J Therm Anal Calorim (2010) 102:1135–1140
DOI 10.1007/s10973-010-0770-4

Evaluation of heat capacity measurements by temperature-modulated differential scanning calorimetry

R. Venkata Krishnan · K. Nagarajan

Received: 28 January 2010 / Accepted: 23 March 2010 / Published online: 9 April 2010

Abstract Temperature-modulated differential scanning calorimetry (TMDSC) is known to have the ability to measure heat capacity of materials more accurately than the conventional differential scanning calorimeter. However, the accuracy of the measured heat capacity displays significant dependence on various experimental parameters such as period of modulation (p), amplitude of modulation (a), geometry of sample (g), heating rate (r), etc. One of the key features of this system is the ability to measure heat capacity under quasi-isothermal conditions. In the present investigation, heat capacity of a well-established system namely sapphire and thoria was measured by TMDSC under dynamic mode and also under quasi-isothermal mode. The experimental parameters, mentioned above p, a, g, and r are varied to establish the conditions for measuring heat capacity accurately.

Keywords TMDSC · Heat capacity · Quasi-isothermal TMDSC

Introduction

Temperature-modulated differential scanning calorimetry (TMDSC) developed by Reading et al. [1] was commercialized shortly afterward and is being widely applied in different fields such as material research, polymeric, food, pharmaceutical, and metallic materials [2–7]. In TMDSC, linear increase or decrease in temperature that is used in conventional differential scanning calorimeter (DSC) is modulated by superimposing upon it, a periodic temperature modulation (generally sinusoidal) of a certain amplitude and frequency. The temperature program of TMDSC could be given as

$$T(t) = T_0 + qt + A_T \sin(\omega t) \quad (1)$$

where T_0 is the initial temperature, q the underlying linear heating rate, and A_T the corresponding oscillation amplitude. The frequency of oscillation is $\omega = 2\pi/p$, where p being the period of oscillation. By differentiating Eq. 1, we obtain the instantaneous heating rate $\beta(t)$, which is given as

$$\beta(t) = \beta_{\text{mean}} + A_\beta \cdot \cos(\omega t) \quad (2)$$

where $A_\beta = A_T \cdot \omega$ (A_β, the amplitude of the heating rate) and β_{mean} corresponds to the underlying heating rate. There exists different evaluation methods for deriving heat capacity in TMDSC from the raw data obtained. Reading et al. [1] showed that by superimposing periodic temperature oscillation to the conventional linear heating program and by performing suitable mathematical manipulations it is possible to separate reversible and irreversible heat flow components in the heat flow signal [8]. The "reversing component" is obtained from the periodic component of heat flow rate and "non-reversing component" is the difference between the underlying heat flow (static heat flow) and the "reversing component" [8]. An alternative evaluation method by Schawe et al. [9–12] is based on linear response theory where the heat capacity obtained is complex in nature containing real and imaginary parts. The former method is used by M/s. T.A. Instruments, whereas M/s. Mettler Toledo GmbH uses the latter evaluation method. In this study, STARe software supplied by M/s. Mettler Toledo GmbH was used for analysis. Wunderlich et al. [13, 14] proposed a quasi-isothermal method to measure the heat capacity of a sample by TMDSC.

R. Venkata Krishnan · K. Nagarajan (✉)
Fuel Chemistry Division, Chemistry Group, Indira Gandhi Centre for Atomic Research, Kalpakkam 603102, Tamil Nadu, India
e-mail: knag@igcar.gov.in

It is known in DSC that when the heating rate is large, larger will be the temperature difference between the sample and the reference and therefore higher will be the sensitivity. Although the underlying heating rate is zero in the quasi-isothermal mode, the instantaneous heating or cooling rate is not zero and is a product of amplitude and angular frequency and therefore the sensitivity and the precision are greatly enhanced. If in the temperature interval ($T \pm A_T\omega$, where T temperature of measurement, A_T is amplitude of the heating program, ω angular frequency), the heat capacity of the sample is nearly constant or a slow changing function of temperature, the heat capacity obtained by quasi-isothermal mode is anticipated to be more accurate than that in conventional DSC [13, 14]. Ding and Cheng [15] proposed that the temperature gradients existing within the sample are another important factor, which has to be considered to obtain exact value of heat capacity, and developed a novel quasi-isothermal theory. Ding et al. suggested that if the heat capacity of the sample is nearly constant within the measured oscillating temperature interval, quasi-isothermal method of TMDSC is better than conventional DSC, otherwise the best tool to measure sample's heat capacity is conventional DSC. Boller et al. [14] suggested that it is possible to measure heat capacity in close thermal and internal equilibrium using TMDSC with a precision better than standard DSC. This is because the correction for the differences in sample and reference heating rates, needed for high-precision data by standard DSC, is not needed for this method. Cao [16] theoretically proved that TMDSC does not offer any advantage over a conventional DSC because it was found that the amplitude of heat flow is a non-linear function of the thermal transfer coefficient, modulation period, the heat capacity of the reference and the sample. However, Cao's theory [16] was latter clarified by Clarke et al. [17] who showed that Cao had incorrectly assumed that the heat capacity from TMDSC is found by dividing the amplitude of modulated component of total heat flow with the amplitude of the modulated block temperature instead of dividing with the amplitude of the modulated sample temperature. This study is aimed to compare the accuracy of the measurement obtained from TMDSC and quasi-isothermal TMDSC with conventional DSC by identifying optimum parameters for the measurement such as modulation frequency (or period), modulation amplitude, sample geometry, and thickness.

Experimental

Equipment

A heat flux type DSC, model number DSC821e/700 with STARe software supplied by M/s. Mettler Toledo GmbH, Switzerland, was used in this study.

Materials and methods

Temperature, heat, and thermal lag calibrations were carried out as explained in our previous publication [18]. High-purity argon was used as the purge gas at a flow rate of 50 mL min^{-1}. The measurements were carried out in 40 μL hermetically sealed aluminum pans with a pinhole on the lid. The measurements were carried out on sapphire and thorium dioxide samples. Sapphire was taken in the form of a disk of 0.2 mm thickness (21.679 mg), which was supplied by M/s. Mettler Toledo GmbH, Switzerland. The thorium dioxide powder was from M/s. Indian Rare Earths. ThO_2 powder was weighed accurately (37.371 mg, 0.5 mm thickness and 108.312 mg, 2 mm thickness) using a microbalance, pelletized, and heat-treated at 1273 K in air before the measurements. The diameter of the sapphire and thoria pellets used was such that the pellets exactly fitted the aluminum pan used. This has been ensured to improve the reproducibility of the measurements.

For each measurement of heat capacity, three runs were performed. The first run was the blank run, during which empty pans without lid were placed on both the sample and the reference sides. This run was carried out to nullify cell asymmetry. The second run was the calibration run where sample pan with lid hermetically sealed and having a pinhole was placed on the sample side. The third run was the sample run where sample pan with lid hermetically sealed and having a pinhole containing sample was placed on sample side. The difference between the mass of the sample pan and that of the calibration pan was chosen to be within 20 μg. In both the sample and the calibration runs, empty pan without lid was placed on the reference side. The ADSC evaluation is based on the following function

$$C_p(\text{sample}) = A(\text{HF})_{s-c}/(m_s\, x A(\beta_{\text{measured}}) \quad (3)$$

where $A(\text{HF})_{s-c}$ is the amplitude of heat flow of sample run minus the amplitude of heat flow of the calibration run, m_s is the mass of the sample, and $A(\beta_{\text{measured}})$ is the measured amplitude of heating rate. This is determined by "calibration run" as follows:

$$A(\beta_{\text{measured}}) = A(\text{HF})_{c-b}/m_c \cdot C_p(\text{pan}) \quad (4)$$

where $A(\text{HF})_{c-b}$ is the amplitude of heat flow of the calibration run minus the amplitude of heat flow of the blank run, m_c is the mass difference between the pan with lid (calibration curve) and the pan without lid (blank curve) or without mass of the lid. Optimization of parameters such as amplitude and period of oscillation was carried out using sapphire sample. Although the optimization studies using sapphire were carried out in the limited temperature range, the TMDSC measurements on ThO_2 sample were carried out in the temperature range 298–800 K using the optimized parameters. Also, each measurement on ThO_2 is

preceded by measurements on sapphire in the same temperature range (298–800 K).

Results and discussion

TMDSC measurements on sapphire

TMDSC measurements were carried out as explained above at modulation periods varying from 30 to 150 s by fixing the amplitude to 0.4 K and at an underlying heating rate of 5 K/min. The value of 0.4 K was chosen for amplitude, because only with 0.4 K amplitude, the experiment could be carried out in "heat only" mode for all the periods chosen. The maximum amplitude that can be chosen to perform the experiment in "heat only" mode is given by the following equation

$$T_{\text{amp}} = H_{\text{r}} \times P/2\pi \times 60$$

where T_{amp} maximum temperature amplitude for "heat only" (K), H_{r} average underlying heating rate (K min^{-1}), and P period in seconds.

Three runs were carried out in each modulation period and the average heat capacity values obtained from the measurements on sapphire were fitted to a polynomial by least squares. The values are shown in Fig. 1. The standard deviation in the measurements was within ±3% and standard error of the fit for all the curves was less than 1 J K^{-1} mol^{-1}. It is seen from Fig. 1 that the heat capacity values measured with the modulation period ≥90 s are in good agreement with the literature data within ±3%, whereas the values measured with periods less than 90 s have an error greater than 8%. Since the reproducibility between different runs under identical conditions is only ±3%, we could substantiate that under this condition of underlying heating rate, amplitude, sample geometry, and thickness the highest accuracy which could be obtained is only ±3%. In other words, there is not going to much improvement in accuracy by increasing the modulation period greater than 90 s. Knopp and Nail [19] also reported a reproducibility of ∼3% for measurements carried out with periods of 100 s when hermetically sealed pans are used.

Experiments were also undertaken to understand the variation in accuracy of the measurement at different amplitudes. If the modulation cannot affect the full sample with the amplitude set for analysis, one cannot expect quantitative data. If on the other hand the modulation is too low, precision suffers [16]. Therefore, maximum amplitude, which delivers more accurate results, has to be chosen. The experiments were undertaken at a period of 60 s, with an underlying heating rate of 5 K min^{-1} and the amplitude were varied from 0.2 to 0.6 K. Although the measured heat capacity data for a modulation period ≥90 s is more accurate, period of 60 s was chosen to effectively study the variation in the accuracy of measurement as a function of amplitude of oscillation. This is because preliminary experiments showed that at period ≥90 s the variation in the accuracy of measurements for varying amplitudes was observed to be within the experimental uncertainty and the amplitude effect could not be studied. The selection of amplitude was restricted to 0.6 K as this is the maximum amplitude, which could be selected for "heat only" mode as explained earlier. The results of the experiments were given in Fig. 2. As can be seen in Fig. 2, the amplitude of 0.2 and 0.4 K are in close agreement with that of literature value within about 3% throughout the measurement range, whereas that measured at an amplitude of 0.6 K yield data with an error in the range 10–12%. As explained earlier the higher amplitude, which delivers more accurate results, i.e., 0.4 K was chosen for further experiments on ThO_2 samples.

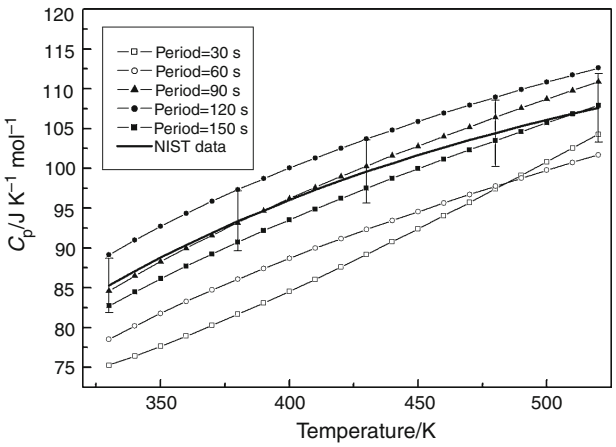

Fig. 1 Effect of modulation period on the accuracy of C_{p} measurement on sapphire

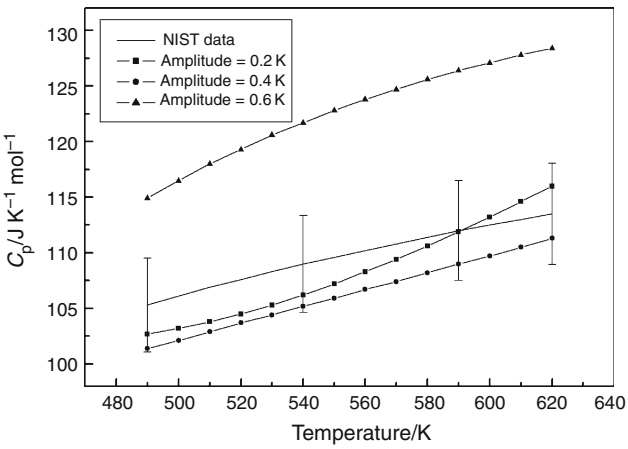

Fig. 2 Effect of amplitude of oscillation on the accuracy of C_{p} measurement on sapphire

TMDSC measurements on ThO_2

Preliminary experiments on sapphire revealed that the modulation amplitude of 0.4 K and the modulation period ≥90 s gave more accurate results with an underlying heating rate of 5 K min^{-1}. Therefore, experiments on ThO_2 were performed with modulation periods 90, 120, and 150 s. The temperature range of measurement is 298–800 K. The ThO_2 sample pellet was heated in the DSC cell at 673 K for 5 min to remove any adsorbed moisture within the sample. Three runs were conducted for each modulation periods and the average values were fitted to a polynomial. The standard error of all these fits is less than 1 J K^{-1} mol^{-1}. A plot of heat capacity of ThO_2 measured at different modulation periods is given in Fig. 3. As could be seen in Fig. 3, the heat capacity values vary in the region of 4–10% that from the literature data for all the three periods. This may be due to the fact that the thermal gradients experienced by ThO_2 pellet (0.5 mm thick) is much higher than that experienced by sapphire disk (0.2 mm thick). However, as each experiment on ThO_2 is preceded by experiment on sapphire, it is logical to correct the measured values of ThO_2 by multiplying with KC_p, where KC_p is the ratio of the literature to measured values of heat capacity of sapphire. This procedure was followed to all the periods of measurements and the corrected values of C_p of ThO_2 are fitted in a polynomial. The plot of corrected values of heat capacity of ThO_2 with temperature at different modulation periods is given in Fig. 4 and the values are listed in Table 1. It is seen from the figure that the corrected values of the heat capacity of ThO_2 for all the modulation periods are in close agreement with that of the literature data [20] throughout the temperature range of measurement within 1–4%. Even though the corrected heat capacity values for period 90 s seems to be in more close agreement with that of the literature data compared to the

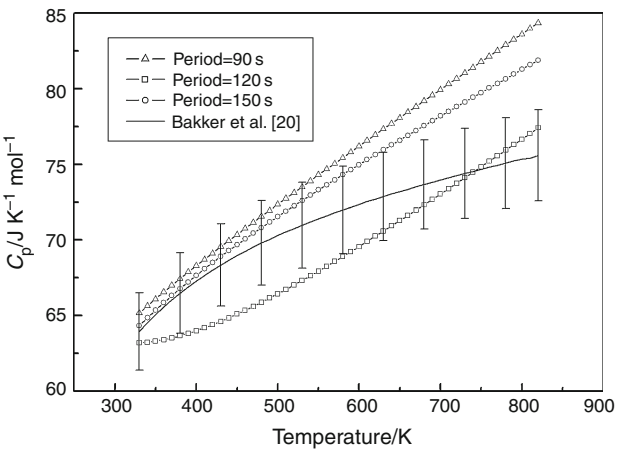

Fig. 3 Effect of modulation period on the accuracy of C_p measurement on ThO_2 at amplitude of 0.4 K

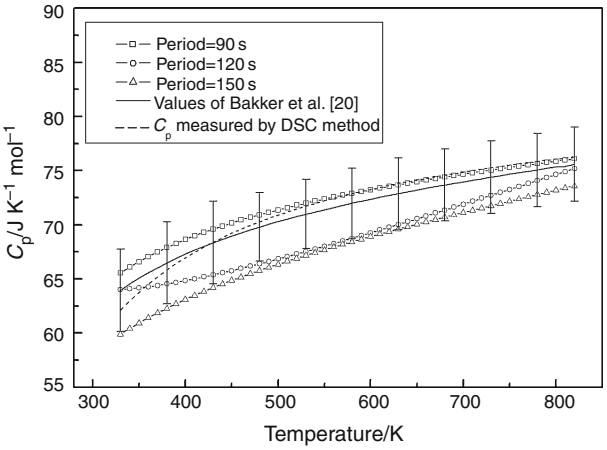

Fig. 4 Corrected C_p data of ThO_2 at different modulation periods

period of 120 and 150 s, we could not consider the period of 90 s to be superior to others as the reproducibility between different runs of the same period is only 3%.

Effect of thermal gradients on TMDSC measurements on ThO_2

TMDSC measurements were carried out on thin (0.5 mm thickness, 37 mg sample size) and thick (2 mm thickness, 108 mg sample size) ThO_2 samples to study the effect of thermal gradients on the accuracy of the heat capacity measurements by TMDSC, several thermal gradients exist within DSC cell during TMDSC measurements namely (1) between heater and temperature sensor, (2) between sensor and block, (3) between the block and the bottom of the sample, (4) between bottom and the top of the sample. Temperature gradients existing due to the first three effects were corrected by thermal lag correction as explained in our previous work [18]. The experiments were carried out in the temperature range 500–670 K at an oscillation amplitude and period of 0.4 K and 90 s, respectively, at an underlying heating rate of 5 K min^{-1}. The measured heat capacity of both thin and thick samples is shown in Fig. 5. As can be seen in Fig. 5, the heat capacity measurements on the thick sample show a large positive bias (10–15%) when compared with that of the literature value. The heat capacity measurements on thin ThO_2 sample are in good agreement within ±2–3% with that of the literature value. This may be due to the fact that the error associated with thermal gradients within the sample is more pronounced for thick sample as it has longer path of diffusion for the heat than that of thin sample. It has been shown in literature both experimentally as well as theoretically [21–25] that the phase lag between block and bottom of the sample and between top and bottom surfaces of the sample increase with sample thickness and therefore results in large error.

Table 1 Heat capacity data of ThO_2 at different modulation period at modulation amplitude of 0.4 K

Temperature/K	C_p corrected/J K^{-1} mol^{-1}			C_p/J K^{-1} mol^{-1} (Bakker et al. [20])
	$P = 90$ s	$P = 120$ s	$P = 150$ s	
400	68.65	64.84	63.11	67.29
500	71.38	66.84	66.36	70.3
600	73.23	69.26	68.92	72.35
700	74.66	71.89	71.14	73.96
800	75.87	74.63	73.19	75.34

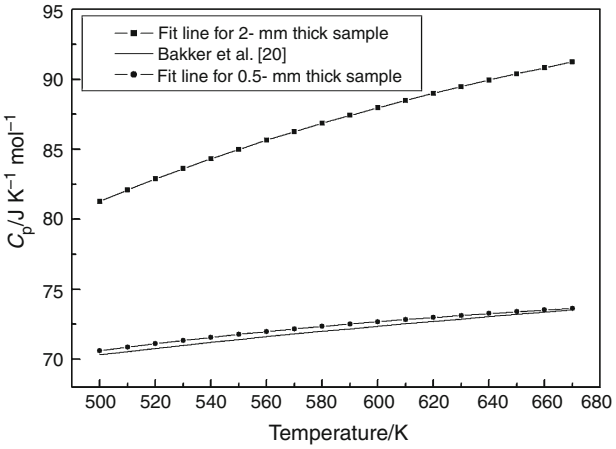

Fig. 5 Effect of thermal gradient on the measured C_p data of ThO_2

Table 2 Effect of period and amplitude on K_c for sapphire and ThO_2

Period/s	Amplitude/K					
	0.2		0.6		1	
	Sapphire	ThO_2	Sapphire	ThO_2	Sapphire	ThO_2
30	1.03	1.09	1.13	1.06	1.09	1.08
60	0.94	0.93	0.98	0.95	1.01	0.89
90	0.93	0.87	1.01	0.93	0.88	0.81
120	0.88	0.86	0.91	0.87	0.95	0.9
150	0.95	0.9	0.96	0.91	1.00	1.09

Quasi-isothermal TMDSC measurements on sapphire

Boller et al. [14] reported that the heat capacity measurements by TMDSC under quasi-isothermal conditions are capable of reducing the average error down to ±1%. To evaluate the claim, heat capacity measurements were carried out by quasi-isothermal mode on sapphire and ThO_2. To understand the influence of period and amplitude of oscillation, initial runs were carried out at 473 K with modulation amplitudes ranging from 0.2 to 1.0 K at different periods ranging from 30 to 150 s. Table 2 lists the calibration constant K_c (C_p literature/C_p measured) for sapphire and ThO_2 for different amplitudes and periods at 473 K. As can be seen from the table, there is no regular variation of K_c with periods, whereas Boller et al. [14] have reported a uniform variation toward unity with increase in period. Further, we find that K_c varies with amplitude of oscillation, whereas Boller et al. [14] found practically no dependence of K_c on amplitude.

From Table 2, it is evident that the highest accuracy of the measurement, which is indicated by the closeness of K_c to unity, is obtained at different periods for different amplitudes. However, 60 and 150 s appear to give an accuracy of ≤5% for all the amplitudes for sapphire. In the case of ThO_2, as seen in Table 2, only 60 s gives the optimum accuracy for all the amplitudes except 1.0 K. It is understandable, since the ThO_2 pellet sample is ~0.5-mm thick, the temperature gradients within the sample will be much higher than in the 0.2-mm thick disk of sapphire especially at higher amplitudes. Table 3 lists the variation of K_c of sapphire and ThO_2, for different periods of oscillation and at different temperatures for temperature amplitude of 0.2 K. It is seen that for both ThO_2 and sapphire, the optimum value for period is 60 s, which gives the optimum accuracy at all temperatures. This is in accordance with the observation with Boller et al. [14] who

Table 3 Variation of the calibration constant K_c as a function of temperature for different periods for sapphire and ThO_2

Temperature/K	Period/s									
	30		60		90		120		150	
	Sapphire	ThO_2	Sapphire	ThO_2	Sapphire	ThO_2	Sapphire	ThO_2	Sapphire	ThO_2
323	1.12	1.08	0.97	1.04	1.03	1.17	0.95	0.84	1.02	1.05
473	1.03	1.09	0.94	0.93	0.93	0.87	0.88	0.86	0.95	0.9
723	1.07	0.96	0.97	0.93	0.9	0.93	0.89	0.9	0.87	0.92

Table 4 Variation of the corrected heat capacity constant, corrected K_c as a function of temperature for different periods for ThO_2

Temperature/K	Period/s				
	30	60	90	120	150
323	0.97	1.02	1.13	0.88	1.02
473	1.05	0.99	0.92	0.97	0.94
723	0.9	0.97	1.03	1.01	1.05

reported that ideal conditions of control and response of the instrument representing the steady state are obtained with a modulation period of 60 s. This could perhaps be just a coincidence, since the instruments used in these investigations are different.

Table 4 lists the corrected K_c of ThO_2 (K_c thoria/K_c sapphire), for different modulation periods and temperatures. It can be seen that the corrected K_c values of ThO_2 in Table 4 are closer to unity than the K_c values of Table 3. Thus, it can be recommended that calibration with sapphire at all the temperatures for the period and amplitude of measurement will be helpful to improve the accuracy of the measured heat capacity value.

Conclusions

The highest accuracy obtained with quasi-isothermal TMDSC and TMDSC with heating ramp is in the range of ±2–4%. The level of accuracy is of the same order as was obtained with conventional DSC [18]. Therefore, from our observation it is evident that the modulated DSC does not offer a great advantage over conventional DSC for heat capacity measurements especially for ceramic samples, which has low thermal conductivity.

References

1. Reading M, Elliott D, Hill V. In: Proceedings of the 21st North American Thermal Analytical Society, 1992. p. 145–50.
2. Dantas HF, Mendes RAS, Pinho RD, Soledade LEB, Paskocimas CA, Lira BB, et al. Characterization of gypsum using TMDSC. J Therm Anal Calorim. 2005;82:565–74.
3. Garden J-L, Richard J, Saruyama Y. Entropy production in TMDSC. J Therm Anal Calorim. 2008;94:585–90.
4. Qiu SJ, Chu HL, Zhang J, Qi YN, Sun LX, Xu F. Heat capacity and thermodynamic properties of CoPc and CoTMPP. J Therm Anal Calorim. 2008; 91(3):841–8.
5. Chau J, Garlicka I, Wolf C, Teh J. Modulated DSC as a tool for polyethylene structure characterization. J Therm Anal Calorim. 2007;90(3):713–9.
6. Heidenreich S, Langner T, Rohm H. Heat capacity of cheese, determination or calculation. J Therm Anal Calorim. 2007; 89:815–9.
7. Danley RL. New modulated DSC measurement technique. Thermochim Acta. 2003;402:91–8.
8. Reading M, Elliott D, Hill VL. A new approach to the calorimetric investigation of physical and chemical transitions. J Therm Anal. 1993;40:949–55.
9. Schawe JEK. A comparison of different evaluation methods in modulated temperature DSC. Thermochim Acta. 1995;260:1–16.
10. Schawe JEK. Modulated temperature DSC: the influence of the experimental conditions. Thermochim Acta. 1996;271:127–40.
11. Schawe JEK. Principles for the interpretation of modulated temperature DSC measurements. Part 1. Glass transition. Thermochim Acta. 1995;261:183–94.
12. Schawe JEK, Höhne GWH. The analysis of temperature modulated DSC measurements by means of the linear response theory. Thermochim Acta. 1996;287:213–23.
13. Wunderlich B, Jin Y, Boller A. Mathematical description of differential scanning calorimetry based on periodic temperature modulation. Thermochim Acta. 1994;238:277–93.
14. Boller A, Jin Y, Wunderlich B. Heat capacity measurement by modulated DSC at constant temperature. J Therm Anal. 1994;42:307–30.
15. Ding EY, Cheng RS. Novel quasi-isothermal method of measuring heat capacity in temperature modulated differential scanning calorimetry. Thermochim Acta. 2001;376:131–9.
16. Cao J. Mathematical studies of modulated differential scanning calorimetry—heat capacity measurements. Thermochim Acta. 1999;325:101–9.
17. Clarke S, Folland P, Matisons J. Clarification about obtaining heat capacities using TMDSC. Thermochim Acta. 2000;351:29–31.
18. Venkata Krishnan R, Nagarajan K. Heat capacity measurements on uranium-cerium mixed oxides by differential scanning calorimetry. Thermochim Acta. 2006;440:141–5.
19. Knopp SA, Nail SL. Experimental considerations for temperature modulated DSC at low temperature. J Therm Anal. 2000;60: 319–32.
20. Bakker K, Cordfunke EHP, Konings RJM, Schram RPC. Critical evaluation of the thermal properties of ThO_2 and $Th_{1-y}U_yO_2$ and a survey of the literature data on $Th_{1-y}Pu_yO_2$. J Nucl Mater. 1997;250:1–12.
21. Buehler FU, Seferis JC. Thermal gradients in TMDSC samples—a comparison of theory and experimental data. J Therm Anal Calorim. 2001;63:21–30.
22. Buehler FU, Seferis JC. Heat diffusion analysis of temperature distribution and phase lag build up in TMDSC specimens. Thermochim Acta. 1999;334:49–55.
23. Buehler FU, Seferis JC. Effect of sample thickness in TMDSC measurements. Thermochim Acta. 2000;348:161–8.
24. Buehler FU, Martin CJ, Seferis C. J Therm Anal Calorim. 1998;54:501–19.
25. Androsch R, Pyda M, Wang H, Wunderlich B. A study of temperature modulated calorimetry with high-resolution infrared thermography. J Therm Anal Calorim. 2000;61:661–79.