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Heat capacity measurement of bulk or inhomogeneous materials [1]

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Abstract

This paper deals with a new, quasi-isothermal method for the measurement of heat capacity in an LKB 2277 heat flow microcalorimeter TAM (thermal activity monitor), following the calibration principle.

The specific heat capacity of a specimen of any material (liquid, solid, bulk, inhomogeneous, etc.) which fits into a 4 ml sample cup can be determined with an uncertainty of less than 5%. With a quasi-isothermal method no heating up or cooling down of the calorimetric unit is needed. The temperature of the thermostat represents directly the test temperature.

INTRODUCTION

In order to measure the heat capacity of inhomogeneous materials, liquid or solid, a technique that abandons the measurement of absolute data is required. Following the simple principle of a calibration, the heat capacity of a liquid or solid specimen can be determined from the experimental data curve recorded with an LKB 2277 heat flow microcalorimeter TAM [1].

Some other techniques for measuring the heat capacity with a heat flow microcalorimeter have been reported. Mikhailik et al. [2] described the measurement of the specific heat capacity in the DAK 1-1 microcalorimeter, based mainly on the same principle of calibration. The specific heat capacity of the specimen is determined by the absorbed thermal energy of the sample during the supply of a constant heat flow rate to the calorimetric cell. The evaluation is based on the integration of the experimental data curve representing the absorbed amount of heat by the sample unit.

Bunyan [3] measured the specific heat capacity of reactive materials

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within an LKB 2277 heat flow microcalorimeter BAM by recording the heat flow rate from a sample during a small rapid drop of the operating temperature of the microcalorimeter. The area below the experimental data curve, when plotted against time, corresponds to the specific heat capacity of the sample, taking the temperature drop into consideration.

The application of the calibration principle to the LKB 2277 heat flow microcalorimeter TAM allows the estimation of the specific heat capacity from the decay time of the experimental data set. This time constant corresponds to the thermal characteristics of the specimen including the heat capacity. Neither a temperature drop of the calorimetric unit nor an integration of the experimental data curve is needed. The experimental procedure taking place in one of the measuring cylinders does not interfere with the series of experiments in adjacent measuring cylinders.

MEASURING EQUIPMENT AND GENERAL PRINCIPLES

This method was developed on the LKB 2277 heat flow microcalorimeter TAM [1]. The measuring unit was linked to a computer working with the TAM software from ThermoMetric, Digitam. It controls the mode of the experimental procedure and stores the obtained data sets.

The analysis of the experimental data was carried out using a software program based on SAS (Statistical Analysation System) [4].

The TAM guarantees a high measurement accuracy due to the stability of the heat sink containing the measuring cylinder. The temperature fluctuation is of the order of $\pm 2 \times 10^{-4}$ °C within the temperature range from 10 to 90°C.

The caloric measurement of the specimen takes place in the sample vessel of a combination measuring cylinder working with the twin principle, in order to establish uniform environment (see Fig. 1). Comparing the signal from the sample cup that contains a specimen with the signal from

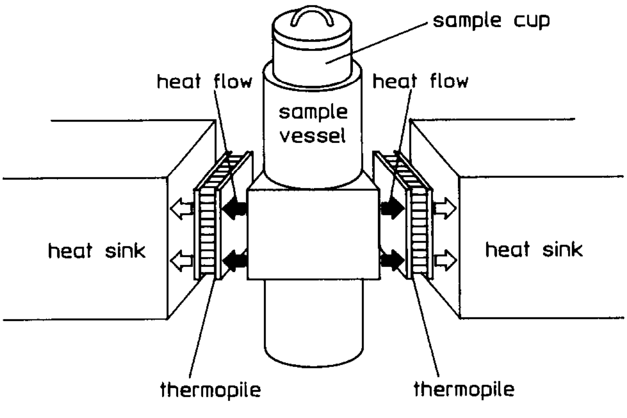

Fig. 1. Scheme of the measuring set up [1].

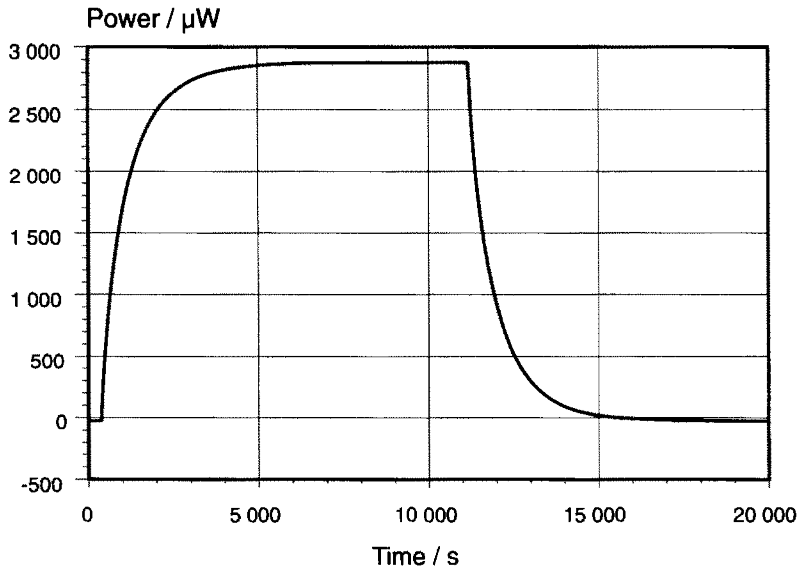

Fig. 2. A typical data curve.

the reference cup representing a blank, the influence of variations in the thermostat temperature during the experiment is eliminated. The heat flow from both cups transferred to the heat sink during the measurement procedure, is detected by highly sensitive thermopiles. Differences of less than 3×10^{-3} μW can be measured.

The experimental procedure follows the calibration principle. The sample cup and the reference cup are lowered into respective sample vessels of the combination measuring cylinder. When thermal equilibrium is established, a constant heat flow of 3000 μW is supplied to the sample cup. The part of the heat not being stored by the sample cup and its contents is transferred to the heat sink, via the thermopiles, where it is detected. The supply of heat is stopped when thermal equilbrium is reached.

A data curve as shown in Fig. 2 is obtained by recording the heat flow rate to the heat sink during the time of measurement. In order to estimate the specific heat capacity of a specimen from this curve, the mathematical function representing the set of data has to be specified. The following heat balance describes the heat flow rate within the system during the calibration procedure

$$\begin{bmatrix}\text{Heat flow rate}\\ \text{supplied to sample}\\ \text{cup and specimen}\end{bmatrix} = \begin{bmatrix}\text{Heat flow rate}\\ \text{transferred to}\\ \text{thermal heat sink}\end{bmatrix} + \begin{bmatrix}\text{Power stored}\\ \text{in sample}\\ \text{cup and specimen}\end{bmatrix}$$

For $t \geq t_0$ (see Fig. 2), when the constant heat flow rate Φ_{feed} was supplied to the sample cup and specimen, the increase in power stored by the measuring cup and the specimen can be expressed as

$$\frac{\partial Q_{\text{storage}}}{\partial t} = \Phi_{\text{feed}} - \Phi_{\text{transfer}}$$

where $\Phi_{\text{transfer}} = \delta Q_{\text{transfer}}/\delta t$ represents the heat flow rate transferred to the heat sink.

Applying the definitions for Q_{storage} and Q_{transfer}, this becomes

$$\frac{\partial}{\partial t}(mc_p\,\Delta T)_{\text{transfer}} = \Phi_{\text{feed}} - B_{\text{transfer}}\,\Delta T$$

where m represents the mass and c_p the specific heat capacity of the measuring cup/specimen system, ΔT is the temperature increment and B_{transfer} represents the thermal characterisation of the apparatus, obtained from the calibration measurements.

This equation corresponds to a differential equation of the form

$$C_1\left(\frac{\partial \Delta T}{\partial t}\right) + C_2\,\Delta T = C_3$$

where C_1, C_2 and C_3 are constants. The solution of this differential equation is

$$\Delta T(t) = (T - T_0)\exp\left(-\frac{t}{\tau}\right)$$

representing a signal of a first-order decay, where T_0 is the temperature at time t_0, T the temperature at time t, and τ represents the decay time constant.

Using this expression for $\Delta T(t)$, the power being stored by the measuring cup and specimen during the calibration can now be written as

$$p_{\text{storage}}(t) = C_4 - C_5\exp\left(-\frac{t}{\tau}\right)$$

where $p_{\text{storage}}(t)$ is the time-dependent curve of the heat stored in the measuring cup and specimen during the calibration, C_4 and C_5 are constants, and τ represents the time constant maintaining the specific heat of the specimen.

Referring to the heat balance, it was found that the time constant τ must be proportional to the product of the mass and specific heat capacity of the specimen and the measuring cup; τ is also linked to the structure and the thermal properties of the measuring equipment.

PERFORMANCE OF THE TEST AND ANALYSIS OF THE EXPERIMENTAL DATA

The curve of $p_{\mathrm{storage}}(t)$ represents the actual profile of an experimental data set. In order to estimate the decay time of this mathematical function, each data set is approximated with the aid of a numerical program, SAS [4].

The first part of the experimental data curve was ignored for the numerical approximation, because of high uncertainty for low $p(t)$ values. The approximation started where

$$\frac{\partial p(t)}{\partial t} \geq 0.8\left(\frac{\partial p(t)}{\partial t}\right)_{\max}$$

This criterion holds for all data sets being analysed (see Fig. 3).

Therefore the approximation only takes place within the range of highest resolution. Nevertheless, the numerical program processes more than 5000 measuring points for this procedure, guaranteeing a high accuracy. The uncertainty for the coefficient τ_i is below 0.1%. One decay time τ_i is derived for every experimental data set (i).

Further analysis of the correlation between decay time τ_i and other parameters (heat capacity and mass of specimen and sample cup, or the influencing factors of the measuring unit) showed that the unknown heat capacity of a specimen can be determined from three measurements: with the sample cup as a blank (index "0"); with the reference material in the sample cup (index "ref"); and with the specimen in the sample cup (index "exp").

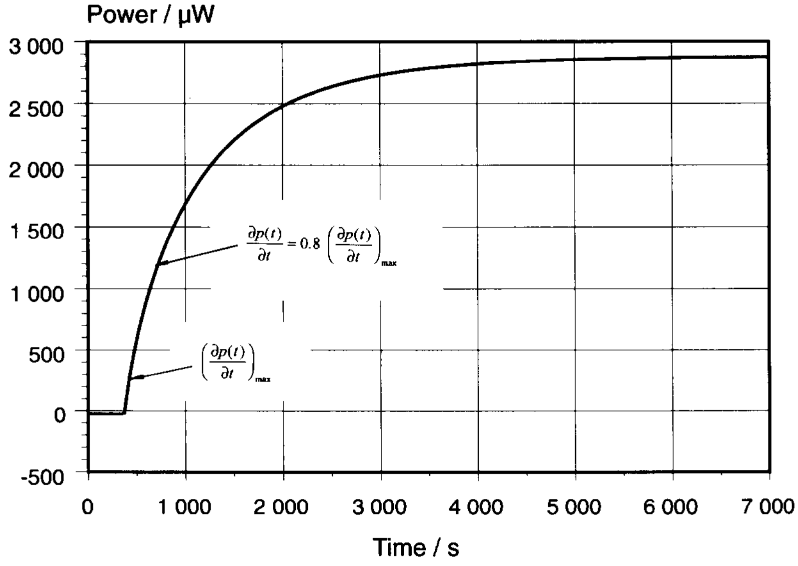

Fig. 3. Data set for the approximation procedure.

The measurements were made in the following way. The sample cup and "blank" reference cup were introduced to the respective sample vessels for thermal equilibration for 3 h. The value of the power $p(t)$ was recorded for baseline control every 20 s. When thermal equilibrium was established, a constant heat flow rate of 3000 μW was supplied to the measuring cup; $p(t)$ was measured every 2 s. After 2 h, the heat input was switched off. This procedure was repeated for the sample cup representing a blank, for the measuring cup containing a sample, and, finally, containing the reference material.

The experimental data of these three tests were analysed using the numerical data analysis program; three functions $p_0(t)$, $p_{\mathrm{ref}}(t)$, and $p_{\mathrm{exp}}(t)$, are obtained, giving the three time constants τ_0, τ_{ref} and τ_{exp}.

In order to determine the unknown specific heat of the sample from these three experimental results, three calculation steps are required.

1. The time constant τ_0 representing the base value is subtracted from τ_{ref} and τ_{exp}. Two new quantities are obtained: $\Delta\tau_{\mathrm{ref}} = \tau_{\mathrm{ref}} - \tau_0$, and $\Delta\tau_{\mathrm{exp}} = \tau_{\mathrm{exp}} - \tau_0$.

2. The correlation between these new quantities and the mass of the respective sample material (reference or specimen) is found to be proportional. Consequently, $\Delta\tau_{\mathrm{ref}}$ and $\Delta\tau_{\mathrm{exp}}$ are divided by the value of the mass of the respective sample material, yielding

$$\Delta\tau^*_{\mathrm{ref}} = \frac{\Delta\tau_{\mathrm{ref}}}{m_{\mathrm{ref}}}$$

and

$$\Delta\tau^*_{\mathrm{exp}} = \frac{\Delta\tau_{\mathrm{exp}}}{m_{\mathrm{exp}}}$$

3. Finally the proportional factor describing the correlation between $\Delta\tau^*$ and the value of the specific heat of the respective sample material is obtained from the known value of the heat capacity of the reference material, yielding

$$c_{\mathrm{exp}} = c_{\mathrm{ref}} \times \frac{\Delta\tau^*_{\mathrm{exp}}}{\Delta\tau^*_{\mathrm{ref}}}$$

RESULTS AND ASSESSMENT

The specific heats of various substances, liquid and solid, were measured in order to evaluate the uncertainty of the new method for measuring heat capacities.

Table 1 lists the measured heat capacities of various solid specimens at 25°C. For all specimens, electrolytic copper was chosen as the reference material.

TABLE 1

Heat capacities of solid specimens

Material	$c_{p,\mathrm{exp}}$/kJ kg^{-1} K^{-1}	$c_{p,\mathrm{lit}}$/kJ kg^{-1} K^{-1}	Uncertainty/%
Stainless steel (X5CrNi188)	0.5082	0.5000 [5]	1.65
Graphite	0.6823	0.7086 [6]	3.72
Fe	0.4493	0.4478 [6]	0.33
Al	0.8876	0.9020 [7]	1.60
Cr	0.4515	0.4475 [6]	0.89
Ti	0.5114	0.5236 [6]	2.32

The uncertainty shows the deviation of the measured value from the literature value, related to the literature value. Table 1 shows a minimum uncertainty for iron of 0.33%, and a maximum error for graphite of 3.72%. The purity of the graphite used was not defined, however, so the literature value of the heat capacity may not be comparable.

Table 2 gives the heat capacities of different bulk materials; the results were calculated with copper as reference material.

TABLE 2

Heat capacities of bulk materials

Material	Particle size/μm	$c_{p,\mathrm{exp}}$/kJ kg^{-1} K^{-1}
Ash	400–700	0.7695
Sand	200–400	0.7683
Glass	800	0.8302

In order to complete the assessment, the repeatability of this measuring procedure was estimated by a series of measurements with n-heptane, as shown in Table 3. The table shows all the experimental data, with m_{exp} being the mass of the sample material and τ_{exp} the time constant from the

TABLE 3

Experimental results for n-heptane tests with different sample masses

Mass/g	τ_{exp}/s	$\Delta\tau_{\mathrm{exp}}$/s	$\Delta\tau^{*}_{\mathrm{exp}}$/s
0.6829	206.587	13.753	20.139
1.3540	219.845	27.011	19.949
1.3560	219.913	27.079	19.970
2.0049	232.543	39.709	19.806
2.4632	242.192	49.358	20.038
2.7091	246.072	53.238	19.652

experimental data curve. The evaluation was made with $\tau_0 = 192.834$ s as the time constant of a "blank" experiment.

Varying the mass of the *n*-heptane samples from 0.68 to 2.71 g, the results of the different tests were compared and the uncertainties were estimated: they were less than 0.8%, guaranteeing a high repeatability.

The method presented in this paper enables the measurement of the heat capacity of any material (liquid, solid, bulk, inhomogeneous) fitting into a 4 ml measuring cylinder, with an uncertainty of less than 5% and a repeatability of more than 99%.

The technique can easily be applied to any LKB 2277 heat flow microcalorimeter TAM in normal operation, because no additional accessories or technical specifications are needed.

In addition, it is possible to measure even reactive or corrosive substances in glass cups, without risk of falsifying the experimental results.

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