



DSC Resolution and Dynamic Response Improvements Obtained by a New Heat Flow Measurement Technique

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ABSTRACT

Differential Scanning Calorimeter heat flow measurements include significant instrument effects that reduce the dynamic response of the signal to sample effects. For example, a sharp first order transition, like a metal melt displays a protracted exponential decay of the heat flow signal following completion of the melt. This exponential decay is the result of heat storage within the DSC sensor and the sample pan. A new technique for measuring DSC heat flow is described that yields greatly improved dynamic response. The new measurement technique accounts for heat storage within the sensor assembly and the sample pan. Dynamic response of the heat flow signal is significantly enhanced, improving the ability of the DSC to separate thermal events that occur within a small temperature range.

INTRODUCTION

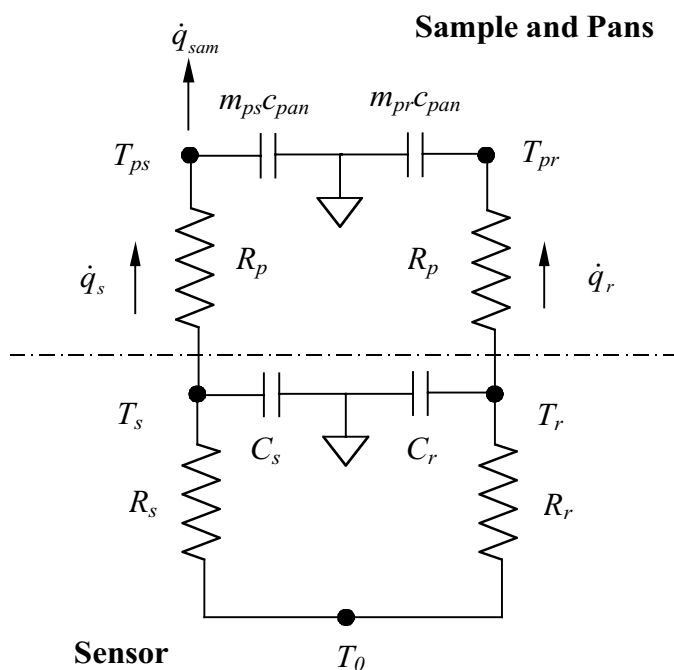
It is well known that the heat flow signal from a DSC during a transition is an inexact representation of the actual sample heat flow. The measured heat flow is delayed and distorted in time (1). This distortion or “smearing” of the heat flow signal is the result of heat storage within the sample pan and the sensor. These heat storage effects are present in all DSCs, heat flux or power compensation. Heat storage within a thermal system is analogous to capacitance within an electrical circuit, so that the heat capacity of the sample pan and the sensor effectively filter the measured heat flow. For many DSC experiments, the smeared heat flow is a sufficiently accurate measurement, for example when heat flow is integrated over a baseline to obtain the enthalpy of a transition. However, in experiments where partial area integrations are required, for example kinetics and purity, the heat flow signal must be de-smear (2). The DSC resolution, i.e. the ability to separate closely spaced transitions is improved when the heat storage effects of pan and sensor are removed from the heat flow signal.

Two de-smearing methods, modeling and numerical deconvolution have generally been used. The modeling approach seeks to represent the DSC by differential equations where the measured signal i.e. the differential temperature and its derivatives are the

inputs and the coefficients of the equations represent the thermal characteristics of the DSC. De-smearing using first and second order differential equations has been demonstrated (3,4). A difficulty in practicing these methods is the determination of appropriate values for the instrument coefficients (2). Numerical deconvolution seeks to reconstruct the sample heat flow by employing the convolution integral equation and the apparatus function, which is determined by the response to an impulsive heat input (1). Numerical deconvolution increases noise in the heat flow signal and can only be performed after the measurement is complete (2).

This paper presents another approach to obtaining the actual sample heat flow, using a new heat flow measurement. It is based on representation of the DSC heat flow measurement by two differential equations that use two differential temperature measurements and the sensor temperature as input signals. A calibration procedure is used to determine the differential equation coefficients representing the instrument. This method also accounts for slight imbalances in the measurement system that contribute to instrument baseline defects (5).

The DSC is a twin instrument comprising two nominally identical calorimeters within an enclosure, the temperature of which is controlled to match a desired thermal program. Heat exchange within the calorimeter may be modeled using the lumped heat capacity method where discrete thermal resistances and heat capacities represent the components of the system (6). Figure 1 shows an electrical network that is analogous to



heat flow within the DSC.

Figure 1 – DSC Heat Flow Measurement Model

The model is divided into two parts, the portion below the broken line (labeled sensor) represents the DSC while the portion above the line represents the sample and

pans. Each calorimeter comprises a thermal resistance and a heat capacity; subscripts s and r indicate the sample or reference calorimeter. T_s and T_r are the measured temperatures of the sample and reference calorimeters and T_0 is the temperature at the base of the sensor, which is representative of that of the DSC enclosure. The measured heat flows are \dot{q}_s , the heat flow to the sample and its pan and \dot{q}_r , the heat flow to the reference and its pan. The actual sample heat flow is \dot{q}_{sam} . A heat capacity C_{ps} and a thermal resistance R_p represent the sample pan and the thermal resistance between pan and sensor. The reference pan is assumed to be empty, a heat capacity C_{pr} and a thermal resistance R_p represent the reference pan and the thermal contact resistance between pan and sensor. The sample and reference pan temperatures are T_{ps} and T_{pr} .

Performing a heat balance gives the measured sample and reference heat flows in terms of measured temperatures T_s , T_r , T_0 and sensor thermal parameters R_s , C_s , R_r , C_r :

$$\dot{q}_s = \frac{T_0 - T_s}{R_s} - C_s \frac{dT_s}{dt} \qquad \dot{q}_r = \frac{T_0 - T_r}{R_r} - C_r \frac{dT_r}{dt}$$

substitute the two measured differential temperatures:

$$\Delta T = T_s - T_r \qquad \Delta T_0 = T_0 - T_s$$

into the sample and reference heat flow equations to obtain the heat flow measurement equations:

$$\dot{q}_s = \frac{\Delta T_0}{R_s} - C_s \frac{dT_s}{dt} \qquad \dot{q}_r = \frac{\Delta T_0 + \Delta T}{R_r} - C_r \frac{dT_s}{dt} - \frac{d\Delta T}{dt} \downarrow$$

Thermal resistances and heat capacities are obtained using a two part calibration method (5). The measured sample heat flow includes the sample and pan heat flow and, likewise, the measured reference heat flow is the sum of the pan and reference heat flows.

The objective of the measurement is to recover the true sample heat flow \dot{q}_{sam} . The measured sample heat flow is the sum of the sample and sample pan heat flows:

$$\dot{q}_s = \dot{q}_{sam} + m_{ps} c_{pan} \frac{dT_{ps}}{dt}$$

The measured reference heat flow is just the pan heat flow because the reference pan was assumed to be empty:

$$\dot{q}_r = m_{pr} c_{pan} \frac{dT_{pr}}{dt}$$

Using the reference heat flow equation to eliminate the pan specific heat capacity and solve for \dot{q}_{sam} :

$$\dot{q}_{sam} = \dot{q}_s - \dot{q}_r \frac{m_{ps} \frac{dT_{ps}}{dt} \downarrow}{m_{pr} \frac{dT_{pr}}{dt} \downarrow}$$

This equation gives the actual sample heat flow and accounts for pan mass imbalances and differences in heating rate between the sample and reference pans. The heat flow measurement equations include imbalances and differences in heating rate between the sample and reference calorimeters. Conventional DSC heat flow measurements do not include the sensor imbalances or the differences in heating rate between the sample and reference calorimeters and pans. The heating rate ratio accounts for the fact that during a DSC experiment the heating rates of the sample and reference pans may be different, for example during a transition. In conventional DSC, the heat

flow measurement is in error because the reference pan always heats at the programmed heating rate. When the sample pan heating rate is higher or lower than the programmed heating rate, the reference heat flow offsetting the sample pan heat flow is too low or too high. The same comments apply to the sensor heat flow. The heat capacity terms in the heat flow measurement equations account for differences between the sample and reference sensor heating rates.

To use this heat flow measurement method, the sample and reference pan temperatures are needed, they are not measured directly but may be obtained from the measured quantities. Heat flow between the sample and reference pans and their sensors are given by:

$$\dot{q}_s = \frac{T_s - T_{ps}}{R_p} \qquad \dot{q}_r = \frac{T_r - T_{pr}}{R_p}$$

Which are solved to find the pan temperatures:

$$T_{ps} = T_s - \dot{q}_s R_p \qquad T_{pr} = T_r - \dot{q}_r R_p$$

Sensor temperatures and heat flows are measured, the pan contact resistance R_p is needed to determine the pan temperatures. A model equation is used to calculate the contact resistance between the pan and sensor. The model assumes that there are two parallel heat conduction paths between the pan and the sensor, one is solid conduction through the sensor and pan where they contact one another and the second is conduction through the gas layer between the pan and sensor. The equation used for the contact resistance is:

$$R_p = \frac{1}{\frac{1}{R_{pan} + R_{sen}} + \frac{1}{R_{gas}}}$$

Where, the component thermal resistances are calculated from:

$$R = \frac{1}{\alpha k}$$

K is the thermal conductivity of the pan, sensor or purge gas and α is a geometric factor for the pan, sensor or purge gas that is equivalent to the ratio of an area to a length. Thermal conductivities for each component as a function of temperature are known, the geometric factors have been determined from a curve fit of experimental data. The geometric factors are dependent upon the pan and sensor shape. Typical values of the geometric factors are supplied in the instrument software for selected pan types. These capabilities are incorporated in the TA Instruments Q1000™ DSC (5,7).

EXPERIMENTAL

A TA Instruments Q1000 with a RCS (mechanical refrigeration cooling system) was used to perform the experiments shown below. The instrument was calibrated per the manufacturer's instructions, including calibration of the sensor thermal coefficients. The DSC cell was purged with nitrogen, crimped aluminum pans were used with 5.64mg indium and 1.13mg dotriacontaine samples.

RESULTS AND DISCUSSION

Figure 2 shows an indium melt at 20°C/min. Two heat flows are plotted, the conventional DSC heat flow and the heat flow according the Advanced Tzero™ heat

flow measurement of this paper. The conventional DSC heat flow signal is proportional to the Difference between sample and reference temperature.

$$\dot{q} = E(T)\Delta T$$

Comparing the Advanced Tzero heat flow to the conventional heat flow, the peak height increased from 23.2mW to 29.9 mW and the peak width at half height has decreased dramatically from 2.26 to 0.82°C, representing a three fold reduction in peak width. The onset and peak temperatures are slightly lower due to the elimination of thermal lag of the sample calorimeter and sample pan. The baseline return at the completion of the melt is much faster, corresponding to improved dynamic response that yields better resolution.

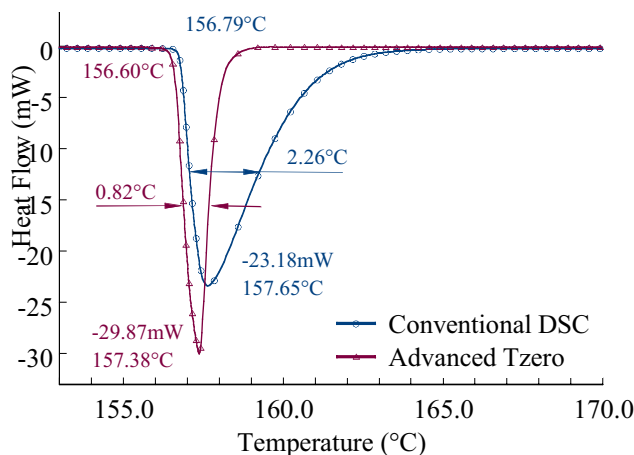


Figure 2 – Indium Melt Tzero vs. Conventional DSC

Figure 3 shows the result of a 10°C/min DSC experiment with a 1.13mg sample of dotriacontane, a C₃₂ hydrocarbon. Two heat flow signals are shown; Advanced Tzero and conventional DSC. This sample has three closely spaced transitions demonstrating the separation ability of a DSC (i.e. the resolution). The first two transitions are barely separated from one another by conventional DSC, whereas Advanced Tzero shows a substantial improvement in the separation. However, between the second and third transitions, Advanced Tzero clearly achieves a baseline, where conventional DSC does not. In this case, the ability to accurately determine the enthalpy of the third transition is improved by Advanced Tzero as compared to conventional DSC. All peak heights are substantially increased while peak width is considerably reduced. Analysis of additional experiments confirms the improved resolution (8).

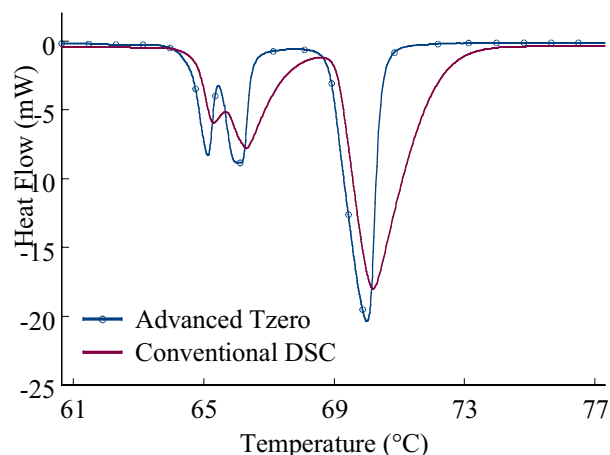


Figure 3 – 1.13mg Dotriacontane at 10°C/min

CONCLUSIONS

A new method of measuring heat flow in DSC is described that improves the measurement by including the heat storage effects of the sensor and the pans. The heat storage effects manifest themselves in any DSC experiment where the sample and reference heating rates are not identical. That includes transitions in DSC and generally all MDSC™ experiments. A key feature of this new measurement is that the sample and reference heat flows may be measured separately, allowing the difference in heating rates between sample and reference sensor and pans to be accounted for. The result is that the actual sample heat flow is measured. A calibration method is used that allows the characteristics of the DSC to be determined.

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