New modulated DSC measurement technique

Robert L. Danley*

TA Instruments, 109 Lukens Drive, New Castle, DE 19720, USA

Abstract

The introduction of modulated DSC (MDSC) increased the utility of DSC by adding the ability to separate the sample heat flows resulting from time dependent and time independent processes. The time independent sample heat flow rate is just that which is due to the sample heat capacity. MDSC is based on conventional DSC where the measured signal is the temperature difference between the sample and reference positions of the sensing apparatus. The measured heat flow rates display significant dependence on the period of the modulation, as demonstrated by the well-known decrease of measured heat capacity with decreasing modulation period. To reduce the frequency dependence, MDSC experiments are usually performed using rather long periods, typically 60 s or more, or various calibration or correction techniques may be applied. Long periods require low average heating rates and result in rather lengthy experiments that reduce the productivity of the DSC. A new MDSC heat flow measuring technique has been developed that greatly reduces the frequency dependence of the heat flow measurement. It includes three components: (1) a new DSC cell that has independent sample and reference calorimeters and includes two differential temperature measurements, (2) a new DSC heat flow measurement method that is based upon independent sample and reference heat flow rates and (3) a new MDSC heat flow calculation method that uses the independent sample and reference heat flow rate measurements. MDSC experiments using this new technique display greatly reduced period dependence, allowing modulation periods as short as 20 s to be used. Higher average heating rates may be used and productivity of the DSC is increased as much as threefold or more.[1]
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1. Introduction

Modulated DSC (MDSC) was initially developed by Reading et al. [1], who showed that by adding a periodic temperature oscillation to the conventional DSC thermal program and performing suitable mathematical manipulations of the measured heat flow rate, the resultant heat flow signal could be separated into time dependent and time independent components.

Numerous benefits have resulted and the technique has enabled researchers to gain additional insight into the behavior of a number of phenomena, for example the glass transition of polymers. However, the technique has been hampered by the inability to obtain high quality results at short modulation periods. Heat capacity measured by MDSC should be independent of the period of modulation and indeed that is the case for sufficiently long periods. Fig. 1 shows the heat capacity correction factor obtained from heat capacity measurements of sapphire made at a constant average temperature of 320 K and modulation periods between 10 and 90 s with 0.05 and 0.2 K amplitudes

* Fax: +1-302-427-4081.
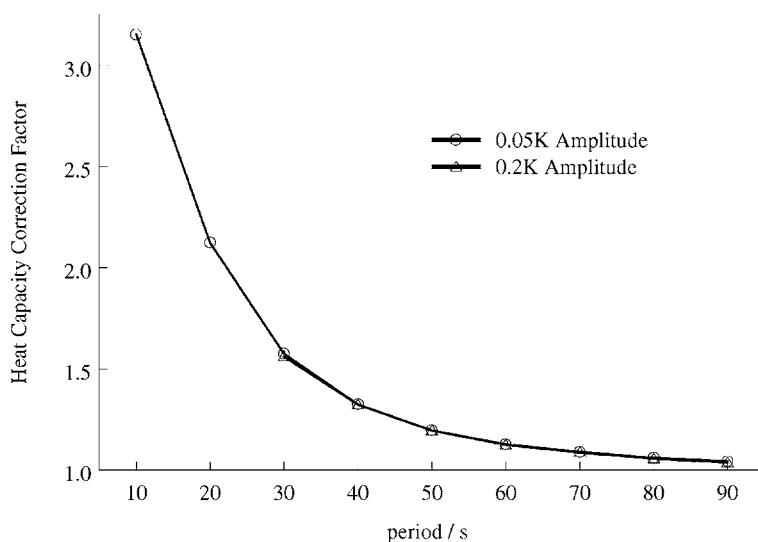*E-mail address:* rdanley@tainst.com (R.L. Danley).

[1] Patents applied for.

Fig. 1. Heat capacity correction factor as a function of modulation period for sapphire samples at 320 K with 0.05 and 0.2 K modulation amplitude [2].

[2]. The heat capacity correction factor is the ratio of the correct heat capacity to the measured heat capacity. The data display a systematic decrease in measured heat capacity as the period is reduced.

A number of researchers have developed methods to correct for this period dependence [3–5]. These methods use heat transfer models of the DSC, sample and pans to apply corrections that are dependent on the frequency and temperature of the experiment. Input signals to the models are the heat flow rate signal and the phase angle between the heat flow rate and the measured sample temperature. All rely upon performing calibration experiments using samples with known heat capacity. In some cases [4,5] the reference position of the calorimeter is empty.

In this paper, it will be shown that a large part of this period dependence is due to instrumental effects and may be eliminated by applying the MDSC heat flow calculation method described here. This new method is implemented in the TA Instruments Q1000 DSC. Because it includes two differential temperature measurements and is constructed such that mutual heat exchange between the sample and reference calorimeters is virtually eliminated it is capable or measuring the sample and reference heat flow rates independently, a necessary condition for application of the method.

2. DSC heat flow rate measurement theory

Generally, the measured signal in DSC is the temperature difference between the twin sample and reference calorimeters. The signal is converted to a heat flow rate by the application of a temperature dependent proportionality factor

$$\dot{q} = E(T)\Delta T \tag{1}$$

The proportionality factor $E(T)$ is the inverse of the thermal resistance between the furnace and the points at which differential temperature is measured. It is a function of temperature and depends upon the geometry and materials of construction of the differential temperature sensing apparatus. However, this relationship is greatly simplified and gives the correct measured heat flow only under restricted conditions. As will be shown below, this expression gives the correct heat flow rate only when the DSC is perfectly symmetrical and the heating rates of both the sample and reference sides of the instrument are the same, in which case the signal corresponds to the sample heat capacity.

An alternate technique for measuring the heat flow rate in DSC has been described that uses a more complete heat flow measurement equation which accounts for asymmetry and the differences in heating rate
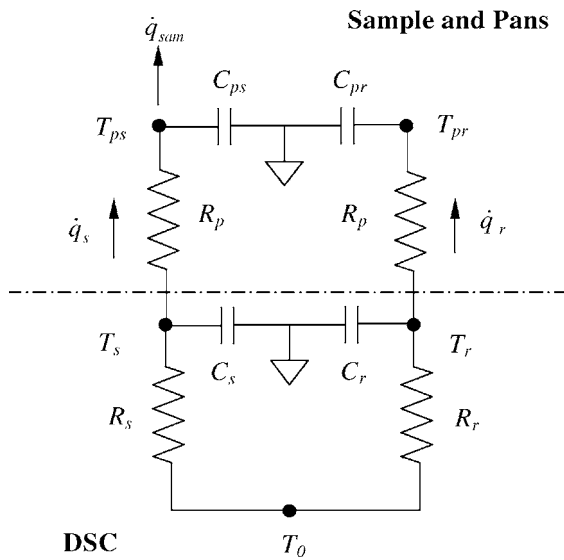
Fig. 2. Network model of DSC. Pans and sample are above and calorimeters are below the broken line.

between the sample and reference calorimeters and pans [6]. It is based on a lumped heat capacity heat transfer model [7], Fig. 2 shows an electrical network analogue of the DSC. The sample and reference calorimeters are each represented in the model by a thermal resistance R and a heat capacity C, subscripts s and r indicate sample and reference calorimeters. The sample and reference pans are represented by heat capacities, C_{ps} and C_{pr}, thermal resistances R_p represent heat exchange between the pans and the DSC sensor. The reference pan is assumed to be empty. The heat flow rate between the sample and it's pan is q_{sam}, the measured sample and reference heat flow rates are q_s and q_r. The model does not include a heat flow path between the sample and reference calorimeters, because the TA Instruments Q series DSC sensor is constructed so that there is no direct heat exchange between the sample and reference calorimeters. T_s and T_r are the measured sample and reference calorimeter temperatures and T_{ps} and T_{pr} the sample and reference pan temperatures. Perform a heat balance on each calorimeter and substitute the measured differential temperatures ΔT and ΔT_0 to obtain the measured sample and reference heat flow rates:

$$\dot{q}_s = \frac{\Delta T_0}{R_s} - C_s \frac{dT_s}{dt} \tag{2}$$

$$\dot{q}_r = \frac{\Delta T_0 + \Delta T}{R_r} - C_r \left(\frac{dT_s}{dt} - \frac{d\Delta T}{dt} \right) \tag{3}$$

where ΔT is the temperature difference between the sample and reference calorimeters and ΔT_0 the temperature difference across the thermal resistance of the sample calorimeter. The measured heat flow rates q_s and q_r are the heat flow rates to the sample and its pan and to the reference pan. The sensor thermal resistances and heat capacities are temperature dependent and are determined by a two-step calibration procedure [6]. Unlike other DSC heat flow rate measurements; the sample and reference calorimeter thermal resistances and heat capacities are not assumed to be equal. The calibration method determines the individual values.

To obtain the heat flow rate between the sample and its pan, a heat balance is performed on the pan

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

where m_{ps} is the sample pan mass and c_{pan} the specific heat capacity of the pan material. It shows that the measured sample heat flow rate is the sum of the sample and pan heat flow rates. The measured reference heat flow rate is just that of the reference pan

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

The measured reference heat flow rate equation is used to eliminate the pan specific heat capacity from the measured sample heat flow rate equation yielding

$$\dot{q}_{sam} = \dot{q}_s - \dot{q}_r \left(\frac{m_{ps}(dT_{ps}/dt)}{m_{pr}(dT_{pr}/dt)} \right)$$

The sample heat flow rate is seen to be the difference between the measured sample and reference heat flow rates of Eqs. (2) and (3) with a factor applied to the reference heat flow rate that accounts for the difference between the sample and reference pan heating rates and masses. The temperatures of the pans are calculated from

$$T_{ps} = T_s - \dot{q}_s R_p \tag{4}$$

$$T_{pr} = T_r - \dot{q}_r R_p \tag{5}$$

The value of the contact resistance is obtained from a temperature dependent contact resistance function that

uses empirically determined coefficients [6]. When the equations for q_s and q_r are substituted, the sample heat flow rate equation becomes

$$\dot{q}_{\text{sam}} = -\frac{\Delta T}{R_r} \frac{m_{\text{ps}}}{m_{\text{pr}}} \frac{\mathrm{d}T_{\text{ps}}/\mathrm{d}t}{\mathrm{d}T_{\text{pr}}/\mathrm{d}t}$$
$$+ \Delta T_0 \left(\frac{1}{R_s} - \frac{1}{R_r} \frac{m_{\text{ps}}}{m_{\text{pr}}} \frac{\mathrm{d}T_{\text{ps}}/\mathrm{d}t}{\mathrm{d}T_{\text{pr}}/\mathrm{d}t} \right)$$
$$- \frac{\mathrm{d}T_s}{\mathrm{d}t} \left(C_s - C_r \frac{m_{\text{ps}}}{m_{\text{pr}}} \frac{\mathrm{d}T_{\text{ps}}/\mathrm{d}t}{\mathrm{d}T_{\text{pr}}/\mathrm{d}t} \right)$$
$$+ \frac{\mathrm{d}\Delta T}{\mathrm{d}t} C_r \frac{m_{\text{ps}}}{m_{\text{pr}}} \frac{\mathrm{d}T_{\text{ps}}/\mathrm{d}t}{\mathrm{d}T_{\text{pr}}/\mathrm{d}t} \qquad (6)$$

Term 1 includes the conventional DSC heat flow equation (1). Terms 2 and 3 include the differences between the sample and reference thermal resistances and heat capacities and express the effects of asymmetry within the DSC sensor on the measured heat flow rate. Term 4 includes the time derivative of ΔT and expresses the effect of differences in heating rates between the sample and reference calorimeters. All four terms include the pan mass ratio and the sample and reference pan heating rate ratio. Those factors express the effects of pan mass imbalance and heating rate differences on each term of the sample heat flow rate. All of the right hand side terms in the equation involve only the measured signals and the properties and heating rates of the sample and reference calorimeters and pans. This equation reduces to Eq. (1) when the sample and reference calorimeters have the same heating rates, the sample and reference calorimeter thermal resistances and heat capacities are identical, and the sample and reference pans have the same mass and the same heating rate. Under those conditions, the measured heat flow rate corresponds to the sample heat capacity. Under any other conditions, the sample heat flow rate is not proportional to the difference between the sample and reference calorimeter temperatures. Thus, only under very restrictive conditions, which are almost never achieved in practice does Eq. (1) give the correct sample heat flow rate. In general, during an MDSC experiment, the sample and reference calorimeter heating rates are not the same and the sample and reference pan heating rates are not the same, consequently Eq. (1) does not give the correct sample heat flow rate. The impact on an MDSC measurement is quite clear, the measured heat flow rate may be significantly in error and hence, also the MDSC result.

3. MDSC measurement method

The method developed by Reading consists of performing a DSC experiment with a periodic temperature oscillation impressed on the typical DSC experiment comprising constant heating rate segments and constant temperature segments. The resulting heat flow rate signal is separated into a total or underlying part, a reversing part and a non-reversing or non-rapidly reversing part. The total, or underlying heat flow rate corresponds to the DSC heat flow result that would be obtained from the same DSC experiment without the superposed oscillation. The reversing part of the signal is due to the heat capacity of the sample. The non-rapidly reversing part of the signal is due to time dependent processes in the sample.

Both the heat flow rate and the sample temperature signals are processed in the same manner [2,8]. A discrete Fourier transform is performed on each of the two signals to separate the sine and cosine components from which the amplitudes and the phase angles of the modulated heat flow rate and temperature are found. A one cycle moving average of both signals is taken to remove the modulation and recover the underlying signals. The heat capacity is determined using the following equation from AC calorimetry:

$$C = \frac{\bar{q}}{\omega \bar{T}}$$

where $\bar{q}$ and $\bar{T}$ indicates the amplitude of the modulating part of the heat flow signal and temperature, respectively, and ω the circular frequency $2\pi/p$, where p is the period of the modulation. The reversing heat flow is calculated by multiplying the measured heat capacity by the underlying heating rate, which is calculated from the moving average of the sample temperature. The total heat flow rate is just the underlying heat flow rate. The non-reversing heat flow rate is the difference between the total and reversing heat flow rates. The phase angle between the heat flow rate and the temperature is the difference between their phase angles.

As was shown above, the conventional heat flow rate measurement of Eq. (1) does not give the ac-

tual sample heat flow rate unless the heating rates of both the sample and reference calorimeters are the same. In general, this condition is never obtained in an MDSC experiment, but it is approached as the period is lengthened. When the period is decreased, the difference between the heating rates of the sample and reference calorimeters increases because of the heat capacity of the calorimeters, the sample and the pans and the thermal resistances between them. Consequently, the amplitude of the measured sample heat flow is attenuated and the measured heat capacity decreases. The measured temperature is never the actual sample temperature, but rather it is measured at a location remote from the sample and so, at shorter periods suffers less attenuation than the actual sample does. Because of this the measured temperature amplitude used to determine the heat capacity is too large. The consequence of these two shortcomings is a systematic reduction of measured heat capacity with decreasing period. The total heat flow rate is generally unaffected by the modulation period, however, it may be in error due to the imbalance effects described above, especially during transitions when the sample and reference heating rates differ. The non-reversing heat flow signal becomes too large to the extent that the reversing signal is too small.

A fundamental assumption underlying the DSC heat flow measurement is that the sample temperature is uniform [9,10]. Because it has finite thermal conductivity and it is subjected in all cases to a dynamic temperature boundary condition, the temperature within the sample cannot be uniform. In conventional temperature scanning DSC, this is generally a minor problem when measuring heat capacity because the heat capacity changes slowly with temperature and the temperature distribution within the sample is very nearly stationary [11]. The result is a slight temperature error due to the inhomogeneous temperature distribution and the sample temperature lag resulting from temperature scanning. In MDSC, however, the temperature distribution within the sample is not stationary, which may result in reduction in the measured real heat capacity as the period is decreased [11,13–15]. Proper selection of the sample thickness, depending upon the thermal conductivity of the sample can reduce this uncertainty sufficiently to allow heat capacity to be measured within 1% accuracy [13].

4. New MDSC measurement method

The DSC is a twin instrument, comprising a sample and a reference calorimeter within a common thermal enclosure, where the two calorimeters are usually assumed to be identical. The nominal output of the DSC is the difference between the heat flow rates measured by each of the calorimeters. Advantages gained by the use of twin calorimeters include cancellation of heat leakage and temperature disturbances common to both calorimeters [12]. This MDSC heat flow rate measurement uses a variation of the twin principle, rather than measuring the difference between the sample and reference heat flow rates, the difference is taken between the components of the heat flow rates. The total heat flow rate is the difference between the sample and reference total heat flow rates, likewise reversing and non-reversing heat flow rates are the differences between the sample and reference reversing and non-reversing heat flow rates. To accomplish this, the sample and reference heat flow rates are measured separately, as indicated by Eqs. (2) and (3). Experiments demonstrate the reduction of the period dependence of the heat flow rates.

Using the method of Reading described above, sample and reference heat flow rates measured in accordance with Eqs. (2) and (3) are separated into their sine and cosine components, which are used to determine the amplitudes of the periodic component of the signals and the phase angle of the sample heat flow rate. Sample and reference pan temperatures are treated the same way and the amplitudes of the periodic parts of the pan temperatures are found as well as the phase angle of the sample pan temperature. Moving averages of both of the temperature and heat flow rate signals are taken over one period to remove the periodic components. The temperatures of the sample and reference pans are found using Eqs. (4) and (5). The sample and reference heat capacities are measured using the AC calorimetry heat capacity equation

$$C_{sa} = \frac{\bar{\tilde{q}}_s}{\omega \bar{T}_{ps}}, \qquad C_{ra} = \frac{\bar{\tilde{q}}_r}{\omega \bar{T}_{pr}}$$

The measured sample heat capacity includes that of the sample and pan, the measured reference heat capacity is just that of the empty pan. The reversing

heat capacity is calculated by

$$C_{p\,rev} = C_{sa} - C_{rs}\frac{m_{ps}}{m_{pr}}$$

The total heat capacity is calculated by

$$C_{p\,tot} = \frac{\langle \dot{q}_s \rangle}{\langle dT_{ps}/dt \rangle} - \frac{\langle \dot{q}_r \rangle}{\langle dT_{pr}/dt \rangle}\frac{m_{ps}}{m_{pr}}$$

The angular brackets indicate quantities that are averaged over one period to remove the periodic component. The pan mass ratio accounts for mass differences between the sample and reference pans. The non-reversing heat capacity is simply the difference between the total and the reversing heat capacity

$$C_{p\,non} = C_{p\,tot} - C_{p\,rev}$$

The total heat capacity must be regarded as an apparent heat capacity, because it includes the heat capacity and an "excess heat capacity" that corresponds to the non-reversing sample heat flow. Heat flow rate components are determined as follows:

$$\dot{q}_{tot} = C_{p\,tot}\left\langle \frac{dT_{ps}}{dt} \right\rangle, \qquad \dot{q}_{rev} = C_{p\,rev}\left\langle \frac{dT_{pr}}{dt} \right\rangle,$$

$$\dot{q}_{non} = \dot{q}_{tot} - \dot{q}_{rev}$$

The reported phase angle is the difference between the phase angles of the sample pan temperature and the sample heat flow rate.

5. Experimental results and discussion

All experiments were performed using a TA Instruments Q1000 DSC with an RCS mechanical cooling system, which uses the heat flow rate measurement and MDSC techniques described in this paper. TA Instruments standard crimped aluminum pans were used for all samples and the DSC cell was purged with nitrogen.

Fig. 3 shows the result of a quasi-isothermal MDSC experiment at 100 °C with periods between 20 and 100 s, the sample was 30.95 mg of aluminum oxide powder. The maximum variation of heat capacity correction factor is 5% between 20 and 90 s, compared to the results of Fig. 1, where over the same range of periods, the heat capacity correction factor varied by 108%. Fig. 1 result was obtained using a TA Instruments 2920 DSC employing the heat flow rate measurement equation (1) and the MDSC method described by Reading. The results of Fig. 3 were obtained using the individual sample and reference heat flow rate measurements of Eqs. (2) and (3) and the MDSC method described in the previous section. The reduction in variation of measured heat capacity with period is the result of accounting for the effects of the heat capacity of the calorimeter and the pans on the measured heat flow and in measuring the amplitude of the pan temperature, which is much closer to the
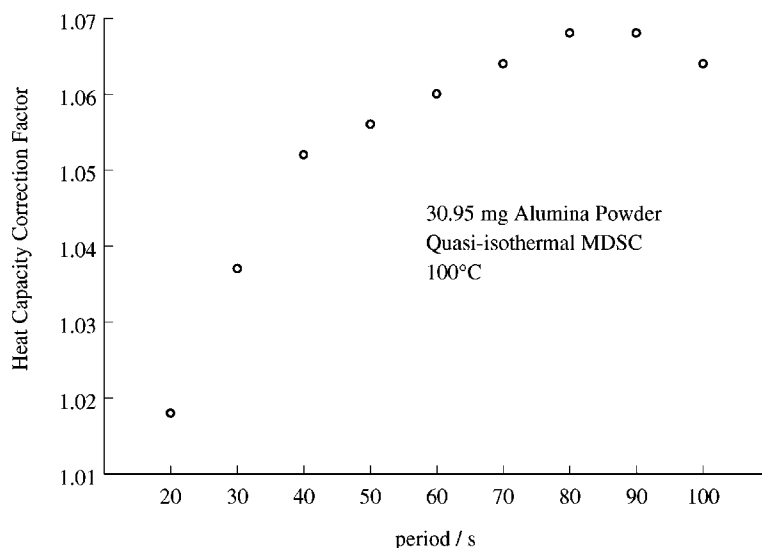

Fig. 3. Heat capacity correction factor as a function of modulation period, 30.95 mg alumina powder at 100 °C.
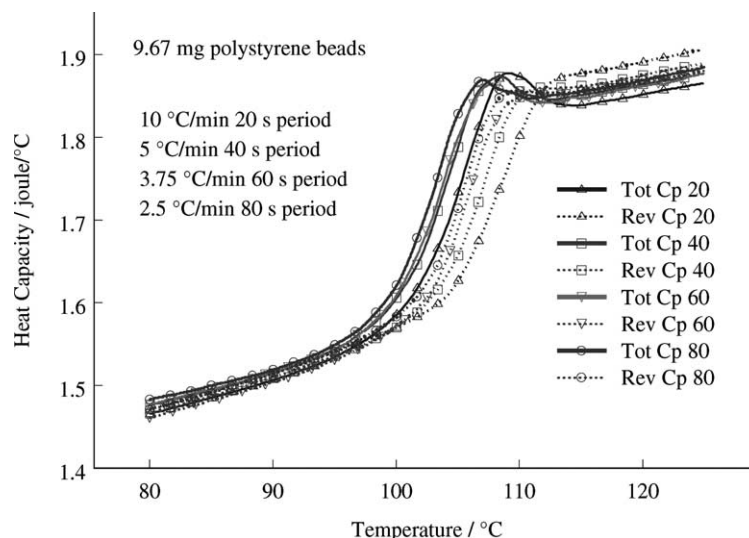
Fig. 4. The 9.67 mg polystyrene beads, total and reversing heat capacities as a function of temperature determined using the new MDSC method.

sample temperature amplitude than is the sensor temperature amplitude.

Fig. 4 shows the result of an MDSC experiment showing the total and the reversing heat capacities for a 9.67 mg sample of polystyrene beads. Four different sets of MDSC conditions were used: 10 °C/min heating rate with a 20 s period, 5 °C/min heating rate with a 40 s period, 3.75 °C/min heating rate with a 60 s period, and 2.5 °C/min heating rate with an 80 s period. Both the total and reversing heat capacities show very little influence of period on the measurement. Below the glass transition at 80 °C the variation of total heat capacity is 1.1%, while the variation of reversing heat capacity is 1.4%. Above the glass transition, at 125 °C the variation of total heat capacity is 1.1% while the variation of reversing heat capacity is 0.75%. Above and below the glass transition, the total and reversing heat capacities should have the same value. At 80 °C, the mean values of the reversing and total heat capacity differ by 0.8% while at 125 °C, the mean values differ by 0.5%.

6. Conclusions

A new MDSC method has been described that substantially reduces the effect of period on the mea-

sured reversing and non-reversing heat capacities and heat flow rates. It was shown that the conventional DSC heat flow measurement based on the temperature difference between the sample and reference calorimeters incorrectly measures the sample heat flow rate when the heating rates of the calorimeters is different. In general, during an MDSC experiment, the heating rates of the calorimeters are different, and the difference becomes more pronounced as the modulation period is decreased. The result is that the heat flow rate amplitude used to determine the sample heat capacity is too low and hence, the measured heat capacity is too low. A similar problem exists with the temperature amplitude, which in conventional MDSC is that of the sample temperature sensor, consequently because of heat exchange between it and the sample its amplitude is too large. The combined effects of low heat flow rate amplitude and high temperature amplitude result in measured heat capacity decreasing with modulation period. These instrumental effects are greatly reduced by the new method. The sample and reference heat flow rates are measured separately using a measurement method that accounts for calorimeter and pan heat storage effects and instrumental imbalances. The temperature of the sample and reference pans is calculated from the measured temperatures and heat flow rates. The resultant heat

flow rates and temperatures are much closer to the true sample heat flow rates and temperature than those measured by conventional DSC. Each of the heat flow rate signals is separated into total, reversing and non-reversing parts. In a variation of the twin principle that is fundamental to DSC, the difference between the measured sample and reference total, reversing and non-reversing heat flow rates are taken to give the sample total, reversing and non-reversing heat capacities and heat flow rates. The variation of the measured quantities with modulation period is greatly reduced, allowing shorter periods to be used. One must still be aware that sample thermal diffusivity may also cause a similar period dependence. Problems of that nature may be avoided by preparing thin, flat samples.

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