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# Fast scanning power compensated differential scanning nano-calorimeter: 2. Heat capacity analysis

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ABSTRACT

Fast scanning calorimetry is an attractive tool to study kinetics and thermodynamics of materials created or used far from thermodynamic equilibrium. In the first part of this paper we describe a differential fast scanning nano-calorimeter utilizing a new power compensation scheme. The device is suitable for calorimetric experiments at controlled cooling and heating rates between 1 and 100,000 K/s. This part of the paper focuses on determination of specific heat capacity out of the measured data. Assuming time independent heat losses for sample and reference sensors at heating and cooling makes possible a heat capacity analysis based on symmetry arguments. The described procedure is not limited to chip-based fast scanning devices but can be applied to common DSC too. Due to the differential scheme and power compensation heat capacity of polymer samples with sample mass of a few 10 ng is available. Reproducibility of heat capacity is in the order of ±2% at optimum scanning rates. Uncertainty of specific heat capacity strongly depends on sample mass determination and is in the order of ±10%. Adding a small particle of a temperature calibration standard, e.g. indium or tin, on top of the polymer sample reduces uncertainty of temperature to about ±4 K.

## 1. Introduction

In polymers, pharmaceuticals, and metal alloys metastability is the rule rather than the exception, and the study of the kinetics of such systems has become an important issue [1,2]. For a thorough understanding of the kinetics of all kinds of temperature- and time-dependent processes related to metastability there is an urgent need for new (calorimetric) techniques enabling the use of high cooling and heating rates [3].

Conventional DSC is one of the few techniques that have already a relatively large dynamic range of scanning rates. They allow (quasi) isothermal measurements and scanning rates up to 10 K/s for power compensated DSCs [1,4]. Several approaches are known how to overcome these limitations. Most of them are based on thin film techniques. Quasi-adiabatic scanning calorimetry at high heating rates, ca. 500 K/s, was developed by Hager [5] and even for rates up to $10^7$ K/s, by Allen and co-workers [6,7] and others [8,9]. Heat capacity determination in these quasi-adiabatic calorimeters is relatively simple because heat losses can be neglected in first approximation. Nevertheless, a more quantitative analysis requires quite some corrections also for these calorimeters [7–12]. But as mentioned above, further investigation of metastable phase formation can be obtained only if the same high controlled cooling rates are available too. Therefore a single sensor non-adiabatic fast scanning calorimeter [13–16] was developed.

The main problem for heat capacity determination for the non-adiabatic single sensor device is the subtraction of the heat loss function. It is realized as a subtraction of a 3rd to 5th order polynomial function [16]. But as soon as several sharp events in the sample occur, the error in determination of the loss polynomial increases dramatically (Fig. 1).

A differential power compensated fast scanning calorimeter was set up to overcome these problems at least in part. It covers the scanning rate range between 1 and $10^5$ K/s in heating and cooling. The device, as described in the first part of this paper [17], uses the same low addenda heat capacity sensors [18] as previously used for the single sensor device [14,16,19]. The presence of an empty reference sensor reduces the influence of heat losses and addenda heat capacity on the obtained data. For a better sample temperature control, particularly in the transition regions, a power compensation was introduced, this way following the work by Rodriguez-Viejo and co-workers [20]. To improve signal to noise ratio and resolution of the device, even under fast scanning conditions, an analog power compensation technique was implemented. A differential power compensation scheme provides, under conditions of ideal symmetry of both sensors, directly the heat flow rate into the sample, which simplifies heat capacity calculation. Furthermore, user-friendly experiment management software and a software package for data evaluation were developed.

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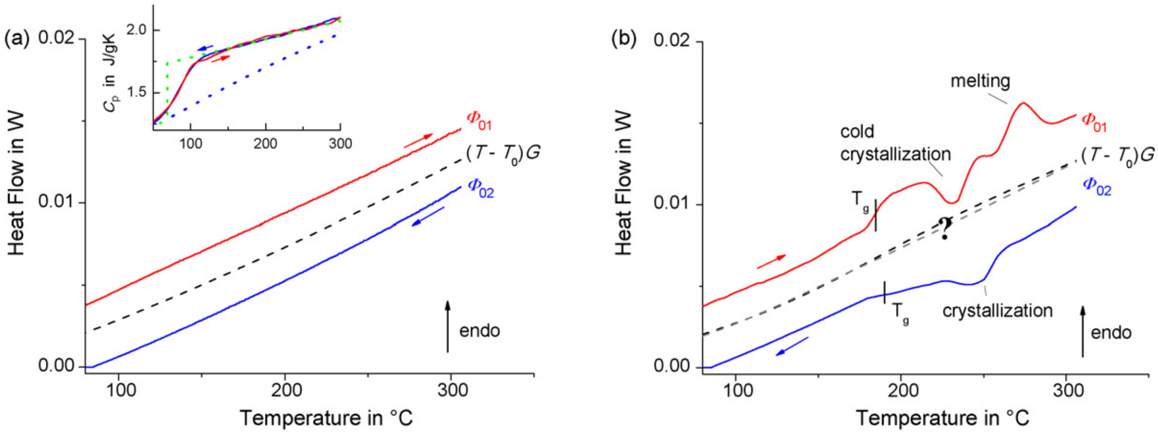

**Fig. 1.** (a) Heat flow rate at heating $\Phi_{01}$ and cooling $\Phi_{02}$ for a heating–cooling scan at 2000 K/s for ca. 480 ng poly (ethylene terephthalate) (PET) sample [15]. The heat loss curve $(T-T_0)G$ is determined outside the transition regions as the symmetry line between $\Phi_{01}$ and $\Phi_{02}$. (b) Problems of heat loss determination in case of complex overlapping events in the sample during heating and cooling.

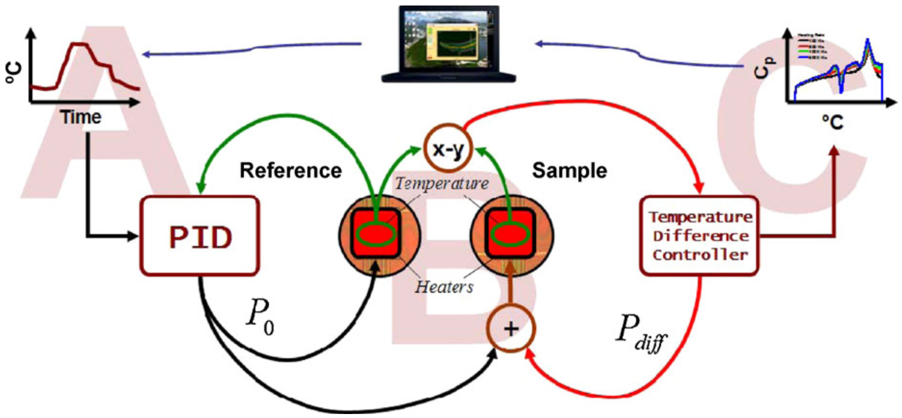

**Fig. 2.** Scheme of the power compensated fast scanning calorimeter. A, the time-temperature profile is generated by the user and is provided to the PID controller through a DAC board. B, sample temperature is made to follow precisely the required profile by means of control loop. C, the resulting temperature difference can be recalculated to heat flow rate and sample heat capacity as shown below.

The developed new power compensation scheme realizes such separate control loops as shown in part 1 [17,21]. It was already successfully applied to the study of polymers [22–25] and metals [26–28]. Compared to the PerkinElmer power compensation scheme [29] the new scheme allows a more precise control of the temperature of both sensors. But the proportionality between the remaining temperature difference in the differential control loop and the differential heat flow rate is lost. Therefore the new scheme requires the measurement of more than only one signal to allow recalculation of the power difference as it is described in part 1 [17].

The practical realization of the control scheme described in Ref. [17] is shown in Fig. 2. The user defined time-temperature profile is recalculated into a voltage and provided as the setpoint for the PID controller. The PID controller makes the temperature of the reference sensor to follow the profile by adjusting power $P_0$ to its heater. The same power $P_0$ is applied to the sample loaded sensor. The difference between the temperatures of reference and sample side is minimized by the differential controller by adding power $P_{\text{diff}}$ to the sample side. The actual realization of this scheme using thin film chip calorimeter sensors is shown in Fig. 2.

The resistive film-heaters of the sensors provide the power, which is supplied to the membrane/sample interface and propagates through the sample, membrane and the ambient gas. For a perfectly power compensated system power is distributed in a way that both sensors are always at the same temperature, $T$, and scanned at the programmed rate, $\mathrm{d}T/\mathrm{d}t$, independent of any heat effect in the sample. Assuming an ideally symmetric differential system, which means equal addenda heat capacities $C_0$ on both sides and equal heat losses $P_{\text{loss}}(T)$ to the surrounding on both sides, the heat balance equations for both sensors are as follows:

$$\text{reference}: \quad C_0(T)\frac{\mathrm{d}T}{\mathrm{d}t} = P_0(T) - P_{\text{loss}}(T) \tag{1.1}$$

$$\text{sample}: \quad (C_0(T) + C(T))\frac{\mathrm{d}T}{\mathrm{d}t} = P_0(T) + P_{\text{diff}}(T) - P_{\text{loss}}(T) \tag{1.2}$$

where $C$ is sample heat capacity. In this particular case the difference between Eqs. (1.2) and (1.1) yields:

$$C(T)\frac{\mathrm{d}T}{\mathrm{d}t} = P_{\text{diff}}(T) \tag{1.3}$$

where $P_{\text{diff}}$ is the difference between the power supplied to the sample and the reference sensors.[1] Consequently, the aim was to set up a system with near to perfect power compensation, which allows determination of $P_{\text{diff}}(T)$ and finally to correct for unavoidable asymmetries between both sides in real measurements at high scanning rates. The hardware was designed for that aim having in mind anticipated scanning rates of up to 100,000 K/s [17].

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[1] These considerations also hold for conventional DSCs and therefore the procedure described below can be applied to conventional DSC too.