

## Heat capacity measurement by calibration with dynamic correction of the calorimetric output signal of a thermopile heat conduction calorimeter

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### Abstract

This paper deals with a new quasi-isothermal method for the measurement of heat capacities of good thermal conductors in an LKB 2277 heat flow microcalorimeter TAM (Thermal Activity Monitor), applying a calibration technique with dynamic correction for the calorimetric output signal.

The specific heat capacities of materials with good thermal conductivities, e.g. metals, can be determined with an uncertainty of less than 4%. This new method provides a fast and simple procedure for the measurement of the specific heat capacity in less than 30 min.

With a quasi-isothermal method, no heating or cooling of the calorimetric unit is needed. The temperature of the thermostat represents directly the test temperature.

### INTRODUCTION

In a previous study by Löwen et al. [1], the measurement of the heat capacities of bulk or inhomogeneous materials using a simple calibration technique was presented. The application of this calibration principle to the LKB 2277 heat flow microcalorimeter TAM allows the determination of the specific heat capacity from the time constant of the experimental calorimetric data. This time constant corresponds to the thermal characteristics of the specimen, including the heat capacity, and can be evaluated by computer analysis of the experimental data.

A similar technique has already been applied to the LKB 2277 microcalorimeter by the manufacturers, i.e. the dynamic correction of the calorimetric output signal with properties describing the inertia characteristics of the calorimetric system [2]. With this simple and fast calibration technique one obtains an additional experimental tool with which to determine the specific heat capacity of good thermal conductors, e.g. metals. Neither a temperature drop of the calorimetric unit, nor an integration of the experimental data curve is needed.

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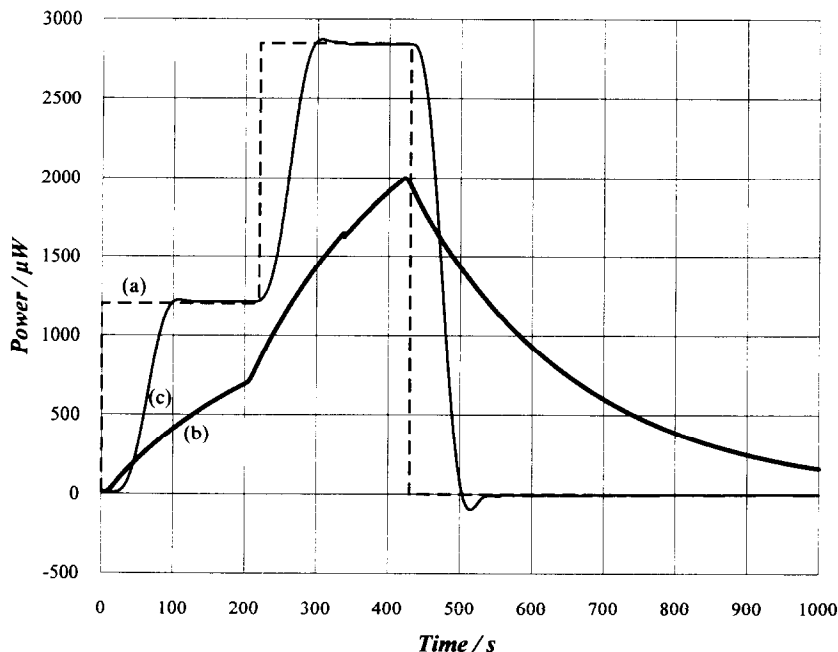


Fig. 1. Dynamic correction of the measured signal by means of a two-step calibration. Curve a, power input; curve b, power output; curve c, dynamically corrected power according to eqn. (1).

#### MEASURING EQUIPMENT AND GENERAL PRINCIPLES

The method was developed on the LKB 2277 microcalorimeter TAM. The measuring unit was linked to a computer working with the TAM software DIGITAM from ThermoMetric [1] which controls the mode of the experimental procedure and stores the data sets obtained [1–3].

Thermopile heat conduction calorimeters have large time constants. Thus, the voltage–time curve will lag behind the input power–time curve except in steady-state conditions. In order to get an accurate measure of the power variation with time, e.g. in biological systems or technical materials, the calorimetric signal can be corrected with a frequency-response method applied to the LKB 2277 microcalorimeter. This method is an automatic procedure that records the response of the measuring system initiated by two calibration heat flowrate levels. A dynamic correction takes about 10 min and can be divided into three steps. First, the thermal input from the calibration heater is set to 40% of full scale, e.g.  $1200 \mu\text{W}$  if the full scale value is  $3000 \mu\text{W}$ , see Fig. 1, curve a. This part takes about 3 min. Second, the input signal is increased to 95% of full scale for about 4 min. Finally, the calibration heat is switched off automatically. While these events are taking place, data on the response of the system to the thermal input from the

calibration heater are being collected and stored in the memory. The response of the system is the measured power output, curve b in Fig. 1. The output signal increases in a steady curve while the first two steps are taking place, and decreases when the calibration heat is switched off.

The digital calibration unit of the LKB 2277 TAM incorporates a microprocessor to provide automatic dynamic correction and filtering of the signal output. The output power signal  $P_{\text{out}}$  from the thermal effect is compared to data in the memory in order to make the dynamic correction, i.e. calculating the dynamically corrected power  $P_{\text{corr}}$  according to eqn. (1), below. The calorimetric response of any thermal event can then be compared to the information in the memory. Curve b in Fig. 1 shows the raw output signal as a response to the above-described calibration heat flowrate levels given as curve a. The dynamically corrected signal that is calculated from the raw output signal is shown as curve c.

The time constants  $\tau_1$  and  $\tau_2$  of the observed system are determined according to eqn. (1), where  $\varepsilon$  is the calibration constant,  $V$  the thermopile voltage, and  $t$  time. The time constants  $\tau_i$  are stored in the memory. They can be used subsequently to calculate the dynamically corrected signal that is a fair representation of the true thermal effect in the measuring cup

$$P_{\text{corr}} = \varepsilon \left( V + (\tau_1 + \tau_2) \frac{dV}{dt} + \tau_1 \tau_2 \frac{d^2V}{dt^2} \right) \quad (1)$$

The dynamic correction leads to two time constants describing the inertia characteristics of the system. As a first approximation,  $\tau_1$  is related to the ratio between the heat capacity of the calorimetric vessel and its heat exchange coefficient with the surrounding heat-sink. The second time constant is related to internal temperature gradients [3]. For more theoretical details, see refs. 4 or 5.

#### PERFORMANCE OF THE TEST AND ANALYSIS OF THE EXPERIMENTAL DATA

From the statements above, it follows that a dynamic correction takes approximately 10 min, plus at most 20 min for reaching the baseline. After 10 min of operation, one obtains the two time constants automatically and no additional analysis of experimental data is necessary. Before a test can be performed, the system needs approximately 2 h to reach thermal equilibrium, i.e. the baseline, after inserting the sample cup.

Three tests are necessary in order to calibrate the time constant  $\tau_1$ :

- (i) With a totally empty sample cup, yielding the time constant  $\tau_0$ .
- (ii) With the reference material in the sample cup, yielding  $\tau_{\text{ref}}$ .
- (iii) With the specimen in the sample cup, yielding  $\tau_{\text{exp}}$ .

Three calculation steps, defined by eqns. (2)–(4), are needed to determine the heat capacity:

TABLE 1

Time constants from a series of blank tests

No. of tests	$\tau_0/s$
1	334.69
2	333.89
3	335.69
4	334.23
5	333.67
Mean value/s	334.434
Standard deviation	$\pm 0.24\%$

- (i) The time constant  $\tau_0$  representing the based value is subtracted from  $\tau_{\text{ref}}$  and  $\tau_{\text{exp}}$ . Thus, two new quantities are obtained

$$\Delta\tau_{\text{ref}} = \tau_{\text{ref}} - \tau_0 \quad \text{and} \quad \Delta\tau_{\text{exp}} = \tau_{\text{exp}} - \tau_0 \quad (2)$$

- (ii) These two quantities are divided by the mass of the respective sample material and one obtains

$$\Delta\tau_{\text{ref}}^* = \frac{\Delta\tau_{\text{ref}}}{m_{\text{ref}}} \quad \text{and} \quad \Delta\tau_{\text{exp}}^* = \frac{\Delta\tau_{\text{exp}}}{m_{\text{exp}}} \quad (3)$$

- (iii) Finally, the unknown specific heat capacity is calculated from

$$C_{p,\text{exp}} = C_{p,\text{ref}} \frac{\Delta\tau_{\text{exp}}^*}{\Delta\tau_{\text{ref}}^*} \quad (4)$$

## RESULTS AND ASSESSMENT

The specific heat capacities of solid and liquid substances were measured in order to verify the applicability of this new method.

Table 1 shows the results for the measurement of a series of blank tests. The values for the time constant  $\tau_0$  have a mean value of 334.434 s and a standard deviation of 0.24%. This indicates the good repeatability of the dynamic correction.

Table 2 summarizes the results of copper, titanium and chromium. These tests were performed at 70°C with different masses of specimen.

Table 3 lists the calculations of the heat capacity of titanium and chromium. Electrolytic copper was chosen as the reference material, guaranteeing high purity, with a  $C_{p,\text{lit}}$  value of 0.390 kJ kg<sup>-1</sup> K<sup>-1</sup>. In this paper, values for  $C_{p,\text{lit}}$  are taken from ref. 6. Deviations are calculated as the deviation of the measured value from the literature value related to the literature value. The results in Table 3 show deviations below 4%.

Table 4 gives the results for the measurements with *n*-heptane and bidistilled water at 70°C. Values from the literature for the specific heat

TABLE 2

Experimental results for some metals of different sample masses

Material	Mass/g	$\tau_{\text{exp}}/\text{s}$	$\Delta\tau_{\text{exp}}/\text{s}$	$\Delta\tau_{\text{exp}}^*/\text{s g}^{-1}$
Cu	16.6918	422.02	87.586	5.2472
	33.2863	516.28	181.841	5.4629
Ti	8.4402	396.91	62.476	7.4022
	16.8577	460.03	125.596	7.4504
Cr	13.4556	423.88	89.446	6.6475
	26.9076	517.38	182.946	6.7990

TABLE 3

Heat capacities of titanium and chromium

Material	$C_{p,\text{lit}}/\text{kJ kg}^{-1} \text{K}^{-1}$	Mass/g	$C_{p,\text{exp}}/\text{kJ kg}^{-1} \text{K}^{-1}$	Deviation
Ti	0.533	8.4402	0.550	+3.16%
		16.8577	0.532	-0.27%
Cr	0.476	13.4556	0.494	+3.88%
		26.9076	0.485	+2.05%

TABLE 4

Heat capacity measurements of liquids

Material	Mass/g	$\tau_{\text{exp}}/\text{s}$	$C_{p,\text{exp}}/\text{kJ kg}^{-1} \text{K}^{-1}$	Deviation
<i>n</i> -Heptane	1.346	415.69	4.308	+77.9%
	1.657	429.42	4.091	+68.9%
	2.305	453.08	3.674	+51.7%
	2.722	471.10	3.538	+47.9%
Bidistilled water	1.016	402.166	4.757	+13.6%
	2.043	468.368	4.680	+11.8%
	3.050	525.576	4.473	+6.9%
	4.195	586.606	4.290	+2.5%

capacities are 2.422 and 4.186 kJ kg<sup>-1</sup> K<sup>-1</sup> for *n*-heptane and water, respectively. Again, electrolytic copper was chosen as the reference material. The calculated specific heat capacity decreases with increasing mass. Deviations are positive and in the range 2.5–14% for bidistilled water and approximately 50–80% for *n*-heptane.

Table 4 shows that this method is not applicable to liquids, i.e. species with low thermal conductivities. The theory assumes the calibration heat to be distributed immediately in the sample cup. In the case of liquids, where

the thermal conductivity is about  $10^{-3}$  times lower than that of metals, there is an additional heat transfer resistance which depends on mass and cannot be calibrated.

Tables 1–3 show that with this new method the heat capacities of good thermal conductors can be determined with good repeatability. The deviation from literature values is below 4%. The advantage of this method is that it is simple and fast.

If materials with low thermal conductivities are to be investigated, the method described in ref. 1 should be selected, especially if the heat capacities of bulk or inhomogeneous species have to be measured.

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