

SLOVENSKI STANDARD

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**Sodobna tehnil' na keramika - Monolitna keramika - Termofizikalne lastnosti - 3.
del: Ugotavljanje posebne toplotne kapacitete**

Advanced technical ceramics - Monolithic ceramics. Thermo-physical properties - Part 3:
Determination of specific heat capacity

Hochleistungskeramik - Monolithische Keramik - Thermophysikalische Eigenschaften -
Teil 3: Bestimmung der spezifischen Wärmekapazität

Céramiques techniques avancées - Céramiques monolithiques. Propriétés
thermophysiques - Partie 3: Détermination de la chaleur spécifique

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**Advanced technical ceramics - Monolithic ceramics. Thermo-
physical properties - Part 3: Determination of specific heat
capacity**

Céramiques techniques avancées - Céramiques
monolithiques. Propriétés thermophysiques - Partie 3 :
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der spezifischen Wärmekapazität

This European Standard was approved by CEN on 9 December 2004.

CEN members are bound to comply with the CEN/CENELEC Internal Regulations which stipulate the conditions for giving this European Standard the status of a national standard without any alteration. Up-to-date lists and bibliographical references concerning such national standards may be obtained on application to the Central Secretariat or to any CEN member.

This European Standard exists in three official versions (English, French, German). A version in any other language made by translation under the responsibility of a CEN member into its own language and notified to the Central Secretariat has the same status as the official versions.

CEN members are the national standards bodies of Austria, Belgium, Cyprus, Czech Republic, Denmark, Estonia, Finland, France, Germany, Greece, Hungary, Iceland, Ireland, Italy, Latvia, Lithuania, Luxembourg, Malta, Netherlands, Norway, Poland, Portugal, Slovakia, Slovenia, Spain, Sweden, Switzerland and United Kingdom.

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Foreword

This document (EN 821-3:2005) has been prepared by Technical Committee CEN/TC 184 "Advanced technical ceramics", the secretariat of which is held by BSI.

This European Standard shall be given the status of a national standard, either by publication of an identical text or by endorsement, at the latest by August 2005, and conflicting national standards shall be withdrawn at the latest by August 2005.

EN 821 *Advanced technical ceramics — Monolithic ceramics - Thermo-physical properties* consists of the following parts:

Part 1: *Determination of thermal expansion*

Part 2: *Determination of thermal diffusivity by the laser flash (or heat pulse) method*

Part 3: *Determination of specific heat capacity*

This document supersedes ENV 821-3:1993

According to the CEN/CENELEC Internal Regulations, the national standards organizations of the following countries are bound to implement this European Standard: Austria, Belgium, Cyprus, Czech Republic, Denmark, Estonia, Finland, France, Germany, Greece, Hungary, Iceland, Ireland, Italy, Latvia, Lithuania, Luxembourg, Malta, Netherlands, Norway, Poland, Portugal, Slovakia, Slovenia, Spain, Sweden, Switzerland and United Kingdom.

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1 Scope

This document specifies two methods for the determination of specific heat capacity of advanced monolithic technical ceramic materials based on drop calorimetry (Method A) and differential scanning calorimetry (DSC, Method B) over a temperature range from room temperature upwards, depending on the design of the equipment.

NOTE 1 The methods described apply in the case of test materials free from phase transformations, annealing effects or partial melting. If any such effect occurs in a material over the temperature range of the test, spurious results will be obtained unless the data are carefully analysed. In such cases it is usually necessary to conduct repeat tests at a number of temperatures close to the discontinuity, in order to estimate correctly its contribution to the apparent heat capacity.

NOTE 2 Care should be exercised in both methods over the selection of the cell or crucible material and in the selection of the test atmosphere, especially at high temperatures. Test pieces can react with the crucible or the atmosphere, leading to spurious results. In general, an awareness of such problems should be maintained at all times. Especially with regard to Method B, awareness should also be maintained of radiation effects at temperatures above 1000 °C, and of the reproducibility of the output signal.

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.

EN 60584-1, *Thermocouples* Part 1: *Reference tables*

EN 60584-2, *Thermocouples* Part 2: *Tolerances*

EN ISO/IEC 17025: 2000, *General requirements for the competence of testing and calibration laboratories* (ISO/IEC 17025:1999)

3 Terms and definitions

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

3.1

enthalpy, ΔH

heat content of an object in joules released or absorbed as a result of a temperature change.

3.2

specific heat capacity, c_p

amount of heat (q) in joules required to raise the temperature of a 1 g mass by 1 °C at temperature T at constant pressure, in accordance with the equation

$$c_p = \frac{dq}{dT} = \frac{1}{m} \frac{dQ}{dT} \quad (1)$$

where Q is the total heat required for a test piece of mass m .

3.3

mean specific heat capacity, $\overline{c_p}$

amount of heat (q) required to raise the temperature of a 1 g mass from temperature T_1 to temperature T_2 , divided by the temperature interval in degrees Celsius at constant pressure, i.e:

$$\overline{c_p} = \frac{q(T_1 \rightarrow T_2)}{T_2 - T_1} = \frac{Q(T_1 \rightarrow T_2)}{m(T_2 - T_1)} = \frac{\Delta H}{m(T_2 - T_1)} \quad (2)$$

3.4

calorimeter

device for measuring the amount of heat input to or output from a test piece.

3.5

drop calorimeter

calorimeter into which a test piece at initially high temperature is dropped and allowed to cool, and the total heat content (enthalpy) of the test piece is measured as a temperature rise or other parameter in the calorimeter.

3.6

differential scanning calorimeter

device in which the difference in energy input into a test piece and into a calibrant may be measured as a function of temperature while subjected to a temperature controlled heating or cooling schedule. This difference is related to the difference in heat capacity between the test piece and the calibrant.

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4 Method A – Drop calorimetry

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4.1 General

This method may be used for measurements up to a temperature of 2000 °C.

4.2 Principle

A test piece, sealed in a crucible where necessary, is heated to the required temperature suspended in a vertical tube furnace positioned above a receiving calorimeter. A shutter prevents radiative heat from the furnace from reaching the calorimeter. The calorimeter may be any suitable device for recording the total amount of heat extracted from the test piece to cool it to the ambient temperature. The test piece, or crucible containing the test piece, is allowed to drop through the shutter into the calorimeter. The response of the calorimeter is monitored continuously. The output curve is analysed, incorporating the calibrated response of the calorimeter and of the crucible if used, and the mean specific heat capacity is calculated.

NOTE Using several determinations of c_p over different temperature ranges, the true c_p at temperature T can be estimated by curve-fitting routines (see 4.6).

Adherence to the procedure described below should provide results with an accuracy of better than 5% up to 1600 °C.

4.3 Apparatus

4.3.1 A vertical tube furnace of suitable design and maximum temperature capability is controlled by a Pt/Pt 13 % Rh or Pt/Pt 10 % Rh thermocouple (for temperatures to 1650 °C) or other suitable type (for higher temperatures) connected to a temperature controller capable of maintaining a given temperature to a constancy of ± 1 °C. The temperature profile of the furnace shall be such as to contain a section of at least twice the length of the crucible or test piece which is at constant temperature to within $\pm 0,5$ °C (see 4.4).

A capability for operating with an inert atmosphere is required for the testing of non-oxide materials at elevated temperatures.

4.3.2 The calorimeter may comprise any suitable device for receiving the hot test piece and for recording the total heat transmitted to it from the test piece. An example based on a massive copper block is shown in Figure 1. Other examples include an ice calorimeter in which the heat transmitted is recorded as the melting of ice through the volume decrease incurred, observed using a capillary level indicator.

NOTE A simple water immersion calorimeter is not recommended for initial test piece temperatures above 100 °C.

Whichever type is employed, it shall be capable of calibration using reference materials or a known amount of electrical power. In the example of a massive copper block, the tapered central hole is designed to mate with the crucible or test piece to provide intimate thermal contact. The block contains a resistance heater and a platinum resistance thermometer. It is supported on three adjustable locating pins incorporating thermally insulating sections.

4.3.3 The calorimeter is placed inside a vessel in a temperature-controlled environment, such as an oil bath as shown in Figure 2. The temperature of the environment shall be constant to within $\pm 0,1$ °C over periods of 15 min.

4.3.4 The test piece shall be either a solid test sample of size and shape appropriate to the calorimeter, or shall comprise fragments or a powder. It may be either:

- a) enclosed in a platinum crucible with a tight-fitting or sealed lid, with geometry suitable for making intimate thermal contact with the calorimeter, and with the capability of being sealed and suspended by a platinum wire (all samples); or
- b) in a form capable of having a platinum suspension wire attached at its upper end (solid samples only).

NOTE The use of a crucible enables the test to be employed on powdered samples, which is especially advantageous for calibration purposes using a reference powder.

4.3.5 There shall be an arrangement whereby either the crucible or the test piece (depending upon the design and operation of the apparatus) suspended in the furnace may be dropped through a radiation screen, such as a shutter mechanism timed to open for the passage of the test piece and to close after its passage.

NOTE This minimizes the heat flux directly radiated from the hot furnace to the calorimeter.

4.3.6 A balance is required to weigh the test piece to the nearest 0,001 g.

4.4 Temperature measurement and calibration

4.4.1 For furnace temperatures below 1650 °C, the initial temperature of the test piece in the furnace shall be measured by a Pt/Pt 13 % Rh (Type R) or Pt/Pt 10 % Rh (Type S) thermocouple with a tolerance conforming to EN 60584-2, allowing use of the reference tables in EN 60584-1, or alternatively calibrated in a manner traceable to the International Temperature Scale.

For furnace temperatures above 1650 °C, an alternative thermocouple type shall be required.

A thermocouple shall be sited with its junction on the inside of the furnace tube in order to record furnace wall temperature. A similar thermocouple shall be placed inside a platinum capsule or a dummy test piece. The furnace wall temperature shall be allowed to equilibrate for at least 15 min. The capsule or dummy test piece shall then be raised or lowered through the thermal centre of the furnace in steps of not more than 10 mm in order to plot the temperature distribution. This procedure is used to establish the optimum position of the capsule or test piece in the furnace and to calibrate the difference between capsule or test piece and the furnace wall. This calibration is performed at a series of temperatures at intervals not exceeding 100 °C up to the maximum furnace temperature, and is used as an indirect measure of initial test piece temperature.

4.4.2 The procedure for a massive copper block calorimeter or similar device in which a temperature rise is recorded is as follows. The calorimeter temperature is measured using a platinum resistance thermometer (PRT) connected into an a.c. bridge circuit, on the opposite arm of which is a matching standard resistor kept at a known stabilized temperature $\pm 0,1$ °C, which may conveniently be the temperature of the controlled environment. In order to calibrate the calorimeter, a known electrical power is dissipated in the heating resistor for a known time period, Δt , determined either using a stopwatch or other calibrated timing device. The output of the a.c. bridge is monitored continuously and the data are recorded at intervals of not less than 30 s. The electrical input power is measured by recording the voltage, V , across the heating resistor, and across a series standard resistor to measure the current, I (Figure 3). A typical bridge output trace is shown in Figure 4. To determine the calorimeter calibration, the following procedure is used. The output curve is extrapolated at X and Y as shown in Figure 4 using line-fitting routines. A time t_{mid} is chosen such that the areas A and B are equal. The output ΔV_e is taken as the distance between lines X and Y at time t_{mid} . The calibration factor for the calorimeter, C , is given by:

$$C = \Delta V_e / VI\Delta t \quad (3)$$

in units of volts output per joule input. The value of C shall be taken as the mean of 10 determinations.

For an ice calorimeter, or other device operating at a fixed temperature, the same procedure is followed, except that the output response recorded and analysed is appropriate to the device, such as the fall in liquid level. The same basic principle shall be used.

4.4.3 To check that the apparatus is functioning correctly, and that the calibration procedure is accurate, the test may be performed with a reference material of known specific heat capacity. The usual material for performing this function is α -alumina (often in the form of sapphire single crystals), and appropriate data are given in reference [1].

4.5 Test determinations

Determine the mass of the test piece, m_s (and of the capsule if used) to an accuracy of $\pm 0,001$ g. Suspend the test piece and/or capsule in the drop tube, and bring into position at the predetermined thermal centre of the furnace. Allow the test piece temperature to equilibrate at the set furnace temperature such that there is no change in furnace wall temperature over a period of at least 15 min. Record this temperature, and read the test piece temperature from the calibration curve.

Drop the test piece into the calorimeter block through the radiation screen, ensuring that the screen is replaced as soon as the test piece has passed. Record the output of the calorimeter as described in 4.4.2.

Repeat the test twice at the same furnace temperature in order to determine a mean result. Repeat the procedure at other furnace temperatures as required.

4.6 Calculations

Calculate the total heat input to the calorimeter from the calorimeter calibration. The temperature change of the test piece is calculated from:

$$\Delta T_g = T_{initial} - T_{final} \quad (4)$$

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where $T_{initial}$ is the test piece temperature calculated from the furnace wall temperature by calibration, and T_{final} is the extrapolated calorimeter temperature at time t_{mid} determined from the calorimeter output, e.g. PRT temperature rise or liquid level fall.

Calculate the mean specific heat capacity, $\overline{c_p}$, over the temperature range ΔT_s from:

$$\overline{c_p} = \frac{\Delta H_s}{m_s \Delta T_s} = \frac{\Delta V_{s+c} - \Delta V_c}{m_s \Delta T_s C} \quad (5)$$

where:

4.7 ΔH_s is the heat content of the test piece,

ΔV is the output change from the calorimeter determined by extrapolation to time t_{mid} for the capsule (subscript c) and for the test piece + capsule (subscript s+c),

C is the calibration factor for the calorimeter.

Use this procedure for each test, and calculate the mean result for each temperature range. If required, the true specific heat capacity, c_p , may be determined as follows. The enthalpy data, ΔH_s over the temperature range, ΔT_s , from the final calorimeter temperature, T_f , is curve-fitted to the polynomial:

$$\Delta H = \overline{c_p} \Delta T = a'T + b'T^2 + c'T^3 + d'T^{-1} \quad (6)$$

where T is the temperature in K.

Hence:

$$c_p = a' + 2b'T + 3c'T^2 - d'T^{-2} \quad (7)$$

5 Method B – Differential scanning calorimetry (DSC)**5.1 General**

This method may be used for measurements up to a temperature of 2000 °C.

5.2 Principle

A cell comprising a test piece in an enclosing platinum or other suitable test piece holder incorporating a lid shall be heated at a defined temperature rise rate, dT/dt , from an initial temperature, T_i , to a final temperature, T_f . The differential output between a temperature sensor, such as a PRT or thermocouple contained within the test piece cell and that from a similar device in a similarly heated but empty reference cell shall be recorded. This output is directly related to the heat capacity of the test-piece. In order to calibrate this output, the test piece shall be replaced by a calibrant of known specific heat. The baseline behaviour is determined by a test with an empty test piece cell. The calibrant is normally α -alumina for which calibration data are given in [1].

Adherence to the procedure described below should give results accurate to better than 5 %.

5.3 Apparatus

5.2.5.3.1 Generally, specialised commercially available apparatus is employed for specific heat measurement using this principle. Operating practices vary according to the manufacturer's design, and the output signal S may be obtained either from the differential power required to maintain the set heating rate (power-compensation DSC) or from differential heat fluxes determined by the use of thermopiles, PRTs or thermocouples between the test piece holders and their cells.

5.3.2 A balance is required, which is capable of weighing the cell and its contents to $\pm 0,1$ mg or 0,1 % of the test piece mass, whichever is the smaller.

5.4 Test piece

A test piece may be a powder, granules or solid material of size and mass appropriate to the size of the test piece holder, but is typically 10 mg - 100 mg. Before any test, the test piece shall be dried at $110\text{ }^{\circ}\text{C} \pm 5\text{ }^{\circ}\text{C}$ to constant mass. Solid materials machined to fit the capsule shall first be cleaned with a suitable solvent to remove grease or other contaminants. The dry mass of the test piece shall be determined to an accuracy of $\pm 0,1$ mg or $\pm 0,1\%$ whichever is the smaller. Care should be taken when using powders that none is lost in handling the capsule. The mass of the cell plus specimen should be checked after measurement of specific heat, and if different by more than 0,1 %, the test should be repeated.

The calibrant shall normally be α -alumina, for which reference data are available (see [1]).

NOTE In general it is desirable to prepare the calibrant in an identical geometrical condition to that of the test piece in order to obtain reproducible and accurate results.

5.5 Test procedure

Record the mass of the empty cell, and of the cell plus test piece and cell plus calibrant both before and after the test runs.

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Choose a heating rate between 5K/min and 20K/min. Make at least two test runs with an empty test piece holder, two with the test piece and two with the calibrant over temperature range required. Recording of output shall either be continuous or at temperature intervals of not more than 1 $^{\circ}\text{C}$. Record also the isothermal outputs before and after the temperature ramp.

NOTE If it is known that the response of the instrument with the empty cell, or with the cell plus calibrant, is repeatable such that when incorporated in the final calculated specific heat the result is constant to within 2 %, it is not necessary to perform runs with the empty cell or with the cell plus calibrant with every new test piece. Regular checking every few runs may be adequate. However, if the apparatus does not behave consistently, or if the cell is changed or becomes contaminated by the specimen or the atmosphere in which the run is performed, then the above procedure should be adhered to.

If the isothermal response before and after a temperature ramp is independent of whether the cell is empty or contains a test piece or calibrant, and the calculated results are independent of the start and finish temperatures of the temperature ramp, baseline shift corrections are not required.

If the isothermal response before and after a temperature ramp with the test piece or calibrant in place is different from the response of an empty cell at a level of significance of greater than 2 % in calculated specific heat capacity, corrections for baseline drift shall be made (see 5.6). The temperature ramp range shall not exceed intervals of more than 200 $^{\circ}\text{C}$.

In either case, if the difference in output between similar test runs results in calculated specific heat capacity data (see 5.6) which are different by more than 2 %, repeat the tests until reproducibility of result to this level is achieved.