming to ISO 679.

5 Determination of the heat of hydration

5.1 Laboratory

The laboratory where the mortar is mixed shall be maintained at a temperature of (20 ± 2) °C.

The room where the test is carried out shall be maintained at a temperature of (20,0 ± 1,0) °C. The measured temperature of the reference calorimeter shall be considered to be the ambient temperature and shall be maintained during the test within ± 0,5 °C. The distance between each of the calorimeters shall be approximately 120 mm. The velocity of the ventilation air around the calorimeters shall be less than 0,5 m·s⁻¹.

When several tests are being carried out simultaneously, at least one reference calorimeter shall be provided for every six test calorimeters; where several test calorimeters are used with one reference calorimeter, a hexagonal arrangement shall be used with the reference calorimeter in the centre.

5.2 Procedure

5.2.1 Mortar composition

The composition of the mortar shall be in accordance with ISO 679 and the test sample shall have a total mass of $(1\,575 \pm 1)$ g. Each batch of mortar being mixed shall consist of $(360,0 \pm 0,5)$ g of cement; $(1\,080 \pm 1)$ g of sand from a sample of standard sand in accordance with the requirements of ISO 679; and $(180,0 \pm 0,5)$ g of distilled or deionized water.

Since it is not possible to recover all the material added to the mixer bowl, the mortar batch being mixed should be slightly more than 1 575 g, the proportions by mass of the various constituents being maintained.

5.2.2 Mixing

The cement, the water, the sand, the mortar box, the mixer bowl and the other instruments coming into contact with the mortar shall be stored in the test room.

With the mixer in the operating position, pour the sand and then the cement into the mixer bowl; homogenize the mixture of sand and cement for 30 s at low speed; pour in the water, record the time, and mix immediately at low speed for 60 s; set the mixer to high speed and mix for a further 60 s.

In order to avoid thermal losses, it is recommended to carry out the mixing in a relatively short time. It is for this reason that the mixing time prescribed in ISO 679 has been shortened.

5.2.3 Positioning of the test sample

Immediately after mixing, weigh $(1\,575 \pm 1)$ g of mortar into the box (4.4), which has previously been weighed, with its lid, to an accuracy of $\pm 0,5$ g. Place the lid in position, making sure that it seals tightly. Fill the thermometer pocket with $(2,5 \pm 0,5)$ cm³ of oil (e.g. thin mineral oil) in order to improve the thermal contact between the test sample and the thermometer.

Weigh the filled mortar box, to an accuracy of $\pm 0,5$ g, in order to be able to check at the end of the test for any leakage of water vapour. Immediately after weighing, place the mortar box in the test calorimeter (4.1) and close with the stopper. Immediately place the thermometer (4.3) in position in the thermometer pocket, so that it is approximately in the centre of the test sample. Seal the opening across the stopper by means of the locking device.

NOTE The stopper can also be sealed by means of a flexible sealant or mastic.

Do not take more than 6 min for the mixing and the positioning of the test sample.

At the end of the test, weigh the mortar box with its contents again, to an accuracy of $\pm 0,5$ g. If a reduction in mass of more than 2 g is found, the test is not valid and shall be repeated.

5.3 Measurement of heating

The time of addition of water shall be taken as the start of timing. The measurement of heating consists of reading, at specific moments in time, the temperature of the test sample and that of the inert sample located in the reference calorimeter (4.2).

At least one reading shall be taken in the first 30 min followed by readings at least every 1 h for the first 24 h; every 4 h during the second day; and every 6 h until the expiry of the selected test period. The frequency of these measurements may be increased according to the characteristics of the cement being tested. The time of each temperature reading shall be recorded in hours and minutes.

At each temperature reading, the temperature rise of the test sample, θ_t , shall be determined as the difference between the temperature of the test sample, T_s , and that of the inert sample, T_r , in the reference calorimeter.

6 Calculation of the heat of hydration

NOTE A worked example is given in Annex B.

6.1 Principles of calculations

The heat of hydration, Q_{hyd} , expressed in joules per gram of cement, at elapsed time, t , is calculated from Equation (1):

$$Q_{\text{hyd}} = \frac{c}{m_c} \theta_t + \frac{1}{m_c} \int_0^t \alpha \cdot \theta_t dt \quad (1)$$

where

- m_c is the mass of cement contained in the test sample, expressed in grams;
- t is the hydration time, expressed in hours;
- c is the total thermal capacity of the calorimeter (see 6.2), expressed in joules per kelvin;
- α is the coefficient of heat loss of the calorimeter (see 6.3), expressed in joules per hour per kelvin;
- θ_t is the difference in the temperature of the test calorimeter compared with that of the reference calorimeter (see 5.3) at time, t , expressed in kelvin.

The first term in Equation (1) represents the heat, Q_A , accumulated in the calorimeter, and the second term represents the heat, Q_B , lost into the ambient atmosphere, both expressed in joules per gram of cement.

Equation (1) can be simplified to Equation (2):

$$Q_{\text{hyd}} = \frac{c}{m_c} \theta_t + \frac{1}{m_c} \sum_{i=1}^n \bar{\alpha}_i \cdot \bar{\theta}_i \cdot \Delta t_i \quad (2)$$

where

- $\bar{\alpha}_i$ is the mean value of the coefficient of heat loss of test sample during period of time, Δt_i ;
- $\bar{\theta}_i$ is the mean value of the temperature rise of test sample during period of time, Δt_i .

6.2 Calculation of the heat accumulated in the calorimeter

The heat, Q_A , expressed in joules per gram of cement, accumulated in the calorimeter shall be calculated from the total thermal capacity, c , of the calorimeter, the mass of cement, m_c , and the difference in the temperature of the test calorimeter compared with that of the reference calorimeter, θ_t , at point in time, t , by Equation (3):

$$Q_A = \frac{c}{m_c} \theta_t \quad (3)$$

where the total thermal capacity of the calorimeter, c , including the mortar box and mortar sample under test is expressed by Equation (4):

$$c = 0,8(m_c + m_s) + 3,8m_w + 0,50m_b + \mu \quad (4)$$

where

- 0,8 is the thermal capacity per unit of mass of cement plus sand, expressed in joules per kelvin per gram;

- 3,8 is the average thermal capacity per unit of mass of water, expressed in joules per kelvin per gram;
- 0,50 is the thermal capacity per unit of mass of the mortar box, expressed in joules per kelvin per gram;
- μ is the thermal capacity of the empty calorimeter, expressed in joules per kelvin;
- m_c is the mass of cement, expressed in grams;
- m_s is the mass of sand, expressed in grams;
- m_w is the mass of water, expressed in grams;
- m_b is the mass of empty mortar box plus lid, expressed in grams.

NOTE Bound water has a thermal capacity per unit of mass lower than $4,18 \text{ J}\cdot\text{K}^{-1}\cdot\text{g}^{-1}$.

6.3 Calculation of heat lost to ambient atmosphere

Heat lost shall be calculated for known periods of hydration represented by the time elapsed between successive measurements of the temperature of the test sample; see 5.3.

The coefficient of heat loss, α , expressed in joules per hour per kelvin, of the calorimeter is given by Equation (5):

$$\alpha = a + b \cdot \theta \quad (5)$$

where

a and b are the calorimeter calibration constants; see A.3.1.1;

θ is the temperature rise, expressed in kelvin.

The heat lost into the ambient atmosphere, Q_B , expressed in joules per gram of cement, during the period of hydration, t_n , is given by Equation (6):

$$Q_B = \frac{1}{m_c} \sum_{i=1}^n \bar{\alpha}_i \cdot \bar{\theta}_i \cdot \Delta t_i \quad (6)$$

where

Δt_i is the elapsed time between the measurement of temperature at point in time, t_{i-1} , and the next measurement at point in time, t_i , expressed in hours;

$\bar{\theta}_i$ is the average of the temperature rise of the test sample, between times t_i and t_{i-1} , expressed in kelvin, as given by Equation (7):

$$\bar{\theta}_i = \frac{\theta_i + \theta_{i-1}}{2} \quad (7)$$

where $\bar{\alpha}_i$ is the average coefficient of total heat loss of the calorimeter (see Equation 5) in the period of time, Δt_i , expressed in joules per hour per kelvin, as given by Equation (8):

$$\bar{\alpha}_i = a + b \cdot \bar{\theta}_i \quad (8)$$

6.4 Calculation of heat of hydration

The heat of hydration, Q_{hyd} , expressed in joules per gram of cement, shall be calculated as the sum of the heat accumulated in the calorimeter and the heat lost into the ambient atmosphere, as given by Equation (9):

$$Q_{\text{hyd}} = Q_A + Q_B \quad (9)$$

7 Expression of results

The results of the measurements shall be set out in a test report, normally in the form of a table, indicating: the heat of hydration, expressed in joules per gram of cement, at the specified hydration age and including intermediate results (e.g. at 12 h, 1 d, 2 d, 3 d, 5 d and 7 d), as applicable.

The results reported for the heat of hydration shall be expressed in joules per gram of cement, to the nearest whole number.

8 Precision

8.1 Repeatability

The standard deviation of repeatability, σ_r , of the heat of hydration determination is $5 \text{ J}\cdot\text{g}^{-1}$.

Therefore, if the results of two properly conducted tests from the same laboratory on samples of the same cement are compared, they should not differ from each other by more than $14 \text{ J}\cdot\text{g}^{-1}$.

8.2 Reproducibility

The standard deviation of reproducibility, σ_R , is $15 \text{ J}\cdot\text{g}^{-1}$.

Therefore, if the results of two properly conducted tests from two different laboratories on samples of the same cement are compared, they should not differ from each other by more than $42 \text{ J}\cdot\text{g}^{-1}$.

9 Test report

9.1 The report shall include the following:

- a) identification of the test specimen;
- b) date of test;
- c) test results as detailed in Clause 7;
- d) any deviations from the standard method of testing;
- e) declaration from the person technically responsible for the test that the testing was carried out in accordance with this part of ISO 29582, except as detailed in item d).

9.2 The report may include the following:

- a) mass of the specimen;
- b) condition of the specimen on receipt.

Annex A (normative)

Calibration of the calorimeter

A.1 Principle

The calibration method consists of replacing the mortar box and test sample in the calorimeter being calibrated with a calibration cylinder (see A.2.4) of equivalent dimensions. A known electrical supply is applied to the calibration cylinder causing it to increase in temperature. The amount of electrical energy applied is equal to the increased heat in the calorimeter and the heat lost to atmosphere. The determination of heat lost is made from the electrical energy required to maintain a constant temperature. The determination of the thermal capacity is made by disconnecting the electrical supply and measuring the rate of fall in calorimeter temperature.

NOTE The time required for a calorimeter to reach thermal equilibrium (steady state) is at least 8 d. When moving from one calibration temperature to the next, by applying the new input voltage at the resistor terminals, the time required to reach a new steady state condition is approximately 6 d.

A.2 Apparatus and power supply

A.2.1 Reference calorimeter (see 4.2), placed approximately 120 mm from the calorimeter being calibrated.

A.2.2 Voltmeter, DC, with an accuracy of $\pm 0,1\%$, operable between 0 V and 100 V.

A.2.3 Resistor measuring bridge or ohmmeter, with an accuracy of $\pm 0,2\%$.

A.2.4 Calibration cylinder (see Figure A.1), composed of an aluminium core on which is wound a resistor of known value of at least 2 000 Ω , using a material with a high resistivity (e.g. constantan wire of 0,2 mm diameter).

The characteristics of the aluminium used for the core shall be designated: EN AW 1080 A, in accordance with EN 573-3, which corresponds to 99,8 % aluminium of specific heat $900 \text{ J}\cdot\text{kg}^{-1}\cdot\text{K}^{-1}$.

The core shall be screwed into a jacket having the same dimensions as the mortar box (see Figure 1 and 4.4); the connecting wires of the resistor shall have a small sectional area ($0,05 \text{ mm}^2$ maximum) in order to avoid thermal losses.

A.2.5 Thermometers, platinum resistance, fitted with conductors complying with the requirements for maximum sectional area set out in 4.3 for the part that passes through the stopper of the calorimeter and accurate to $\pm 0,15 \text{ }^\circ\text{C}$ over the temperature range $20 \text{ }^\circ\text{C}$ to $60 \text{ }^\circ\text{C}$.

A.2.6 Power supply, stabilized, with a voltage adjustable between 2 V and 60 V minimum; a stability as a function of load of $\Delta V/V \leq 2 \cdot 10^{-4}$; and a stability as a function of the mains voltage of $\Delta V/V \leq 1 \cdot 10^{-4}$.

A.2.7 Test room, with conditions maintained in accordance with 5.1.

A.3 Calibration procedure

A.3.1 Determination of the coefficient of total heat loss, α

A.3.1.1 Procedure

The coefficient, α , shall be obtained by measuring, in steady state conditions

- a) the heat output emitted by Joule effect in the calibration cylinder (see A.2.4) previously placed in the calorimeter being calibrated;
- b) the temperature of this cylinder in relation to the temperature of the inert test sample placed in the reference calorimeter located close by; see A.2.1.

When steady state conditions are achieved, the heat supplied is equal to that lost to the ambient atmosphere. Rate of loss of heat, P , expressed in watts, is given by Equation (A.1):

$$P = V^2 \cdot R^{-1} = \alpha \cdot \theta_c \quad (\text{A.1})$$

where

V is the input voltage at resistor terminals, expressed in volts;

R is the resistance of the heating coil, expressed in ohms;

θ_c is the temperature difference between the calibration cylinder and the inert reference sample, expressed in kelvin;

α is the coefficient of total heat loss of the calorimeter at temperature difference, θ_c , expressed in joules per hour per kelvin.

Equation (A.1) can be rearranged to give the coefficient of total heat loss, expressed in watts per kelvin as given by Equation (A.2) or expressed in joules per hour per kelvin as given by Equation (A.3):

$$\alpha = V^2 \cdot R^{-1} \cdot \theta_c^{-1} \quad (\text{A.2})$$

$$\alpha = 3\,600 \cdot V^2 \cdot R^{-1} \cdot \theta_c^{-1} \quad (\text{A.3})$$

The measurement of rate of loss of heat shall be made with an accuracy of $\pm 0,5\%$. Since the coefficient, α , approximates a linear function of θ , it can be determined with the required accuracy by calculation at five points within the temperature range anticipated during tests; see Table A.1.

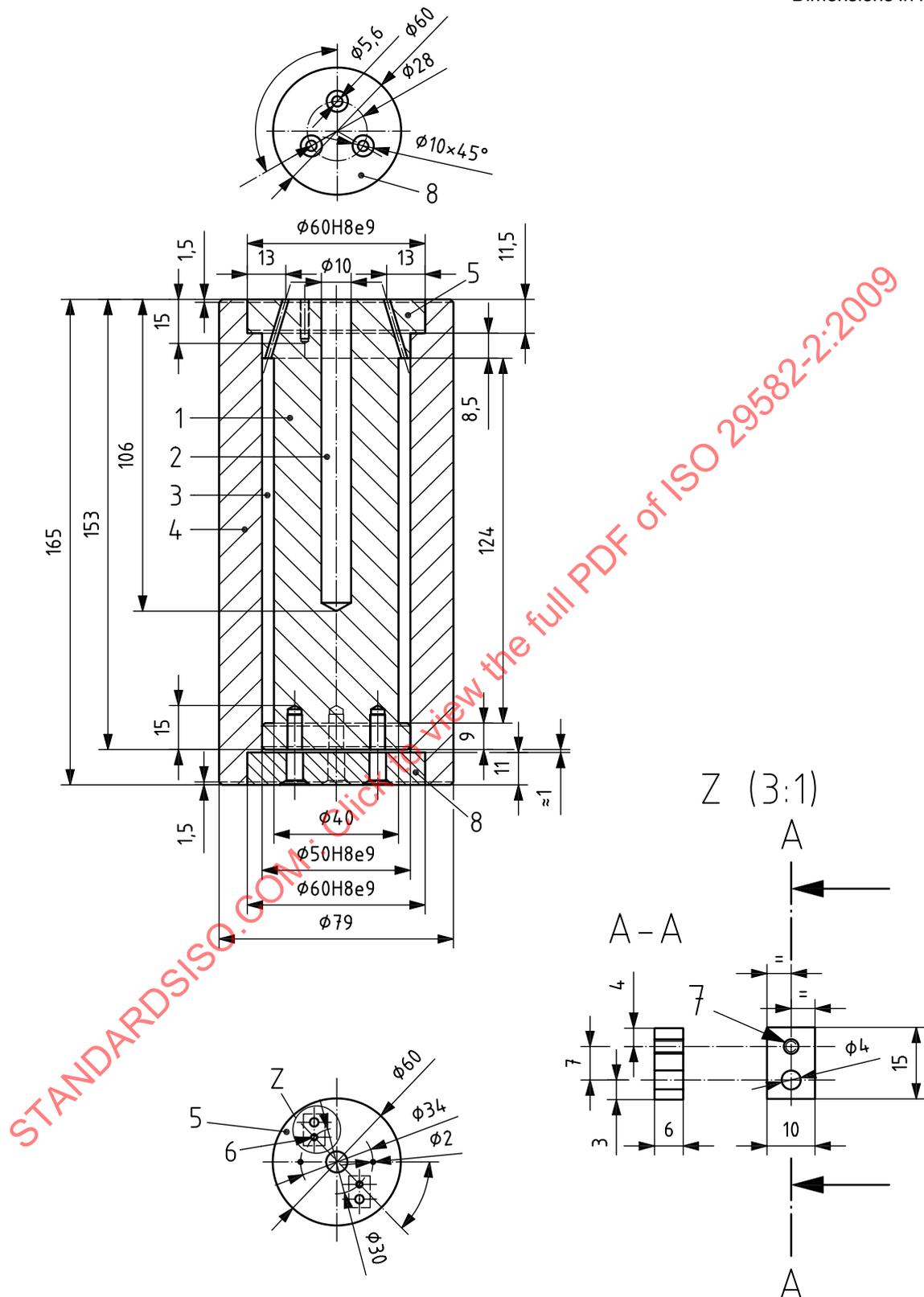
For example, measurements may be made for temperature rises of approximately 10 K, 17 K, 24 K, 31 K and 38 K.

Having determined the five values of α , the equation for the calibration line can be written as Equation (A.4):

$$\alpha = a + b \cdot \theta_c \quad (\text{A.4})$$

and the constant terms a and b shall be calculated by the method of least squares. The calibration points shall approximate a straight line; if the coefficient of linear correlation is less than 0,97, the calibration shall be repeated. The coefficient, α , shall not exceed $100 \text{ J} \cdot \text{h}^{-1} \cdot \text{K}^{-1}$ for a temperature rise of 20 K.

Dimensions in millimetres



Key

- | | | | |
|----------------------|------------|------------------------|------------------|
| 1 aluminium core | 3 resistor | 5 capping plate | 7 tapped hole m4 |
| 2 thermometer pocket | 4 jacket | 6 connector (plastics) | 8 base plate |

Figure A.1 — Typical calibration cylinder

A.3.1.2 Example calculation

The following worked example [see Table A.1 and Equation (A.3)] sets out the calculation stages:

Table A.1 — Measurement of coefficient of total heat loss, α

Temperature of calibration cylinder, °C	31,60	37,10	41,70	48,40	58,70
Reference temperature, °C	19,97	19,83	19,77	19,80	19,88
Temperature difference θ_c , K	11,63	17,27	21,93	28,60	38,82
Voltage V , V	20,78	25,52	28,95	33,48	39,60
Resistance R , Ω	2 036	2 036	2 036	2 036	2 036
Output P , W	0,212 1	0,319 9	0,411 6	0,550 5	0,770 2
Coefficient α , J·h ⁻¹ ·K ⁻¹	65,65	66,68	67,57	69,30	71,43

Analysis of the straight line equation, $\alpha = a + b \cdot \theta$ results in the values of 63,0 for a and 0,216 for b with a coefficient of linear correlation of 0,99.

The value of the coefficient of total heat loss for the calorimeter, α , for a temperature rise of 20 K, is calculated as $(63 + 0,216 \times 20) = 67,3 \text{ J}\cdot\text{h}^{-1}\cdot\text{K}^{-1}$ and, as the coefficient of linear correlation is 0,99, the calibration is, therefore, valid and the calorimeter meets the performance requirements.

A.3.2 Determination of the thermal capacity

A.3.2.1 Procedure

The measurement of the thermal capacity, μ , of the empty calorimeter shall be carried out by the method of spontaneous cooling. For this purpose, the calibration cylinder shall be disconnected from its electrical power supply after reaching the steady state condition for the last point of calibration to determine α ; see A.3.1. Determine the total thermal capacity, c_T , of the calorimeter containing the calibration cylinder (see A.2.4) of known thermal capacity, c_c , from which that of the empty calorimeter itself, μ , shall be calculated.

The thermal capacity of the calibration cylinder shall be calculated by weighting by mass the specific heats of the different elements which constitute the cylinder.

During cooling, the heat exchange, $-c_T d\theta$, is given by Equation (A.5):

$$\begin{aligned}
 -c_T \cdot d\theta &= \alpha \cdot \theta \cdot dt \\
 &= (a + b \cdot \theta) \cdot \theta \cdot dt
 \end{aligned}
 \tag{A.5}$$

The total thermal capacity, c_T , of the calorimeter containing the calibration cylinder, in joules per kelvin, can be calculated from Equation (A.5) as expressed by Equation (A.6):

$$c_T = \frac{\alpha \cdot t_d}{\text{Ln}[(\theta_0 \cdot \alpha_t) / (\theta_t \cdot \alpha_0)]}
 \tag{A.6}$$

where

t_d is the elapsed time since disconnecting the power supply, expressed in hours;

θ_0 is the temperature difference between the calibration cylinder and the inert reference sample, expressed in kelvin;

θ_t is the temperature difference at a point in time, t_d , expressed in kelvin;

α_0 is the coefficient of total heat loss, expressed in joules per hour per kelvin, for the temperature difference, θ_0 ;

α_t is the coefficient of total heat loss, expressed in joules per hour per kelvin, for the temperature difference, θ_t .

The initial temperature difference, θ_0 , shall be between 35 K and 40 K. The value of the thermal capacity of the empty calorimeter, μ , in joules per kelvin, shall be calculated from Equation (A.7):

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The cooling period shall be between 22 h and 30 h.

A.3.2.2 Example calculation

The following worked example (see Table A.2) sets out the calculation stages:

Table A.2 — Measurement of thermal capacity of empty calorimeter, μ

Time, h	0	22	24	26	28
Temperature of calibration cylinder, °C	58,70	39,50	38,32	37,23	36,20
Reference temperature, °C	19,88	19,81	19,79	19,79	19,77
Temperature difference, θ , K	38,82	19,69	18,53	17,44	16,43
Coefficient of total thermal loss, α , J·h ⁻¹ ·K ⁻¹	71,39	67,25	67,00	66,77	66,55
Total thermal capacity, c_T , J·K ⁻¹	—	2 238	2 236	2 234	2 234
Thermal capacity of cylinder, c_C , J·K ⁻¹	—	1 852	1 852	1 852	1 852
Thermal capacity of empty calorimeter, μ , J·K ⁻¹	—	386	384	382	382

The thermal capacity of the cylinder is calculated as 1 852 J·K⁻¹; see A.3.2.1. From the above, the average thermal capacity of the calorimeter is 384 J·K⁻¹.

The initial temperature rise was 38,82 K and the test period was 28 h; therefore, the determination meets the requirements for a valid calibration.