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Simultaneous measurement of heat capacity, thermal conductivity, and thermal diffusivity

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Abstract. A new instrument is presented for the simultaneous measurement of the specific heat, thermal conductivity, and thermal diffusivity of solids and powdery materials in very wide ranges of their thermal conductivity (0.01 to 200 W $\mathrm{m^{-1}\ K^{-1}}$) at temperatures between 100 °C and 1750 °C. These properties are usually determined by means of transient hot-wire methods, transient hot-strip methods, step-wise or pulse transient plane-source methods. With these methods either thermal diffusivity and thermal conductivity or specific heat and thermal diffusivity can be determined, but with the new procedure all thermophysical properties can be measured simultaneously.

The principle of the new method consists of a quasistationary scanning of the sample temperature under adiabatic conditions, which means the chosen temperature transient is constant through the whole sample.

By measuring the heat flow rate into the sample and the radial temperature difference in the sample during temperature scanning with a constant heating rate, the absolute values of the specific heat, the thermal diffusivity, and the thermal conductivity can be determined as a function of temperature in a very simple manner. Additionally, kinetic investigations are possible.

1 Overview of applied methods for simultaneous measurements

Knowledge of the thermophysical properties of materials at temperatures well above 2000 °C has become extremely important for the development of new high technologies such as aeroengines, coating systems for turbine blades, and computer components, where the determination of thermal conductivity, thermal diffusivity, and specific heat together with the enthalpy and temperature of some transitions and/or chemical reactions of the applied materials is needed. The enthalpy behaviour is understood to be the change in the enthalpy during some phase and chemical transitions.

The following well-known methods are available for the simultaneous determination of these thermophysical properties (see, eg, Kubicar and Bohac 1998):
(i) transient hot-wire method (THW);
(ii) transient hot-strip method (THS) (Gustafsson and Karawacki 1983; Groß et al 1992);
(iii) step-wise transient plane-source method (step-wise TPS) (Karawacki and Suleiman Bashir 1991);
(iv) pulse transient plane-source method (pulse TPS) in an infinite medium (Kubicar 1990);
(v) pulse transient plane-source method (pulse TPS) in a semi-infinite or finite medium (laser-flash) (Parker et al 1961).

These transient methods are characterised by generation of the dynamic temperature field by the passage of electric current through a line or plane electrical resistance by means of either a pulse of heat or a heat flux in the form of a step-wise function.

With the THW and the THS methods, the thermal conductivity, λ, and the thermal diffusivity, a, are measured whereas with the other mentioned methods the specific heat, c, and the thermal diffusivity, a, are measured. The absent third thermophysical property must be calculated by $a = \lambda/(\rho c)$, in which ρ is the density.

The peculiarity of the transient methods consists in the sometimes incomplete agreement between the ideal preconditions of the mathematical model and the practical

Table 1. Laser-flash instruments for simultaneous measurements of the thermal diffusivity (*a*) and the specific heat (*c*).

Producer	Type	Temperature range	Given uncertainty/%			Uncertainty/% tested at 1000 °C		
			a	c	λ	a	c	λ
Holometrix (USA)	Thermaflash	up to 2000 °C	±3	±5	±8	±3	+75	
Sinquriku (Japan)	TC 700 HNG	up to 1500 °C	±3	±7	±10	±3	+55	
CompoTherm (Germany)	LP 80	up to 2700 °C	no values			±3	+17	

conditions of the measurement. Therefore, the transient methods are often much less accurate than the stationary ones. A further disadvantage of the transient methods is the fact that they cannot be used for temperature scanning, which allows a quick and clear representation of the thermophyiscal data dependent on the temperature and an easy kinetic analysis.

In particular, we have tested a few laser-flash instruments. On the world market we found three laser-flash instruments for the simultaneous measurement of both the thermal diffusivity, *a*, and the specific heat, *c* (see table 1). For checking the uncertainties the producers of these instruments were supplied with identical samples with properties which had been measured earlier by the Physikalisch – Technische Bundesanstalt (PTB) in Braunschweig (Germany). Typically the uncertainties in measured specific heat, *c*, increase with temperature (possibly because of changes of emissivity) which is not the case for thermal diffusivity, *a*. In order to avoid the difficulties in the course of simultaneous measurements of *a* and *c* with the laser-flash method, most of the producing companies, for example Netzsch in Selb, Germany, suggested separate measurements of these properties with different methods.

Because of the typical disadvantages mentioned of the transient methods, it is our aim to develop a new quasi-steady cylinder method showing sufficiently good agreement between the preconditions of the mathematical model and the practical conditions of the measurement.

2 New simultaneous quasi-steady cylinder method

2.1 *Principle*

The scheme of the new method is illustrated in figure 1.

Within an outer furnace, *2*, with three independent coils, *4*, *5*, and *6*, the sample container, *3*, with the sample, *1*, is positioned. In the sample container a radially wound coil is fixed. Above and below the sample container, special multiple heat conduction shield systems, *7*, and conventional multiple radiation shield systems, *8*, are positioned. The temperature of the outer furnace of the sample container at $z = 0$ is T_C and the temperature of the inner surface of the outer furnace at $z = 0$ is T_F. The temperatures of the inner surfaces of the outer furnace in $z = \pm h_2$ are marked T_FA (furnace above) and T_FB (furnace below).

All four separated coils of the sample container and the outer furnace are heated independently with four special controllers, so that the following relationships are valid at every moment:

$$T_\mathrm{F} = T_\mathrm{C} = T_\mathrm{FB} = T_\mathrm{FA} = \dot{T}t \ , \tag{1}$$

where $\dot{T}$ is the programmed scanning rate, and t is time.

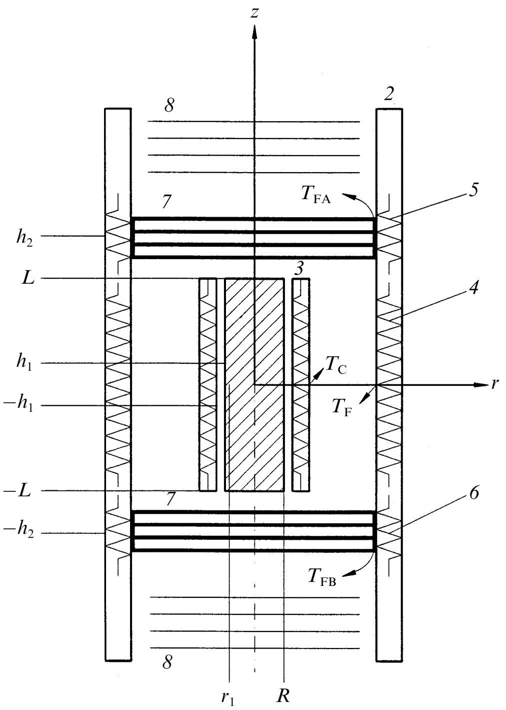

Figure 1. Scheme of the principle of the new method: *1*, sample; *2*, outer furnace; *3*, sample container; *4*, *5*, *6*, independent coils; *7*, multiple heat conduction shield system; *8*, multiple radiation shield systems.

The heat flow rates into the sample container with and without a sample are marked $\dot{Q}_F$ and $\dot{Q}_E$, respectively. The heat flow rate, $\dot{Q} = UI$, is measured in a small central range between $z = h_1$ and $z = -h_1$ (where U is electric voltage, and I is electric current).

If the condition

$$\frac{L}{R} = \frac{L}{h_1} \geqslant 10 \ , \tag{2}$$

and conditions (1) are true, then there exist adiabatic conditions in the r and z directions. This is supported by the multiple shield systems, *7* and *8*.

Additionally to the heat flow $\dot{Q}$, the temperature difference between the positions $r = 0$ and $r = r_1$ or $r = R$ has to be measured.

If the adiabatic conditions are given, the following balance is valid:

$$\dot{Q}_F = C_F \dot{T} = (C_C + C_S)\dot{T} \ .$$

This means that the controlled heat flow rate, $\dot{Q}_F$ (index F for the full sample container) is only consumed for heating to the heat capacity, C_C, of the sample container and to the heat capacity, C_S, of the sample (index S for sample).

Under these adiabatic conditions the temperature field in the sample can be calculated in the following manner. The boundary value problem for an infinite cylindrical sample is given by:

$$T(t = 0, r) = 0 \ ,$$

$$\dot{q} = -\lambda \left(\frac{\partial T}{\partial r} \right)_{r=R} , \quad t > 0 \ ,$$

and

$$\frac{\partial T}{\partial t} = a \left(\frac{\partial^2 T}{\partial r^2} + \frac{1}{r} \frac{\partial T}{\partial r} \right) \ .$$

The quasi-steady-state solution is [see for example Tautz (1971)]:

$$T(r,\,t) = \frac{\dot{q}R}{\lambda}\left[2\frac{at}{R^2} + \frac{1}{2}\frac{r^2}{R^2} - \frac{1}{4}\right] ,$$

with the heat flow rate $\dot{q}$ per unit area at the surface of the cylinder of radius R. From this, it follows that the temperature difference between two radial positions is given by:

$$T(r) - T(0) = \frac{\dot{q}r^2}{2\lambda R} .$$

The scanning rate at an arbitrary position is given by:

$$\frac{\partial T}{\partial t} = \dot{T} = \frac{2\dot{q}a}{\lambda R} .$$

The scanning rate is measured at the position of the thermocouple T_F at the inner wall of the outer furnace (figure 2).

From the quasi-steady-state solution, we obtain the following expressions for thermal conductivity, thermal diffusivity, and heat capacity, respectively:

$$\lambda = \frac{\dot{q}r^2}{2R[T(r) - T(0)]} , \qquad a = \frac{\dot{T}r^2}{4R[T(r) - T(0)]} , \qquad c = \frac{2\dot{q}}{\rho R\dot{T}} . \tag{3}$$

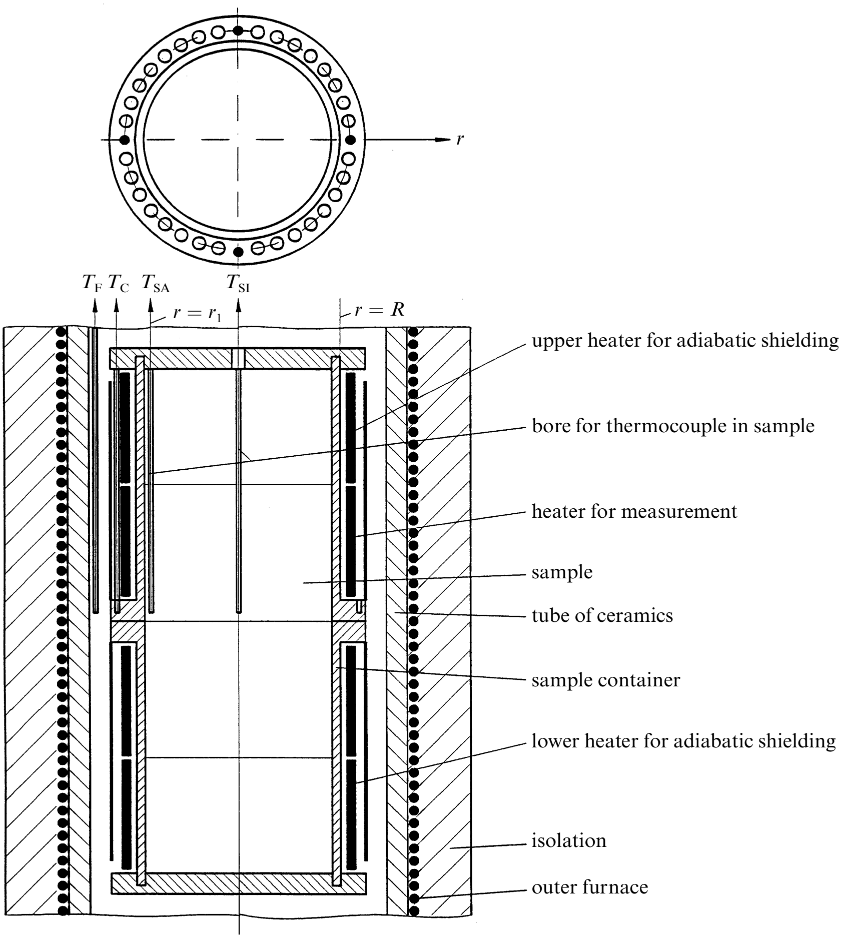

Figure 2. Schematic drawing of the application of the simultaneous method to solid samples.

For the validity of formulae (1), which derived from the solution of the linear parabolic heat equation, it is necessary that the scanning rate and the radius are chosen so that, within the temperature interval $T(r) - T(0)$, the temperature dependence of the thermal conductivity can be neglected.

For the absolute determination of a and c only, measurements of the temperature transient $\dot{T}$, the temperature difference $[T(r) - T(0)]$, and the electrically supplied heat flow rate $\dot{q}$ per unit area are required. From one or several measured curves, $\dot{q}(T)$, at different temperature transients, $\dot{T}$, the kinetic parameters activation energy, frequency factor, and order of reaction can be calculated.

2.2 *Transient behaviour*

Before the quasi-steady state can be established and evaluation of the properties according to equations (1) can start, one has to wait until the initial transient period after starting the experiment has finished. This is an important fact, especially for very poorly conducting materials. The complete solution for all times of the infinite cylinder with the same initial and boundary conditions as used for the determination of the quasi-state solution in section 2.1 (Tautz 1971) is:

$$T(r,\,t) = \frac{\dot{q}R}{\lambda}\left[2\frac{at}{R^2} + \frac{1}{2}\frac{r^2}{R^2} - \frac{1}{4} - 2\sum_{n=1}^{\infty}\frac{J_0(\mu_n r/R)}{\mu_n^2 J_0(\mu_n)}\exp\left(-\frac{\mu_n^2 at}{R^2}\right)\right]\,, \tag{4}$$

where μ_n are the roots of equation $J_1(\mu) = 0$; $J_0(\mu)$ and $J_1(\mu)$ are Bessel functions of order zero and one, respectively. This shows that even for ceramics with $R = 2$ cm and $\lambda = 1\ \mathrm{W\,m^{-1}\,K^{-1}}$, the quasi-steady state is reached within 3 min.

2.3 *Compensation of heat capacities of the sample container*

If $\dot{Q}_\mathrm{F}$ and $\dot{Q}_\mathrm{E}$ are the electrically produced heat flow rates for heating the container with (full) and without (empty) the sample, respectively, and $\dot{Q}_\alpha(T)$ represents the temperature-dependent heat losses and distorting effects, the following energy balances are valid for the determination of the heat flow rate $\dot{Q}_\mathrm{S}$ to the sample itself:

$$\left.\begin{aligned}\dot{Q}_\mathrm{F} &= (C_\mathrm{C} + C_\mathrm{S})\dot{T} + \dot{Q}_\alpha(T)\\ \dot{Q}_\mathrm{E} &= C_\mathrm{C}\dot{T} + \dot{Q}_\alpha(T)\\ \dot{Q}_\mathrm{F} - \dot{Q}_\mathrm{E} &= \dot{Q}_\mathrm{S} = C_\mathrm{S}\dot{T}\end{aligned}\right\}\,. \tag{5}$$

Here, C_C and C_S are the heat capacities of container and sample, respectively. By the subtraction according to equation (5), the desired heat capacity, C_S, can be determined. The terms $\dot{Q}_\alpha(T)$ of the full and empty measurements are compensated.

3 Construction of the test facility

The test facility consists of the outer and the inner furnace with the sample. The sample (solid or powder material, see figures 2 and 3, respectively) is put into a cylindrical container made of molybdenum, which is closed at its ends by means of ceramic disks. In the sample container, the heat flux $\dot{q}$ for the sample is generated by a molybdenum coil divided into three sections and fixed inside the container. The two outer sections provide an adiabatic shield for the inner section in which the measurements are made.

For measuring the temperatures there are small boreholes in the ring flange of the sample container (figures 2 and 3). This provides good thermal contact between the thermocouple and the sample container. For solid samples (figure 2) two boreholes are needed for the inner and outer thermocouple, positioned at radii $r = 0$ and $r = r_1$. In the case of a powdery sample (figure 3), the outer sensor (T_SA) is located in the ring flange of the sample container at $r = R$ and the inner thermocouple (T_SI) is placed into a special small-diameter tube (also made from molybdenum) in the centreline of the container at $r = 0$, fixed in the ceramic end disks.

The sample container is positioned in the interior of the outer furnace which carries three separated coils. According to the measuring principle, the three parts of the outer furnace are heated and controlled separately to provide the given temperature transient. By means of an additional controller, the sample container is heated in such a way that the temperature difference between the outer surface of the sample container and the inner surface of the outer furnace is zero.

The length-to-diameter ratio of the sample is about 10, and the same is true for the ratio between the total heat flow rate to the sample container and that to its central section.

Above and below the sample container, a multiple heat conduction shield system with six shields and a multiple radiation shield system with eight shields are positioned. By all these measures adiabatic conditions in the radial as well as in the axial directions are fulfilled, which is of basic importance for the validity of equations (3).

4 Accuracy and some first results

At this time, for technical reasons, the determination of temperature differences has not been carried out. Therefore, only the measurement of the heat capacity is reported.

The accuracy of the measurement of the heat capacity is in a very decisive manner dependent on the quality of the adiabatic conditions in the radial as well as in the axial directions. This was tested by heating in such a way that the temperature of 500 °C was

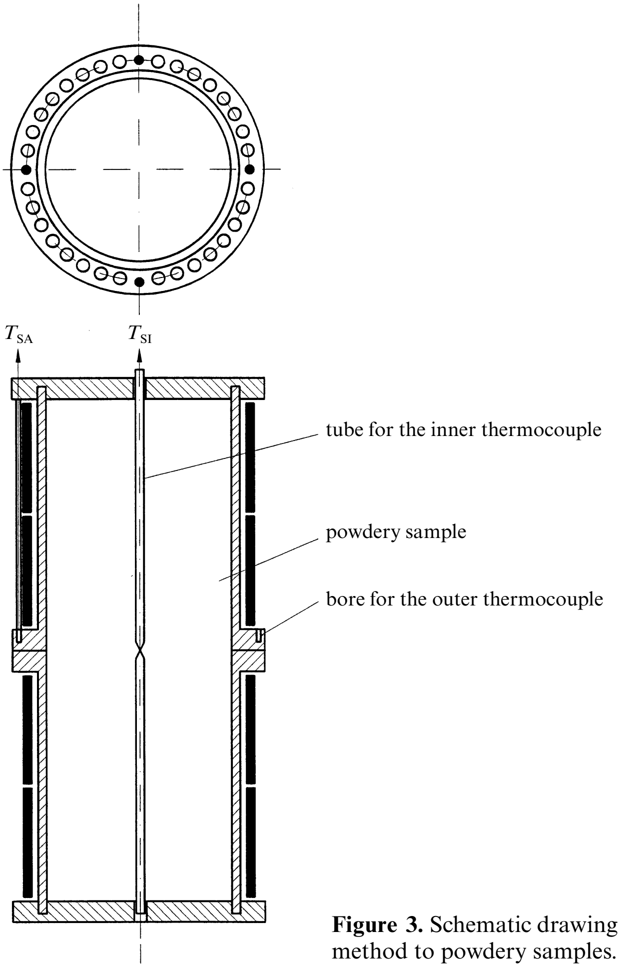

Figure 3. Schematic drawing of the application of the simultaneous method to powdery samples.

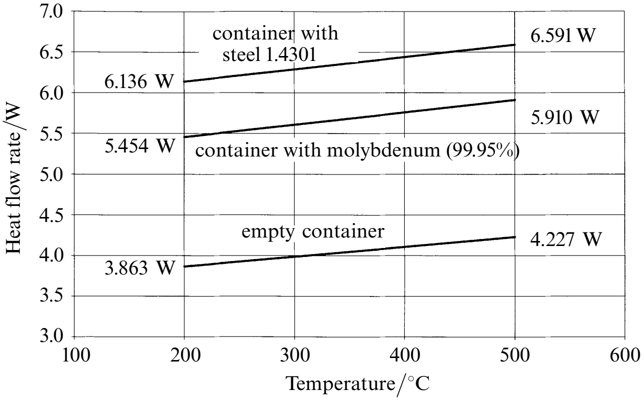

Figure 4. Smoothed measured values of the heat flow rate for the full and empty sample container.

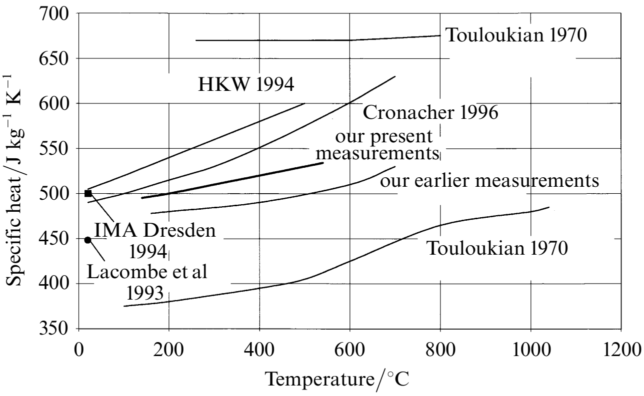

Figure 5. Representation of the measured heat capacity of steel 1.4301 in the temperature range 200 – 500 °C compared with the results of other authors (HKW 1994: *Handbuch der Kennwerte metallischer Werkstoffe*).

kept constant. By continuation of the controlling processes under these circumstances the heat flow rates $\dot{Q}_\mathrm{F}$ or $\dot{Q}_\mathrm{E}$ have to disappear. This was the case, so a high accuracy of specific heat could be expected.

Figure 4 shows the measured and smoothed heat flow rates, $\dot{Q}_\mathrm{E}$ and $\dot{Q}_\mathrm{F}$, for steel 1.4301 (X 5 NiCr 18.10) and molybdenum (99.95% purity) from 200 °C to 500 °C with a scanning rate of 2 K min^{-1}. The length and the diameter of the sample are 400 mm and 24 mm, respectively. By subtracting $\dot{Q}_\mathrm{E}$ from $\dot{Q}_\mathrm{F}$, the heat capacities in accordance with equations (3) can be calculated. They are represented and compared with the results of other authors in figures 4 and 5. Because of the uncertainty in the exact composition of the steel 1.4301, the results of the specific heat measurements show a relatively large variation and our measured curves are situated roughly in the middle of the range. In contrast to the steel, the molybdenum used in our measurements has nearly the same purity as the molybdenum measured by NBS. The deviations are a maximum of 0.1% for 500 °C and 0.4% for 200 °C (figure 6).

5 Conclusions

These results show that quasi-steady methods for the measurement of the specific heat can also be made very accurately. This accuracy is otherwise only typical for steady-state methods which take a long time to reach equilibrium, whereas our method takes only two and a half hours for the temperature range 200 – 500 °C. If the temperature

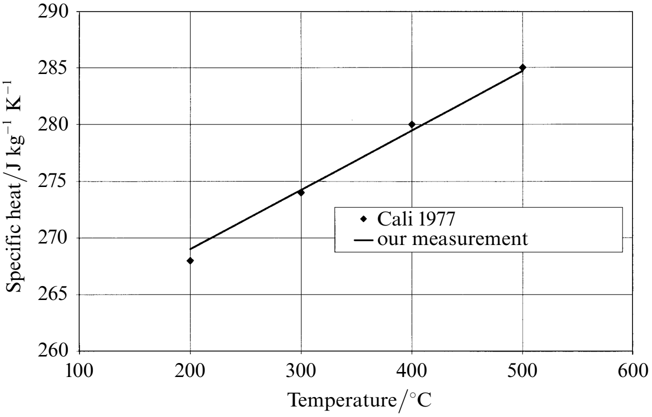

Figure 6. Representation of the measured heat capacity of molybdenum (purity 99.95%) in the temperature range 200 – 500 °C compared with tabulated values of the NBS (Cali 1977) for Standard Reference Maerial 781(purity 99.95%).

difference is measured simultaneously during the measurement and across the temperature range, the values for specific heat, thermal conductivity, and thermal diffusivity can be derived in accordance with equations (3).

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