



# Chip-calorimeter for small samples

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## Abstract

A method for measuring heat capacities of small samples using a chip-calorimeter and a heat pulse technique is described. The theoretical background to calculate the heat transport properties and the heat capacity of the sample from the pulse response function is given. Problems and potentials of the method are discussed. An example is given.

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## 1. Introduction

Traditional calorimeters offer high resolution and precision in measuring heat and heat flow rates only when sample masses and heating rates are not too small. In applications where these conditions are not fulfilled the signal to noise ratio can be very low, in particular, if the heat flow rate into the sample is reduced. Reduction of the masses of the measuring system together with an improvement of the thermal properties can help to increase the resolution and signal to noise ratio such that small samples can be measured even at low heating rates.

Heat pulse technique allows to determine the dynamic behavior of the calorimeter system as well as that of the sample. From the pulse response the heat transport properties can be derived and the measured signals can be corrected properly so that quantitative results for the heat capacity of the sample can be obtained at every moment of the measurement. In this

way the common condition of scanning calorimetry that the calorimeter system should dominate over the sample to reduce the influence of the latter on the measured signal as well as a differential (twin) design can be get past.

Measuring systems with low thermal masses are increasingly used nowadays [1,2], they are normally fabricated on a silicon chip basis and available from several companies and institutes [3–9]. The original purpose of such devices was the use as ac/dc-converters (see also Planar MJTC, Planar Multi-Junction Thermal Converter) for True RMS Conversion. Later on they were optimized for thermal sensing or calorimetric applications. Essential examples showing the possibilities of such calorimeters and the state of the art of the techniques used are given in [10–12]. As far as we know Denlinger et al. [10] were the first who successfully used a self-made calorimeter of silicone chip type to measure heat capacities of small samples (ca. 50 µg) down to 1.5 K. The samples were normally vapor deposited, using different evaporation masks, to ensure reproducible and good contact and sample position. The disadvantage of such a method is that every new sample needs a new calorimeter-chip. Of course such a method is

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not possible with polymer samples and we preferred a method where the sample can easily be exchanged and the calorimeter used for several samples in succession.

## 2. Calorimeter

The calorimeter itself consists of the calorimeter-chip mounted with good thermal contact inside a temperature controlled furnace. The calorimeter-chip in its turn consists of a thin silicon membrane with a heater wire and a thermopile positioned on one side of it. The membrane is embedded into a silicon frame which is glued into a ceramic housing. The latter is mounted inside the furnace.

In our case the following chip types were used, most of them commercially available:

LCM-2506	Chip 5 mm × 5 mm Membrane 3.5 mm × 3.5 mm, mono-Si 6 μm [3]
XI-71	Chip 4 mm × 3 mm Membrane 2.6 mm × 1.6 mm, SiN 0.5 μm, poly-Si 0.3 μm [3]
LCM-2524	Chip 10 mm × 10 mm Membrane 8.3 mm × 8.3 mm, mono-Si 25 μm [3]
PTB-TK	Chip 6 mm × 8 mm Membrane 2 mm × 3 mm, SiO <sub>2</sub> -Si <sub>3</sub> N <sub>4</sub> -SiO <sub>2</sub> 0.8 μm [4]

The LCM-type chips have a reduced temperature range up to 100 °C because of the electrical behavior of the semiconductor material. The types XI-71 and PTB-TK can be used up to 200 °C, but their handling is difficult because of the thin membrane and the smaller membrane area. The handling of the LCM-types is not so sensitive, when special care is taken on positioning or removing samples, so the LCM-types were preferred for most of the measurements.

The geometric construction principle is the same for all four types of chips (Fig. 1). The ceramic housing provides soldering pads so that the thermopile and the heater can be contacted easily (Figs. 2 and 3).

The “underlying” temperature program, typically linear with time, is applied by temperature control of the surrounding furnace in which the calorimeter-chip is connected via a heat transfer path with low thermal resistance. The heater, which is part of the chip, can

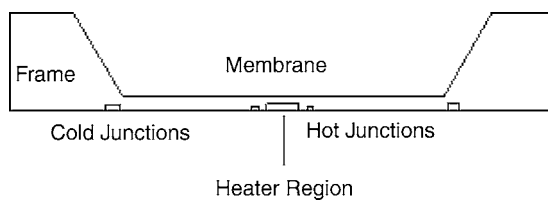


Fig. 1. Construction scheme of the chip-calorimeter without housing. The contacts are on the bottom of the membrane so that the sample must be placed on the upper side above the heater region.

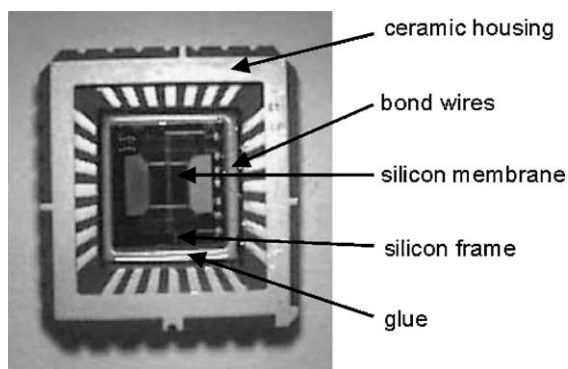


Fig. 2. The chip-calorimeter LCM-2506 from the bottom side. The square in the middle is the heater area, surrounded by the thermopile.

be used for further temperature programs (e.g. step- or pulse-like) superimposed to the underlying one.

Normally the sample has to be placed in the middle of the membrane where a square or rectangle area

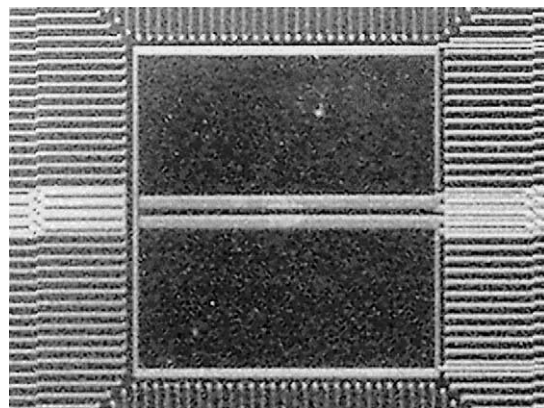


Fig. 3. Silicon membrane of LCM-2506; the square area represents the heater area, it is surrounded by the hot junctions of the thermopile. The membrane size is 3.5 mm × 3.5 mm.

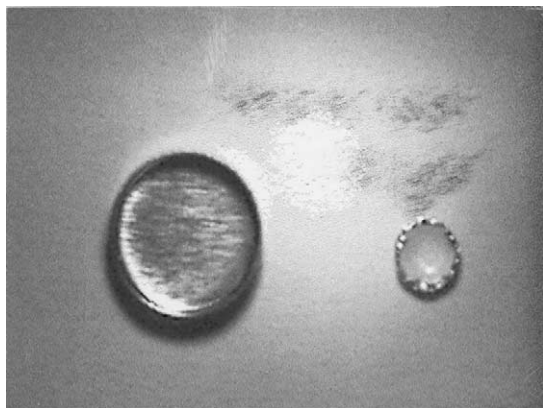


Fig. 4. Comparison of pan sizes; the left pan is a standard DSC pan (mass: 26 mg), the right pan, made for the chip-calorimeter of aluminum foil, has a mass of 0.5 mg; it contains a PCL sample of 0.9 mg.

is surrounded by the heater. Around the heater area the hot junctions of the thermopile are positioned. The cold junctions are located on the silicon chip frame. The LCM-types provide an additional temperature sensor on the chip frame so that the reference temperature for the cold junctions can be measured separately.

As will be seen later, an important point is to have sample and/or pan geometries that are not differing too much because this would have a strong influence on the heat transfer behavior of the sample. Standard DSC pans cannot be used because they are too large and they too have high mass (around 25 mg, see Fig. 4). To ensure that the used pans fit in size to the heater area, a special tool was made to form them of a proper aluminum foil. The mass of such a pan is typically 0.5 mg. Because of the very sensitive and fragile silicon membrane, the use of any contact increasing agent is forbidden. To come to reproducible heat transfer conditions, the sample should be as flat as possible and in good contact with the aluminum foil.

### 3. Model calculations and evaluation method

For small sample sizes, the chip-calorimeter can be described using a network model (Fig. 5) of three thermal nodes (with heat capacity  $C_{P_i}$ , temperature  $T_i$ ) and five heat conducting paths (with thermal resistance  $R_{ij}$ ). The index 1 refers to the

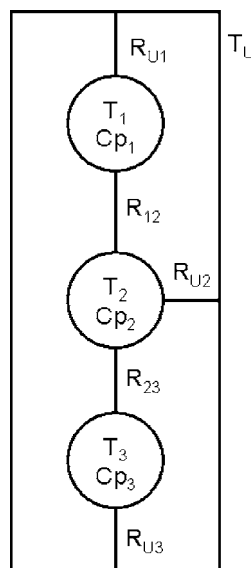


Fig. 5. Network model of the chip-calorimeter with sample ( $C_{P1}$ ), membrane ( $C_{P2}$ ) and silicon frame ( $C_{P3}$ ).  $R_{U3}$  represents the glue between the silicon frame and the ceramic housing. The ceramic housing has a good thermal contact to the temperature controlled surroundings ( $T_U$ ).

sample, index 2 to the heater part of the membrane and index 3 to the silicon frame surrounding the membrane. The index  $U$  refers to the temperature controlled furnace. When heating power is applied to  $C_{P2}$  (via the heater) a rising signal is observed at the thermopile (which measures  $T_2 - T_3$ ). Another temperature rise is observed at the chip frame namely  $T_3 - T_U$ .

These temperature differences, measured in dependence on time, are compared with the respective theoretical curves that are calculated from the model used. The parameters  $R_{ij}$  and  $C_i$  are adjusted so that measured and theoretical curves fit. As the furnace is temperature controlled, an underlying heating rate can easily be realized, e.g. by increasing  $T_U$  linearly.

The model can be described mathematically by a set of coupled differential equations which can be derived making use of Fourier's law for the conservation of energy (heat) for each node in terms of heat flow rate:

$$C_{P1} \frac{dT_1}{dt} + \frac{dQ_{\text{latent}}}{dt} = \frac{T_2 - T_1}{R_{12}} + \frac{T_U - T_1}{R_{U1}} \quad (1)$$

$$C_{P2} \frac{dT_2}{dt} = \frac{T_1 - T_2}{R_{12}} + \frac{T_3 - T_2}{R_{23}} + \frac{T_U - T_2}{R_{U2}} + P \quad (2)$$

$$C_{P3} \frac{dT_3}{dt} = \frac{T_2 - T_3}{R_{23}} + \frac{T_U - T_3}{R_{U3}} \quad (3)$$

with given  $T_U = T_U^0 + \beta t$  and  $Q_{\text{latent}}$  the latent heat connected with reactions or transitions in the sample.

Measurement can be done in a scan mode (with  $P = \text{constant}$ ) as well as in a pulse mode where the heater is used to produce heat pulses by switching an electrical power on and off. From the shape of the pulse response, as measured by the thermopile ( $T_2 - T_3$ ), the sample heat capacity  $C_{P1}$  can be determined.

In both modes of operation the respective application may require a higher resolution in time. Highly time-resolved measurements are, however, difficult to make with the chip-calorimeter in its original state, because the chip frame contributes with a “parasitic time constant” ( $C_{P3}R_{U3}$ ) that affects all thermopile measurements by slowing down the response. To overcome this problem for both modes of operation and cover all ranges of applications, the chip-calorimeter has to be modified. The material that was originally used to glue the silicon frame to the ceramic housing has rather a low thermal conductivity and must be replaced by a glue with a high thermal conductivity, so that  $R_{U3}$  is highly reduced and  $C_{P3}$  better coupled to the furnace.  $C_{P3}$  can then be considered as a part of the temperature controlled environment and the temperature difference between  $C_{P3}$  and the surrounding furnace is very low and does not affect the measurements anymore, even in the case of small samples and pulse mode. For calculations a simplified model (without  $C_{P3}$ ) can then be used. The modification procedure itself is not easy to do because the calorimeter-chip is very sensitive and can easily be destroyed.

The modified calorimeter can then be described using a simpler two-body-model as shown in Fig. 6. In that case we get a solution  $T_{\text{Th}}(t)$  of Eqs. (1) and (2) which has the following form, if we assume the heat capacities involved to be constant within the temperature region in question:

$$T_{\text{Th}}(t) = a_1 e^{-a_2 t} + a_3 e^{-a_4 t} + a_5 \quad (4)$$

with  $T_1(0) = 0$ ,  $T_2(0) = 0$ ,  $T_U(t) = 0$ , where  $T_{\text{Th}}(t) = T_2(t) - T_U(t)$  represents the thermopile signal. The coefficients  $a_1$  to  $a_5$  can be determined, they are rather complex functions of  $C_{P1}$ ,  $C_{P2}$ ,  $R_{12}$ ,  $R_{U1}$ ,  $R_{U2}$  and  $P$ . To fit Eq. (4) properly to the measured thermopile temperatures, information of the calorime-

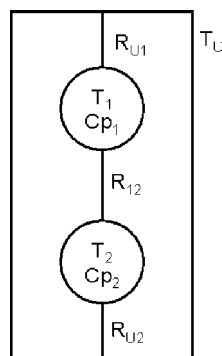


Fig. 6. Simplified model (A) of the chip-calorimeter with sample ( $C_{P1}$ ) and membrane ( $C_{P2}$ ).  $R_{U2}$  represents the membrane resistance between heater and chip frame. The ceramic housing has a good thermal contact both to the temperature controlled surroundings ( $T_U$ ) and to the chip frame.

ter properties (which are not influenced by the sample itself) has to be gained from reference measurements. One of these reference measurements is done with the empty calorimeter. The mathematical description for the empty calorimeter in its turn starts from a two-body-model as well with the membrane and the chip frame as the two components (see Fig. 7). (With the empty calorimeter the quality of the chip modification, mentioned above, can be checked too.)

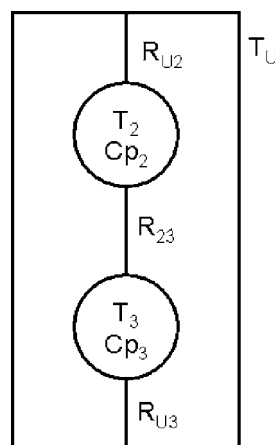


Fig. 7. Network model (B) of the empty chip-calorimeter with membrane ( $C_{P2}$ ) and chip frame ( $C_{P3}$ ).  $R_{U3}$  represents the optimized thermal resistance between chip frame and ceramic housing. The ceramic housing has a good thermal contact to the temperature controlled surroundings ( $T_U$ ).

For this model B we get a solution  $T_{Th}(t)$  of Eqs. (2) and (3) which has a similar form as that of model A, but the coefficient are, of course, different:

$$T_{Th}(t) = a_6 e^{-a_7 t} + a_8 e^{-a_9 t} + a_{10} \quad (5)$$

with  $T_2(0) = 0$ ,  $T_3(0) = 0$ ,  $T_U(t) = 0$ , where  $T_{Th}(t) = T_2(t) - T_3(t)$  represents the thermopile signal. The coefficients  $a_6$ – $a_{10}$  are functions of  $C_{P2}$ ,  $C_{P3}$ ,  $R_{23}$ ,  $R_{U2}$ ,  $R_{U3}$  and  $P$ , which naturally are different from the respective values of model A (containing the sample).

The measured curves for  $T_3(t)$  and  $T_{Th}(t)$  from the empty calorimeter can be fitted to the mathematical solutions of model B, to obtain useful start values for the fit procedure with the measurements done with a sample (the results can even be used to control the quality of the modification of the calorimeter).

Additional calculations, to obtain the heat transfer parameters, can be done for the empty device by means of the known geometry and material parameters using the heat conductivity of silicon:

$$\lambda = 150 \text{ W/mK} \left( \frac{T}{300 \text{ K}} \right)^{-4/3}$$

the thermal resistance between heater and chip frame can be calculated:

$$R_{23} = \frac{D_{Th}}{A_Q} 0.00667 \text{ mK/W} \left( \frac{T}{300 \text{ K}} \right)^{4/3}$$

For the LCM-2506 chip with  $D_{Th} = 8.5 \times 10^{-4} \text{ m}$  and  $A_Q = 4.32 \times 10^{-8} \text{ m}^2$  we find:

$$R_{23} = 131.2 \text{ K/W} \left( \frac{T}{300 \text{ K}} \right)^{4/3}$$

Calculation of the heat transfer through the air above and below the membrane leads to:

$$R_{U2} = \frac{D_O D_U}{D_O + D_U} \frac{1}{\lambda_{Luft} A_M} \quad (6)$$

With  $\lambda_{air} = (5.35 + 0.0695T(\text{K})) \times 10^{-3} \text{ W/mK}$ ,  $A_M = A_{eff} = 6.502 \times 10^{-6} \text{ m}^2$  (effective area with consideration of the temperature profile in the membrane),  $D_O = 1.5 \text{ mm}$  and  $D_U = 1.0 \text{ mm}$  we get:

$$R_{U2} = \frac{9.228 \times 10^4}{5.35 + 0.0695T(\text{K})} \text{ K/W}$$

For  $T = 300 \text{ K}$  we obtain  $R_{U2} = 3522 \text{ K/W}$ .

These values for  $R_{23}$  and  $R_{U2}$  are used as starting values to fit the measurements of the empty calorimeter.

#### 4. Calibration

For quantitative measurements the thermopile of the calorimeter-chip has to be calibrated properly. The calibration is done by measuring a calibration substance in scanning mode. The power applied to the membrane heater has been varied in a wide range to test its influence on the sample temperature, which, depending on the power applied is always higher than the underlying temperature program. As a result, the sample will melt earlier than expected from the underlying temperature program. A calibration curve is gained when plotting the thermopile signal in dependence on the underlying temperature of the chip at the start of melting. Fig. 8 gives an example with a LCM-2506 chip using gallium as calibrant.

The reciprocal slope  $S = U_{Th}/(T_1 - T_3)$  from this calibration would be correct if the sample would be ideally coupled to the chip membrane. This is in reality not the case, any contact medium is forbidden because of the sensitivity of the silicon membrane. The non ideal coupling to the membrane can, however,

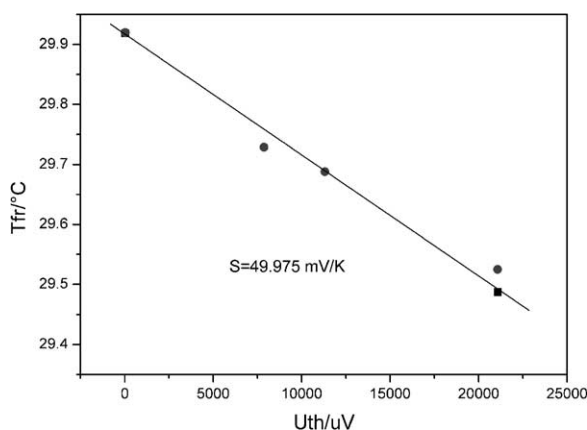


Fig. 8. Thermopile calibration using gallium for a LCM-2506 chip-calorimeter. Flat gallium samples of mass 0.2 mg were measured in scan mode. Different power applied to the heater gives rise to a higher temperature level of the gallium sample compared to the surroundings. The chip frame temperature was measured as reference temperature for the cold junctions and the onset temperatures of the melting peaks plotted against the thermopile signal.

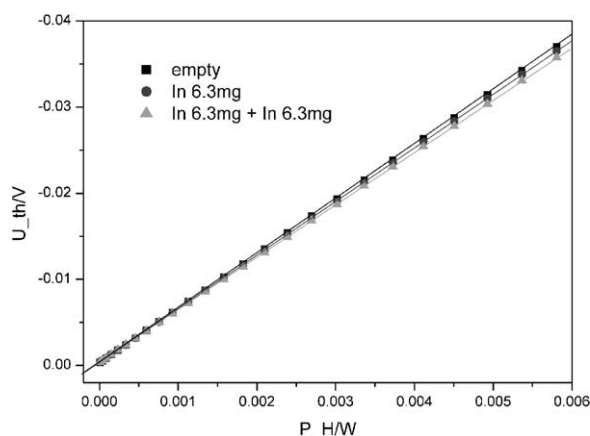


Fig. 9. Linearity-check of the calorimeter using several different samples. The thermopile signal is obviously a linear function of the heating power.

be taken into account by using the respective thermal resistance which can be determined from the shape of the melting peak.

To obtain the correct value for the Seebeck coefficient of the thermopile  $S_{\text{See}} = U_{\text{Th}}/(T_2 - T_3)$ ,  $S$  has to be multiplied with a factor  $K_{\text{Th}} = (T_1 - T_3)/(T_2 - T_3)$  which can be calculated as follows:

$$K_{\text{Th}} = \frac{R_{U1}(R_{23} + R_{U3})}{R_{U3}(R_{U1} + R_{12})} - \frac{R_{23}}{R_{U3}} \quad (7)$$

For the above-mentioned chip this results in:  $S_{\text{See}} = SK_{\text{Th}} = 41.98 \text{ mV/K}$

## 5. Linearity check

Linearity of the system was tested by measuring the amplitude of the thermopile signal of different samples at different amounts of heater power. The results (see Fig. 9) show that there are no relevant nonlinear heat transfer effects regarding the system sample calorimeter.

## 6. Modes of operation

### 6.1. Scanning mode

In scanning mode the chip-calorimeter has the advantage of high resolution with a low time constant on measuring small samples at low heating rates. Fig. 10

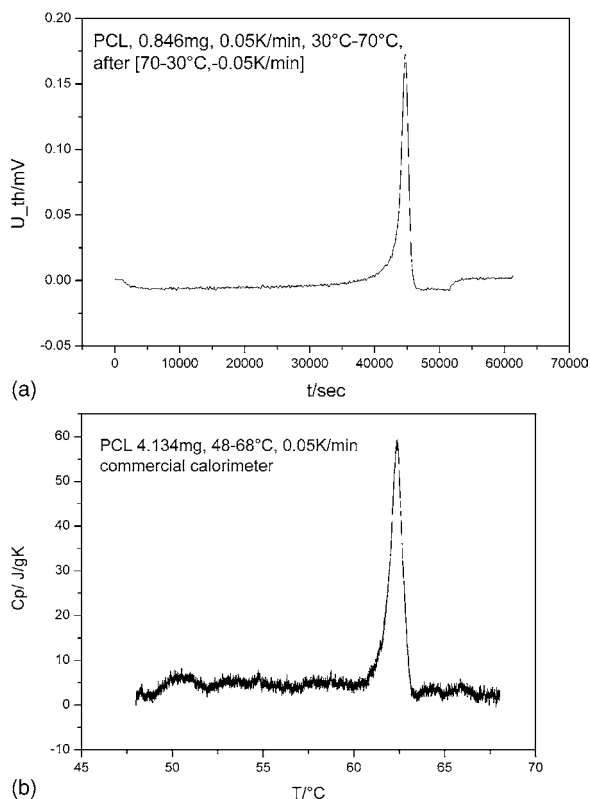


Fig. 10. Comparison of the signals from the chip-calorimeter (a) and a commercial DSC (b); the chip-calorimeter signal shows a better resolution and minor noise although the sample mass was five times smaller.

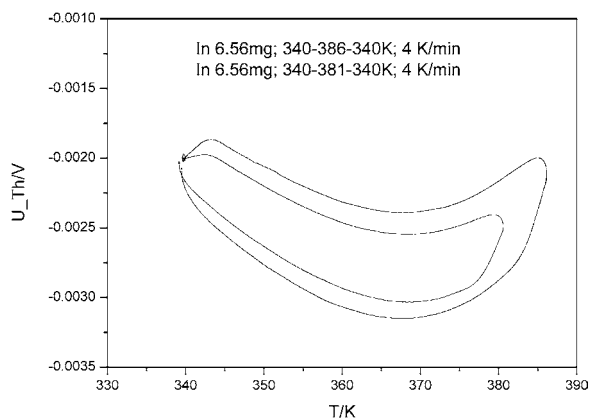


Fig. 11. Measurements of one sample but with varying heat transfer conditions and temperature gradients (for details see text). The measured curves differ significantly.

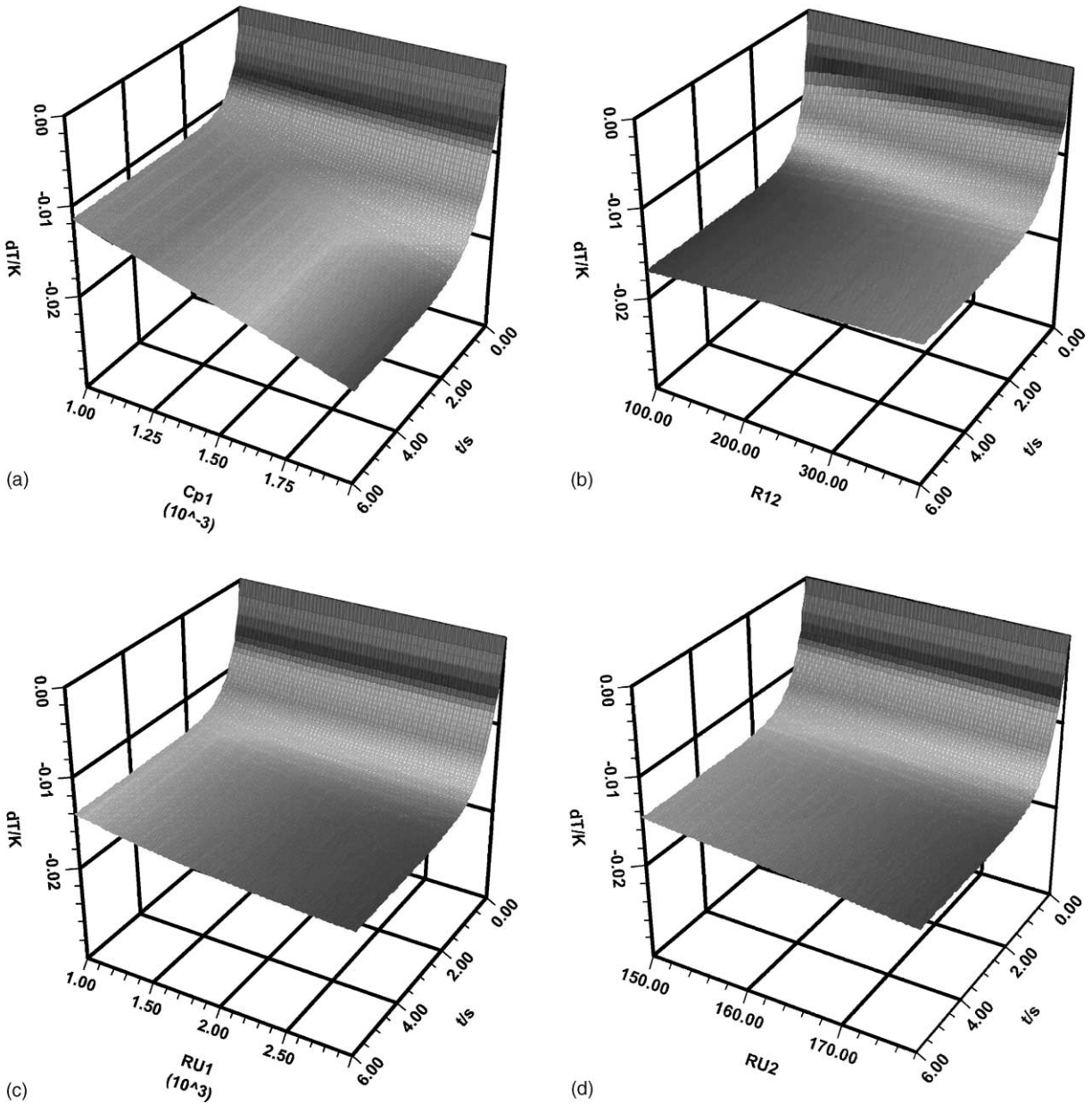


Fig. 12. Simulation of the influence of different heat transfer parameters in scan mode on the chip signal, the other parameters are always kept constant:  $R_{U2} = 163.7$  K/W,  $C_{p2} = 0.00019$  J/K,  $C_{p1} = 0.0015$  J/K,  $R_{12} = 280$  K/W,  $R_{U1} = 1850$  K/W.

shows the comparison of a poly-capro-lactone (PCL) sample [13,14] measured with a commercial differential scanning calorimeter and the chip-calorimeter. Although the sample in the chip-calorimeter is five times smaller than the sample in the commercial

DSC, obviously the resolution and the signal to noise ratio is much better.

The influence of the heat transfer parameters on the measurement plays an important role when quantitative results are needed. Fig. 11 shows the results

for different heat transfer paths between sample and sensor and different temperature gradients in the surrounding of the calorimeter-chip (case 1: flat sample placed plane on the heater; case 2: sample bent so that it lies on three points on the heater with 0.1 mm distance otherwise). Although heat capacity of the sample is the same in both measurements, the amplitude of the measured signal in the second measurement is only half of that of the first measurement.

The influence of the different parameters on the signal becomes obvious from the results of the respective simulation calculations. As shown in Fig. 12, the amplitude depends strongly on  $C_{P1}$ , and on the thermal resistances as well. The influence of the transport parameters can be determined and corrected if an additional heat pulse is applied at the beginning and end of every measurement. The respective values of the parameters at these two temperatures can then be calculated from the shape of the temperature-response signals. In a first approximation the calculated parameters can then be properly interpolated within the scanning temperature range of the measurement and used to calculate the correct heat flow into the sample.

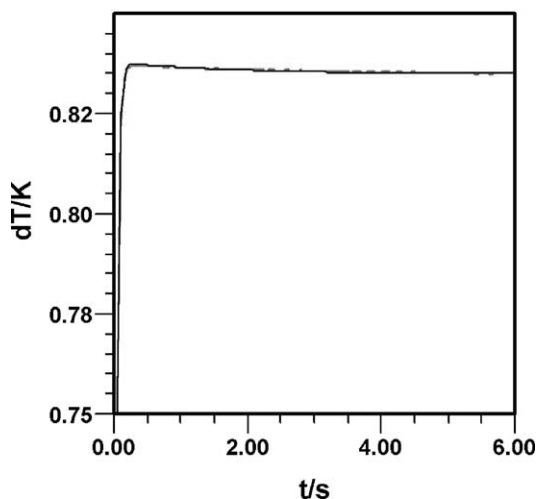


Fig. 13. Fit of a measured thermopile signal for an empty LCM-2506 device (using model B). The fit results were  $R_{23} = 163.7 \text{ K/W}$ ,  $R_{U3} = 12.0 \text{ K/W}$ ,  $R_{U2} = 2430.0 \text{ K/W}$ ,  $C_{P3} = 0.145 \text{ J/K}$ ,  $C_{P2} = 0.00019 \text{ J/K}$  and  $P = 0.00547 \text{ W}$ . The influence of  $R_{U3}$  and  $C_{P3}$  can be seen in the slight long-term decrease of the signal. Measured values and fit data are exactly one on top of the other.

## 6.2. Pulse mode

In pulse mode the heater power is switched on and off periodically within the whole temperature range of the measurement. The temperature-response function of every pulse can be used to calculate the parameters of the system together with the heat capacity of the sample at that moment. Examples for such evaluations of pulse responses are given in Figs. 13 and 14 which show the measured and the calculated curves of the empty chip-calorimeter and two poly-capro-lactone

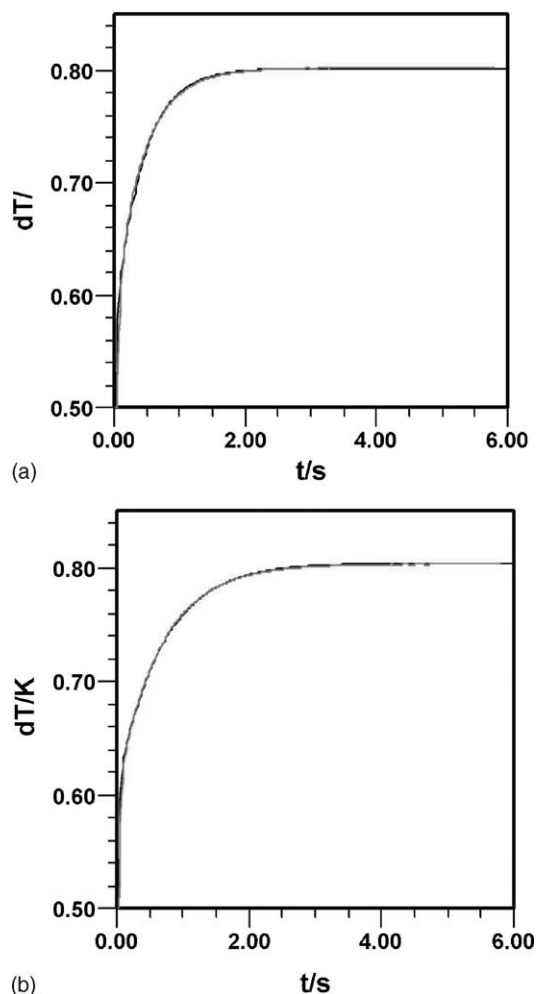


Fig. 14. Measurement and calculated fit curves for of two different PCL samples of (a) 0.52 mg; and (b) 0.96 mg sample (using model A). Both samples were enclosed in an aluminum pans of 0.41 mg mass, respectively. The curves are exactly one on top of the other.



samples. Measured and calculated curves fit very well and in addition the influence of the sample on the signal is clearly visible.

The evaluation on the empty device (Fig. 13) was done with Eq. (5) and model A. As can be seen in  $R_{U3}$ , the thermal coupling between the chip frame and

the ceramic housing is relatively good in this case (improved by a factor of 15 in comparison to the original unmodified state of the calorimeter). The influence of the time constant formed by  $R_{U3}$  and  $C_{P3}$  is small and can be neglected in relation to the other time constants.

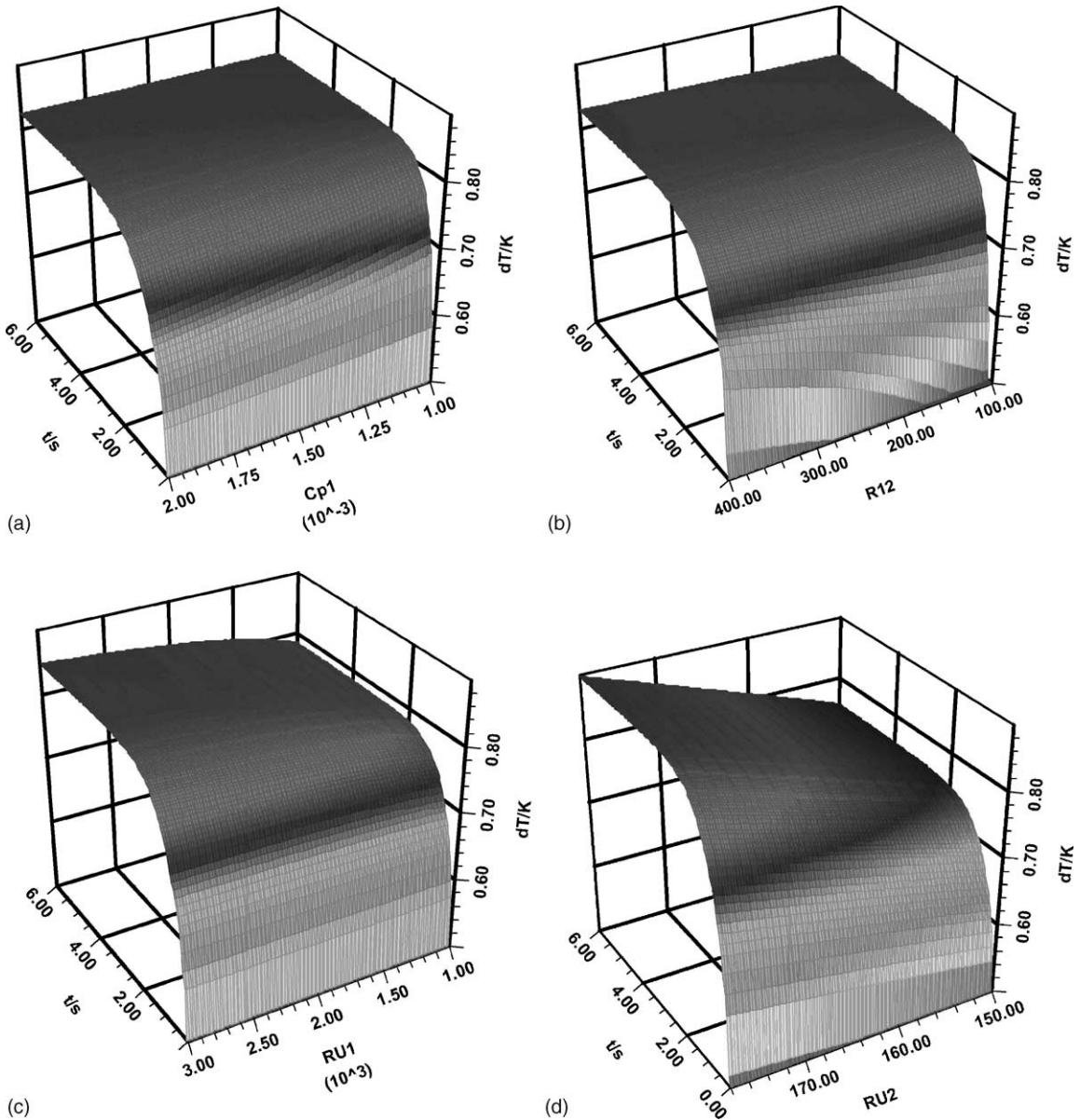


Fig. 15. Simulation of the influence of different fit parameters on the curve shape; the other parameters are kept constant:  $R_{U2} = 163.7$  K/W,  $C_{P2} = 0.00019$  J/K,  $P = 0.00547$  W,  $C_{P1} = 0.0015$  J/K,  $R_{12} = 280$  K/W,  $R_{U1} = 1850$  K/W.

Table 1  
Parameter set of the simulated curves from Fig. 14

	PCL (0.96 mg)	PCL (0.52 mg)
$R_{U1}$ (K/W)	1100.0	1150
$R_{U2}$ (K/W)	163.7	163.0
$R_{12}$ (K/W)	360.0	310.0
$C_{P2}$ (J/K)	0.00019	0.00019
$C_{P1}$ (J/K)	0.0019	0.00122
$P$ (W)	0.00547	0.00547

The evaluation for the measurements with the PCL samples (Fig. 14) is done with Eq. (4) and model B.

The difference of the parameters estimated from the empty device and from the device with sample comes from the different models and the different nomenclature for both models. Thus,  $R_{23}$  in model B for the empty device corresponds to  $R_{U2}$  in model A for the device with sample. The parameters estimated from the measurement of the empty device were used as starting values for the fit calculations of the measurements with the PCL samples. The resulting parameter sets of the fits are collected in Table 1.

After correction for the known heat capacity of the aluminum pan, the specific heat capacities of the samples are found to be 1.60 J/(g K) and 1.63 J/(g K), respectively. A precise measurement using a power compensated commercial DSC with a larger sample gave a value of 1.8 J/(g K) (the measurements were all carried out at room temperature). The results of our measurements are satisfactory if we have in mind the rather simple model as well as that the two values above were obtained from the evaluation of a single pulse only. To increase the accuracy, a series of such evaluations should be averaged.

Simulation calculations shows the influence of the different parameters on the shape of the measured curve more clearly (see Fig. 15). As can be seen, every parameter has an influence on the amplitude as well as on the shape of the curve; therefore it is very important for the simulation to start from suitable initial values and to limit the parameter ranges properly.

## 7. Conclusion

A chip-calorimeter can be a powerful quantitative instrument when used in combination with the heat

pulse method especially in applications where small samples, low heating rates and high time-resolution are needed. Time dependent processes can be monitored and analyzed by using heat pulses as simulation of the system and evaluating the response in time which can be measured with high resolution and amplitude. The prerequisites to get precise and reliable results are the following:

- The thermopile should be calibrated using accepted temperature standards.
- Sample pans should be flat and have always the same size and properties to ensure that the variation of the transport parameters is only small.
- The diameter of the sample or sample pan should match to the heater area.
- The different transport parameters must always be taken into account. Scanning mode measurements that are calibrated with a known heat capacity standard can be accurate only if the geometry and material properties of the standard and the measured sample are similar.
- To fit the calculated curves to the measured curves correctly a lot of extra information should be taken into account. This information can be obtained, with some experience, from other measurements of known samples (with known geometry), from measurements of the empty calorimeter and from direct calculations of the heat transfer (using common methods [15]). All this information should be used to obtain high quality starting values for the fit procedure and to reduce the possible range of variation.
- The average of several pulse responses should be used if possible.
- The originally existing “parasitic time constants” of the system should be eliminated by gluing the chip frame to the ceramic housing with high thermal conductivity.
- The temperature controlled furnace of the chip-calorimeter should be optimized for the intended applications (e.g. high or low heating rates). The quality of the temperature control must be good enough that no additional noise caused by the furnace is measured with the chip-calorimeter.

Taking these points into account, it is possible to measure heat capacities of small samples (down to 1 mg and below) with sufficient accuracy at a

time-resolution well below 1 s. If a proper sample can be positioned directly on the chip, without the special pan, even lower masses and time constants can be achieved. Of course the advantage to take the same chip-calorimeter for several measurements could be loosed in this case because of the irreversible pollution of the chip.

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