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TEMPERATURE MODULATED DSC (TMDSC)
Applications and limits of phase information, c_p determination and effect separation

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Abstract

The ADSC (Alternating DSC [1]) technique superimposes upon the conventional constant heating rate a periodically varying modulation [2–8]. The modulation creates high instantaneous heating rates which increases sensitivity. The low underlying constant heating rate is used to get better resolution. With ADSC it is possible to separate overlapping thermal effects without loss of sensitivity and to determine heat capacities under quasi-isothermal conditions. It has been reported that there are also some limitations for the use of the modulation techniques, i.e. that the accuracy of c_p determination is reduced at higher modulation frequencies due also to thermal diffusivity within the sample itself [9, 10].

In this contribution, the limitations given by the measuring system itself will be discussed. A key value is the limit frequency of the sensor arrangement. In the Mettler Toledo DSC821^e this frequency is approximately 1/3 Hz. From these findings the following recommendations amongst others can be given: for light mass crucibles, 30 s periods are reasonable with amplitudes not exceeding the heating/cooling rates possible. A blank and a calibration measurement will eliminate cell asymmetry and will enhance the accuracy of c_p measurements even at higher modulation frequencies.

Keywords: c_p determination, modulation frequency, recommendations for TMDSC parameters, TMDSC, TMDSC calibration

Introduction to ADSC

The measured heat flow comprises fractions which arise from c_p (sensible heat) and those due to physical transformations or chemical reactions (latent heat). The relation between heat flow (HF), rate (β) and c_p is given in Eq. (1):

$$c_p = \frac{dH}{dT}\frac{1}{m} = \frac{dH/dt}{dT/dt}\frac{1}{m} = \frac{HF}{\beta}\frac{1}{m} \qquad (1)$$

where H enthalpy, T temperature, m sample mass, t time, HF heat flow, β heating rate.

ADSC with its periodic temperature program (Fig. 1) combines the advantages of the following measurement modes:

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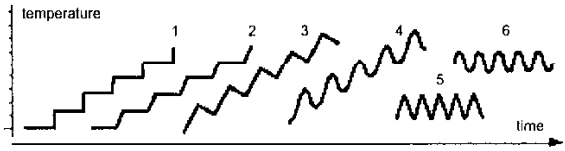

Fig. 1 Some periodic temperature programs used for ADSC. For all wave forms, the mean heating rate, β_{mean} is equal to the temperature increase per period (increment i) divided by the duration of the period, p: $\beta_{mean}=i/p$. The amplitude, A_T, corresponds to half of the peak-peak value of the periodic temperature program

– High sensitivity in respect to c_p changes thanks to the high instantaneous heating rate.

– High temperature resolution thanks to the low mean heating rate.

– Thanks to the separation in reversing and non-reversing curves overlapping phenomena can be resolved.

– c_p determination under quasi-isothermal conditions, e.g. during chemical reactions.

Theory

Sinusoidal ADSC

Instead of constant heating rate, a sine wave is modulated on a low underlying or mean heating rate, β_{mean}:

$$T(t) = T_0 + \beta_{mean}t + A_T\sin(\omega t) \tag{2}$$

where A_T is the amplitude of the temperature modulation, $\omega=2\pi/p$ is the angular frequency and p the period of the modulation.

By differentiation of Eq. (2) we obtain the heating rate:

$$\beta(t) = \beta_{mean} + A_\beta\cos(\omega t) \tag{3}$$

$$A_\beta = A_T\omega \tag{4}$$

where A_β is the amplitude of the heating rate.

The maximum/minimum heating rates are:

$$\beta_{Max} = \beta_{mean} + A_\beta = \beta_{mean} + \frac{A_T 2\pi}{p} \tag{5}$$

$$\beta_{Min} = \beta_{mean} - A_\beta = \beta_{mean} - \frac{A_T 2\pi}{p} \tag{6}$$

β_{Min} may not exceed the maximum cooling rate of the used DSC instruments.

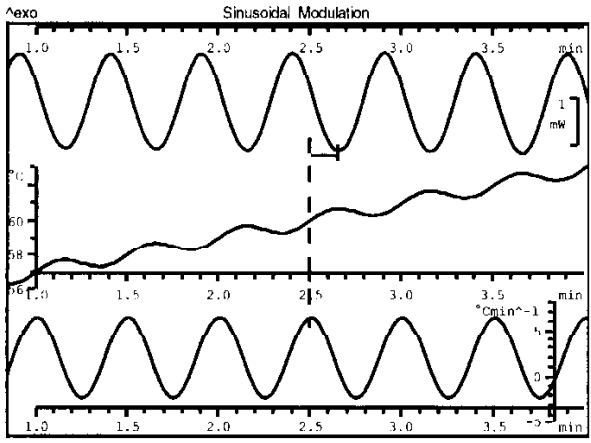

Fig. 2 The sinusoidal temperature program (center) corresponds to a sinusoidal heating rate (bottom). They produce the sinusoidal heat flow (top) with a phase lag

Measuring the DSC signal a modulated heat flow is recorded which is shifted by the phase φ compared to the heating rate. $\beta(t)$. This means that the heat flow is lagging behind the heating rate (Fig. 2).

$$HF = A_{HF}\cos(\omega t + \varphi) \tag{7}$$

Similarly to Eq. (1) c_p can be calculated from the amplitude of the heat flow and the amplitude of the heating rate

$$|c_p^*| = \frac{A_{HF}}{A_\beta m_o} \qquad \text{(complex } c_p\text{)} \tag{8}$$

$$c_p' = |c_p^*|\cos\varphi \qquad \text{(in-phase } c_p\text{)} \tag{9}$$

$$c_p'' = |c_p^*|\sin\varphi \qquad \text{(out-of-phase } c_p\text{)} \tag{10}$$

In addition to c_p, the sensible heat flow usually called the reversing heat flow is calculated. The term 'reversing' comes from the fact that the deflection of the ADSC signal caused by reversing or c_p effects changes when the heating rate changes sign.

Equation (1) solved for the heat flow, now called reversing heat flow, HF_{rev}:

$$HF_{rev} = \beta_{mean} C_p \tag{11}$$

where C_p is the heat capacity of the sample.

From Eqs (4) and (8) the heat capacity is:

$$C_p = \frac{p}{2\pi A_T} A_{HF} \tag{12}$$

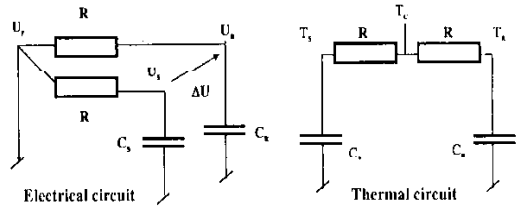

Fig. 3 Analogy of thermal and electrical circuits; U voltage, I current, R resistance, C capacity, U_F furnace temperature, U_S sample temperature, U_R reference temperature, R thermal resistance, C_S heat capacity of the sample side, C_R capacity of the reference side, ΔU potential difference (correlates to the heat flow of the sample), T temperature, dQ/dt heat flow (HF), R thermal resistance, C heat capacity, T_C furnace temperature, T_S sample temperature; T_R reference temperature, R thermal resistance, C_S heat capacity of the sample side, C_R heat capacity of the reference side

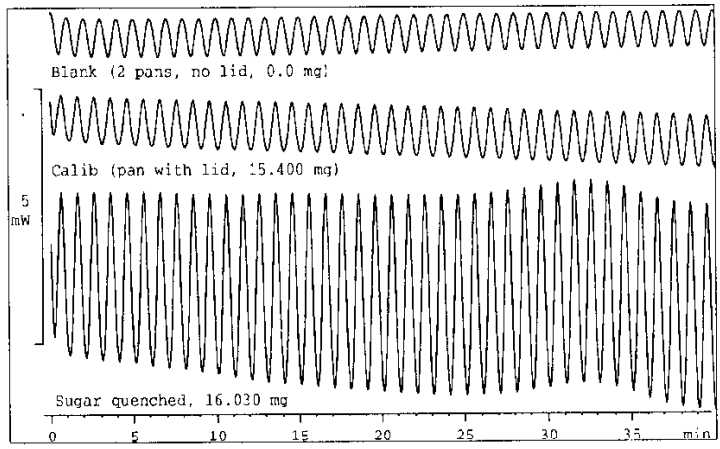

Fig. 4 Sample, blank and calibration curves measured with a mean heating rate of 2 K min^{-1}, an amplitude of 0.5 K and a period of 1 min

The reversing heat flow is:

$$HF_{rev} = -\frac{p\beta_{mean}}{2\pi A_T} A_{HF} \tag{13}$$

(Remark: The negative sign is for the upwards exothermal direction.)

The mean value curve calculated for the ADSC curve is equal to a classical DSC curve without modulation. This curve is called the total heat flow (Fig. 5).

To obtain the non-reversing heat flow the reversing signal is subtracted from the total signal:

$$HF_{non-rev} = HF_{total} - HF_{rev} \tag{15}$$

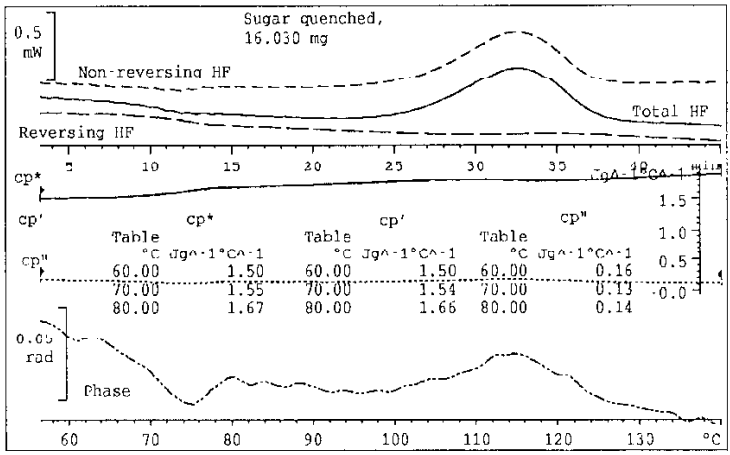

Fig. 5 All curves and some numerical results (c_p values) obtained from the ADSC evaluations of the measurement shown in Fig. 4. The glass transition is detected at 75°C, the cold crystallization at 115°C

Physical model

The accuracy of c_p determinations depends also on the thermal diffusivity within the sample itself [9, 10], but the measuring system has also to be considered. To estimate these limitations, a simple 'RC'-model of the DSC sensor has been used:

Experimental

To compare model calculations with real measurements, the following measurements were performed:

- 3 different masses of sapphire (m1=21.582 mg, m2=42.305 mg, m3=61.612 mg) corresponding to 1, 2 or 3 discs in an aluminum pan. Aluminum reference pan without lid.
- 7 different periods (12 s, 15 s, 30 s, 60 s, 120 s, 240 s, 480 s)
- Blank, Calibration and Sample measurement for every combination (every measurement was repeated 4 times to check the reproducibility)
- 3 different evaluation possibilities were used:

Method 1: just the sample curve:
no correction of asymmetries of the cell, no quantitative c_p values.
Method 2: sample and blank curves:
correction of asymmetries of the cell, no quantitative c_p values.
Method 3: sample, blank and calibration curves:
correction of asymmetries of the cell, quantitative c_p values.

The calibration run is used in a similar way as in ASTM E1296 but the calibration material is aluminum with the known c_p temperature function. Measuring sys-

tem: METTLER TOLEDO STAR^e System with DSC821^e ADSC evaluation. The heat flow curves are shown with exothermic direction upwards.

Results

Typical ADSC curves of a complete measurement (method 3) of quenched sugar are shown in Fig. 4. The respective evaluations in Fig. 5 are given to demonstrate separation of reversing and non-reversing effects (change of c_p during glass transition and cold crystallization from the frozen amorphous state).

The comparison of the c_p values measured ($|c_p^*|$) and model calculated using sapphire, in function of the frequency, is given in Fig. 6. Figure 7 shows the related phase shift. The main deviations are due to the simplified model, neglecting the heat transfer from sensor to sample and within the sample. The furnace itself has also not been considered in the model calculation.

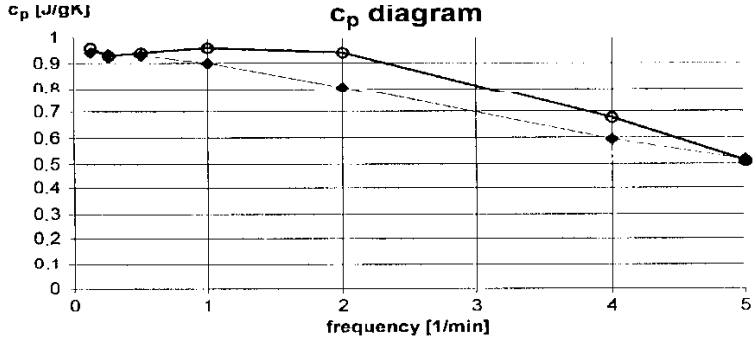

Fig. 6 c_p determination by ADSC in function of the modulation frequency at 125°C (isothermal) with sapphire mass 1; solid line – measured; dashed line – model calculation. Method 1 was used. –o– c_p measured (125°C, m1); –♦– c_p model (125°C, m1)

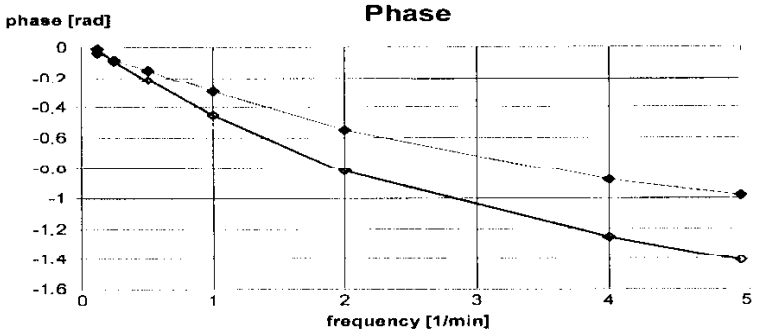

Fig. 7 Phase behaviour in function of the modulation frequency; Fig. 6. Method 1 was used –o– c_p measured (125°C, m1); –♦– c_p model (125°C, m1)

The comparison of the modeling and measurement results show that blank and calibration runs (method 3) are the most important ones for accurate c_p determinations by ADSC, Figs 8 and 9.

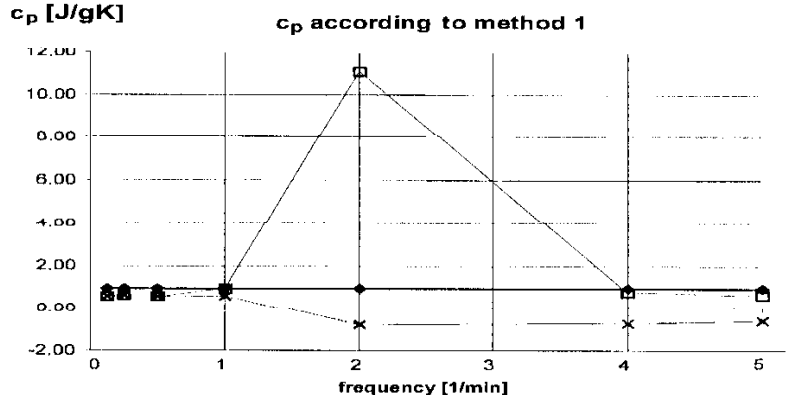

Fig. 8 c_p values of sapphire (mass 1, 125°C) measured and evaluated according to method 1. –♦– Ilit (125°C, m1); –□– measured (125, m1); –x– c_p' (125°C, m1)

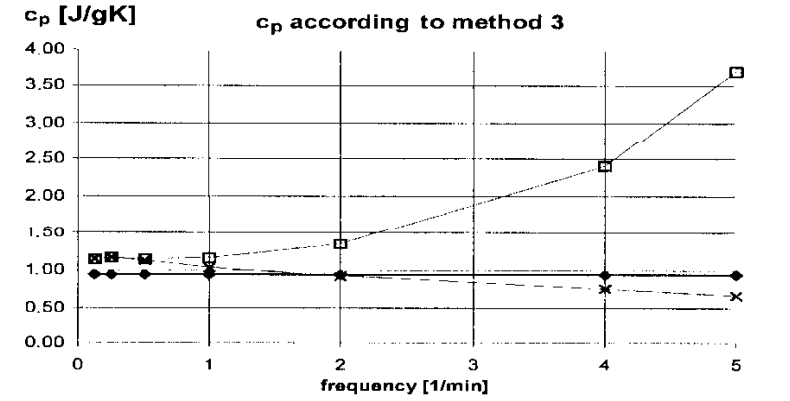

Fig. 9 c_p values of sapphire (mass 1, 125°C) measured and evaluated according to method 3. –♦– Ilit (125°C, m1); –□– measured (125, m1); –x– c_p' (125°C, m1)

The limit frequency given by the model is approximately 1/3 Hz. According to signal theory, a decade smaller frequency should not be exceeded in order to have no distortion. Hence, a period of >30 s is an appropriate period for ADSC, which is confirmed by the sapphire measurements (Fig. 6).

Method 3 is the most accurate method to get the correct c_p values of a substance (c_p') for large and small periods. Here the blank curve is used to correct the calibra-

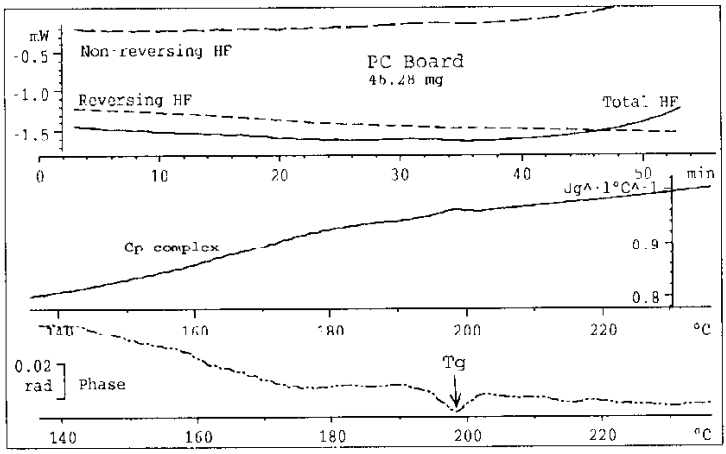

Fig. 10 46.28 mg of a flat piece of a printed circuit board are analyses by ADSC using method 2. c_p and heat flow curves do not show the normal behaviour during glass transition. Only the phase curve identifies the glass transition temperature by a pronounced peak

tion and sample curves with respect to cell asymmetry. With large periods of more than 60 s the aluminum mass should be in a range that the resulting amplitude is bigger than 100 μW, otherwise the online calibration is not very accurate.

If only temperature information is requested, the phase signal itself can be very helpful to detect and localize a glass transition temperature which is not seen by standard DSC measurements: example given in Fig. 10

Conclusions

From the model calculations and measurement results the limiting conditions and recommendations can be summarized as follows:

1. Choose $\omega << \omega_{limit}$	period (no damping is always better than compensation)
P_{limit} (light Al crucible, 10 mg): 3 s	30 s is a reasonable period
P_{limit} (Al standard crucible, 40 mg): 12 s	60 s is a reasonable period
2. Do not exceed the instrument heating and cooling rates	amplitude (no deterioration)
3. There should be 6–10 cycles (n) over the interesting thermal effect (ΔT) $\beta_{mean}=\Delta T/(nP)$	underlying heating rate e.g.: 20 K/(10·1 min)=2 K min^{-1}
4. Use small crucible mass	higher limit frequency

5. Measure with flat samples	good heat transfer (less damping)
6. Use small samples	similar frequency behaviour as for the blank (better accuracy of the c_p' calibration)
7. Make the difference between the sample and reference pan masses big enough (used only for c_p' calibration)	significant blank amplitude (better online c_p' calibration)
8. Avoid signal values (amplitudes) less than 100 μW	amplitude and/or period (smaller c_p' error)
9. Measure a blank curve	to eliminate the cell asymmetry
10. Choose the amplitude much smaller than the interesting thermal effect	good resolution for the non reversing signal

The ADSC technique is used in many applications to separate reversing effects (e.g. glass transition, Curie transition) and non reversing effects (e.g. chemical reactions, crystallization, enthalpy relaxations, evaporations).

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