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MTDSC CALIBRATION
Dependence of the instrumental response upon experimental conditions

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Abstract

The heat capacity calibration 'constants' of a commercial MTDSC system (TA 3100) were determined in a variety of experimental conditions. For a given modulation frequency, the calibration constants are the same within a few percents for different temperatures, and over a wide range of modulation amplitudes and scan rates. This variation decreases below 1% if hidden instrumental constraints are taken into account, which are related with the capability of the control system to achieve the desired temperature program. On the other hand, the calibration constant changes substantially with the period, and takes anomalously high values for the short modulation periods (20÷40 s). Rules to optimize the accuracy of the system are given.

Keywords: calibration, heat capacity, MTDSC

Introduction

MTDSC is a recent evolution of conventional DSC [1–3] where a sinusoidal modulation of temperature is added to the conventional heating/cooling ramp. A major consequence is that instantaneous and average heating rates of the sample may differ substantially. As a consequence, information is retrieved about a sample being heated at rate which is a constant in average, and oscillates around this value with amplitude and frequency determined by the modulation parameters. A first consequence is that it is much easier to accommodate the conflicting requirements of resolution (which needs small scan rates) and sensitivity (which needs high scan rates) of the DSC technique. Another and more fundamental advantage is that, in principle, it is possible to distinguish between thermally reversible phenomena, which follow the modulation, and the irreversible ones, which do not. For this reason, it has been claimed that MTDSC may be invaluable in polymer [4–8] and pharmaceutical [9–12] sciences, where the complex nature of the samples makes determination of thermodynamic equilibria difficult.

The splitting of the total heat flow into two parts is made on the assumption that all thermally reversible phenomena contribute to the heat capacity. However, the significance and the reliability of such a splitting is doubtful; the response to modula-

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tion of a physico-chemical transformation will depend on the nature of the transformation and on the modulation conditions themselves, while the total heat flow has the same meaning as in conventional DSC. From a practical point of view, a very careful heat capacity (c_p^*) calibration is always needed to separate reversible and irreversible effects in MTDSC.

The c_p^* calibration itself, properly performed with a sapphire disk (with optimal thermal transfer – due to the good fitting of the flat surface of the disk and of the bottom of the pan – and no transition in the temperature interval of our interest), may be used to gain insights of basic features of MTDSC, in particular the role of the various experimental parameters. An aim of this article is to provide indications about the expected effects of different choices of amplitude (A_T) and period (P) of the temperature modulation. In this paper, specific heat (c_p) calibration was performed in a variety of experimental conditions to gain knowledge on how the instrument response is affected by the experimental parameters.

Experimental

Measurements were performed with a MDSC 2920 apparatus, connected to a TA 3100 data station (Thermal Solution™ Software). A wide range of experimental conditions was utilized. Namely, average heating rates (<β>) of 0.5, 1.0, 2.0, 3.0 and 5.0°C min^{-1} were applied. Temperature amplitudes were ranging from 0.03 to 3.00°C and periods from 20 to 100 s (in steps of 10 s). The temperature range was between 150 and 200°C. The sapphire disk utilized (mass 60.98 mg) was supplied by TA Instruments Ltd. as a part of the apparatus kit. Standard open pans of aluminium were used as sample holder and reference. Dry nitrogen was flushed through both the purge gas and vacuum ports (25 ml min^{-1} into DSC cell to improve modulation; 50 ml min^{-1} into heat exchanger to prevent moisture freezing). A computer controlled liquid nitrogen cooling accessory (LNCA by TA Instruments Ltd.) was used to improve modulation over all experiments. The specific heat of sapphire was taken from the literature [13].

Results and discussion

The expected relationship between c_p calibration constant and experimental parameters

According to the manufacturer indication, the heat capacity c_p^* is obtained as follows:

$$c_p^* = K_{cp} \frac{A_\varphi P}{A_T 2\pi} \quad (1)$$

where c_p^* – thermal capacity of the sample (J K^{-1}), equal to its mass multiplied by the specific heat, K_{cp} – calibration constant (adimensional), A_φ – amplitude of modulated heat flow (W), computed by the machine software, A_T – amplitude of the temperature modulation (K), computed by the machine software, P – modulation period (s).

We may also write the calibration constant as

$$K_{cp} = c_P^* \frac{A_\beta}{A_\varphi} \quad (2)$$

with

$$A_\beta = A_T \frac{2\pi}{P} \quad (3)$$

where A_β – amplitude of the modulated heating rate (K s^{-1}).

The heat flow is equal to the heating rate times the heat capacity of the sample and an instrumental constant (K_{cp}), which, ideally, does not depend upon the experimental parameters. To better show the connection with the conventional DSC, we recall that the calibration constant is usually written as

$$K_{cp} = c_P^* \frac{\Delta\beta}{\Delta\varphi} \quad (4)$$

where we have the difference between two heating rates (β) and the difference between the corresponding heat flows (φ)

$$\Delta\beta = \beta_{max} - \beta_{min};\ \Delta\varphi = \varphi_{max} - \varphi_{min}$$

In the presence of a perfectly sinusoidal modulation with an average heating rate ⟨β⟩, we should have

$$\beta_{max} = \langle\beta\rangle + A_\beta,\ \ \beta_{min} = \langle\beta\rangle - A_\beta \Rightarrow \Delta\beta = 2A_\beta \quad (5)$$

and the difference between the corresponding heat flows should be

$$\Delta\varphi = 2A_\varphi \quad (6)$$

However, if we retrieve Δβ and Δφ from the peak-to-peak amplitudes of the heating rate and heat flow curves, we have some noticeable differences relative to the ratios of the raw parameters, A_β and A_φ computed by our system. Therefore, in the following, we will mostly refer to Eq. (4), with Δβ and Δφ evaluated directly from the plots of the heating rate and heat flux, a well defined procedure. Relative to the calibration constant determined through Eq. (2), recommended by the manufacturer, some significant differences have been noted only at the highest modulation frequencies (P=20, 30 s).

Table 1 Calibration constants at two temperatures determined from Eq. (2) ($K_{cp,\,Am}$) and Eq. (4) ($K_{cp,\,\Delta}$)

A_T/ °C	P/ s	⟨β⟩/ °C min^{-1}	T=156.85°C		T=186.85°C	
			$K_{cp,\,Am}$	$K_{cp,\,\Delta}$	$K_{cp,\,Am}$	$K_{cp,\,\Delta}$
0.030	20	1	1.794	1.595	1.772	1.609
0.030	20	3	1.782	1.643	1.779	1.585
0.080	30	1	1.462	1.385	1.456	1.382
0.133	30	1	1.502	1.425	1.486	1.409
0.053	40	0.5	1.284	1.250	1.299	1.271
0.106	40	1	1.292	1.257	1.286	1.257
0.212	40	0.5	1.294	1.254	1.288	1.242
0.212	40	1	1.297	1.256	1.290	1.256
0.212	40	2	1.291	1.250	1.293	1.258
0.212	40	2	1.294	1.239	1.285	1.244
0.531	40	5	1.300	1.256	1.291	1.250
0.212	40	5	1.291	1.257	1.290	1.256
0.030	40	3	1.222	1.149	1.248	1.191
3.000	40	3	1.258	1.247	1.252	1.238
0.030	40	5	1.342	1.230	1.232	1.241
3.000	40	5	1.258	1.244	1.251	1.236
0.133	50	1	1.212	1.172	1.217	1.207
0.151	60	1	1.176	1.158	1.176	1.150
3.000	60	3	1.151	1.143	1.149	1.140
3.000	60	5	1.152	1.137	1.149	1.139
0.133	70	1	1.167	1.165	1.168	1.149
0.159	70	1	1.168	1.174	1.170	1.153
0.186	70	1	1.154	1.151	1.155	1.141
0.212	70	1	1.171	1.165	1.166	1.164
0.239	70	1	1.167	1.146	1.166	1.160
0.159	80	1	1.154	1.154	1.151	1.157
0.186	80	1	1.153	1.154	1.148	1.136
0.212	80	1	1.153	1.135	1.151	1.122
0.212	80	1	1.137	1.126	1.142	1.135
0.239	80	1	1.147	1.150	1.150	1.136
0.265	80	1	1.151	1.141	1.150	1.142

Table 1 Continued

A_T/ °C	P/ s	⟨β⟩/ °C min^{-1}	T=156.85°C		T=186.85°C	
			$K_{cp,Am}$	$K_{cp,\Delta}$	$K_{cp,Am}$	$K_{cp,\Delta}$
0.030	80	3	1.111	1.183	1.117	1.256
3.000	80	3	1.114	1.105	1.115	1.110
3.000	80	5	1.114	1.104	1.116	1.109
0.186	90	1	1.137	1.123	1.138	1.146
0.239	90	1	1.138	1.145	1.138	1.124
0.239	90	1	1.132	1.147	1.137	1.140
0.265	90	1	1.140	1.139	1.137	1.145
0.212	90	1	1.136	1.123	1.138	1.143
0.265	100	1	1.128	1.119	1.128	1.129
0.265	100	1	1.119	1.115	1.119	1.134
0.239	100	1	1.126	1.125	1.129	1.137
0.318	100	1	1.130	1.139	1.130	1.116

The observed dependence of K_{cp} on experimental parameters

The K_{cp} values obtained according to Eqs (2) ($K_{cp,Am}$) and (4) ($K_{cp,\Delta}$) at two different temperatures (156.85°C, c_p=0.9770 and 186.85°C, c_p=1.0070 J g^{-1} °C^{-1}) are reported in Table 1. For each measurement A_T, P and ⟨β⟩ are also reported. We note that:

- K_{cp} depends on P and decreases with increasing P;
- the rate of change of K_{cp} decreases with increasing P;
- at first sight it seems there is no dependence of K_{cp} upon average heating rate (⟨β⟩) and temperature amplitude (A_T).

According to Eq. (4), a Δφ–Δβ plot should yield a straight line through the origin, which appears to be mostly the case if data taken with the same period are considered. For 60 s≤P≤100 s, the K_{cp}'s computed through Eq. (2) are the same, within ±2%. However, for P≤40 s, the K_{cp}'s appear to increase systematically with decreasing P. As it can be seen from Table 1, for P=40 s, both β and A_T have been changed over a wide range. Some of the data taken with constant A_T=0.212°C, P=40 s and different ⟨β⟩ are reported in Table 2. No dependence of values upon ⟨β⟩ or temperature (T) can be noted.* However there is a systematic difference between K_{cp} estimated through Eqs (2) and (4) which is larger than the standard deviation.

* Note, however, that our temperature range is too small to show any definite temperature effect on K_{cp}. Indeed, the discussion of such an effect is not among the aims of the present paper. Temperatures were selected in the range 150-200°C because such a range is of interest for many organics.

Table 2 Influence of T and $\langle\beta\rangle$ upon K_{cp} with P=40 s

A_T/ °C	$\langle\beta\rangle$*	T=156.85°C						T=186.85°C					
		$2A_\beta$*	$\Delta\beta$*	$2A_\varphi$+	$\Delta\varphi$+	$K_{cp,Am}$	$K_{cp,\Delta}$	$2A_\beta$*	$\Delta\beta$*	$2A_\varphi$+	$\Delta\varphi$+	$K_{cp,Am}$	$K_{cp,\Delta}$
0.212	0.5	3.9905	3.8490	3.0620	3.0470	1.294	1.254	3.9527	3.8330	3.1400	3.1596	1.288	1.242
0.212	1	3.9923	3.8590	3.0560	3.0510	1.297	1.256	3.9735	3.8694	3.1520	3.1531	1.290	1.256
0.212	2	3.8887	3.7632	2.9900	2.9890	1.291	1.250	3.9716	3.8484	3.1440	3.1319	1.293	1.258
0.212	5	3.6625	3.6770	2.8160	2.9040	1.291	1.257	3.9150	3.7900	3.1060	3.0880	1.290	1.256
				K_{cp} average		1.293	1.254			K_{cp} average		1.290	1.253
				standard deviation		±0.0029	±0.0031			standard deviation		±0.0021	±0.0074

* in °C min^{-1}
+ in mW

Table 3 Influence of A_T upon K_{cp} with P=70 s

A_T/ °C	⟨β⟩*	T=156.85°C						T=186.85°C					
		$2A_\beta$*	$\Delta\beta$*	$2A_\varphi$$^+$	$\Delta\varphi^+$	$K_{cp,Am}$	$K_{cp,\Delta}$	$2A_\beta$*	$\Delta\beta$*	$2A_\varphi$$^+$	$\Delta\varphi^+$	$K_{cp,Am}$	$K_{cp,\Delta}$
0.133	1	1.3895	1.3930	1.1824	1.1872	1.167	1.165	1.4056	1.3760	1.2316	1.2259	1.168	1.149
0.159	1	1.6781	1.6826	1.4270	1.4226	1.168	1.174	1.7018	1.6844	1.4880	1.4946	1.170	1.153
0.186	1	1.9464	1.9320	1.6744	1.6673	1.154	1.151	2.0034	1.9961	1.7746	1.7898	1.155	1.141
0.212	1	2.2307	2.2141	1.8908	1.8886	1.171	1.165	2.2512	2.2466	1.9762	1.9756	1.166	1.164
0.239	1	2.5011	2.4561	2.1280	2.1283	1.167	1.146	2.5420	2.5225	2.2320	2.2254	1.166	1.160
				K_{cp} average		1.165	1.160			K_{cp} average		1.165	1.153
				standard deviation		±0.0066	±0.011			standard deviation		±0.0058	±0.0091

* in °C min^{-1}
\+ in mW

Table 4 Influence of A_T upon K_{cp} with P=80 s

A_T/ °C	⟨β⟩*	T=156.85°C						T=186.85°C					
		$2A_\beta$*	Δβ*	$2A_\varphi$ +	$\Delta\varphi^-$	$K_{cp,Am}$	$K_{cp,\Delta}$	$2A_\beta$*	Δβ*	$2A_\varphi$ +	$\Delta\varphi^+$	$K_{cp,Am}$	$K_{cp,\Delta}$
0.159	1	1.4156	1.4146	1.2176	1.2174	1.154	1.154	1.4778	1.4840	1.3136	1.3124	1.151	1.157
0.186	1	1.6701	1.6687	1.4386	1.4363	1.153	1.154	1.7417	1.7229	1.5530	1.5518	1.148	1.136
0.212	1	1.8868	1.8509	1.6248	1.6192	1.153	1.135	1.9811	1.9304	1.7616	1.7606	1.151	1.122
0.239	1	2.1658	2.1725	1.8750	1.8765	1.147	1.150	2.2129	2.1749	1.9696	1.9598	1.150	1.136
0.265	1	2.4014	2.4000	2.0720	2.0882	1.151	1.141	2.4929	2.4638	2.2180	2.2071	1.150	1.142
				K_{cp} average		1.152	1.147			K_{cp} average		1.150	1.139
				standard deviation		±0.0028	±0.0085			standard deviation		±0.0012	±0.013

* in °C min^{-1}
\+ in mW

Some measurements at P=70 and 80 s were performed with the same $\langle\beta\rangle$ but with different A_T values (Tables 3, 4). It can be seen that the K_{cp}'s are somewhat more sensitive to a change of A_T than to a change of $\langle\beta\rangle$. However the influences of both A_T and $\langle\beta\rangle$ are smaller with respect to those of P.

We now study the dependence of K_{cp} upon the modulation period P. As implied by Eqs (2) and (4), there should be a proportionally between A_β ($\Delta\beta$) and A_φ ($\Delta\varphi$). If we have three or more data points with the same period, we may analyze the data with a linear regression of $\Delta\varphi$ *vs.* $\Delta\beta$: when we find that the standard error of the intercept [$Es(a)$] is larger, or comparable with $|a|$, the proportionality is verified; each data point gives an estimate of K_{cp} and our standard error will be

$$\varepsilon(K_{cp}) = \sqrt{\frac{\sum_{i=1}^{N}(K_{cp} - <K_{cp}>)^2}{N-1}}$$

On the other hand, if $|a|$ is larger than 2 $Es(a)$, some systematic error may be present; the best estimate of K_{cp} may be assumed proportional to the slope of the linear regression; its error should then be proportional to the standard error of the slope.

When we have less than three data points, we may only estimate K_{cp} and, with two points, its error. The results of this analysis are summarized in Table 5. As it can be seen, the standard errors are quite low, meaning that the measurements' precision is good at each P value. However, the expected proportionality between A_β ($\Delta\beta$) and A_φ ($\Delta\varphi$) does not result statistically verified for P=80 s and P=90 s. As noted, this could be due to the presence of some of some systematic error that, as a matter of fact, becomes relevant in the upper range of the permitted P values.

Table 5 Average and standard errors of K_{cp} for different P values

P/s	N	$\|a\|<2Es(a)$	$\langle K_{cp}\rangle$[1]	$\varepsilon(K_{cp})$
20	2	–	1.619	0.024
30	2	–	1.405	0.020
40	12	yes	1.241	0.009
50	1	–	1.172	–
60	3	yes	1.146	0.006
70	5	yes	1.160	0.005
80	9	no	1.102	0.001
90	5	no	1.218	0.043
100	4	yes	1.125	0.005

[1]Computed from $\Delta\varphi$ and $\Delta\beta$

Table 6 Comparison between expected and observed modulations

P/ s	A_T/ °C	⟨β⟩*	T=156.85°C							T=186.85°C						
			$\Delta\beta_{calc}$*	$2A_\beta$*	$\Delta\beta$*	$2A_\varphi$⁺	$\Delta\varphi$⁺	$K_{cp,Am}$	$K_{cp,\Delta}$	$\Delta\beta_{calc}$*	$2A_\beta$*	$\Delta\beta$*	$2A_\varphi$⁺	$\Delta\varphi$⁺	$K_{cp,Am}$	$K_{cp,\Delta}$
40	0.030	3	0.5655	0.5372	0.4860	0.4366	0.4200	1.222	1.149	0.5655	0.5466	0.5190	0.4484	0.4460	1.248	1.191
40	0.030	5	0.5655	0.4756	0.5030	0.3518	0.4060	1.342	1.230	0.5655	0.5278	0.5240	0.4384	0.4320	1.232	1.241
40	3.000	3	56.549	39.546	40.170	31.220	31.990	1.258	1.247	56.549	39.578	40.261	32.440	33.280	1.252	1.238
40	3.000	5	56.549	37.605	38.390	29.680	30.640	1.258	1.244	56.549	39.999	40.470	32.721	33.520	1.251	1.236
60	3.000	3	37.699	34.909	35.171	30.120	30.560	1.151	1.143	37.699	38.780	38.990	34.540	34.991	1.149	1.140
60	3.000	5	37.699	35.902	36.160	30.940	31.580	1.152	1.137	37.699	37.762	37.721	33.620	33.900	1.149	1.139
80	0.030	3	0.2827	0.3156	0.3730	0.2820	0.3130	1.111	1.183	0.2827	0.2343	0.2860	0.2606	0.2330	1.117	1.256
80	3.000	3	28.274	27.417	27.261	24.441	24.490	1.114	1.105	28.274	27.784	27.630	25.501	25.477	1.115	1.110
80	3.000	5	28.274	26.936	26.777	24.000	24.094	1.114	1.104	28.274	27.492	27.291	25.220	25.178	1.116	1.109

* in °C min^{-1}
\+ in mW

The influence of A_T and $\langle\beta\rangle$ on the agreement between calculated and observed quantities

Table 6 summarizes the relevant calculated and observed quantities of some of the measurements performed with very low (0.03°C) or quite high (3.00°C) temperature amplitudes. Here we have defined $\Delta\beta_{calc}$ in terms of the nominal (programmed) modulation amplitude divided P: $\Delta\beta_{calc}=2A_T(2\pi/P)$. Again, the two different ways of computing K_{cp} (Eq. (2) and (4)) yield compatible results. However, for P=40 s and A_T=3.00°C, we have $\Delta\beta/2=0.71A_\beta$ (rather than $\Delta\beta/2=A_\beta$), meaning that the experimental modulation parameters are substantially different form the selected ones. For A_T=0.03°C there is apparently some dependence of the calibration constant from $\langle\beta\rangle$ and T. However, with such a low amplitude, $\Delta\beta$ is of the order of 0.56°C min^{-1} or an order of magnitude smaller than a typical average heating rate of 5°C min^{-1}. It seems the instrument is unable to add accurately a small temperature variation to large heating rates, as if its actuator has a quite limited dynamic range.

Instrument limitations

A major limitation is the maximum heating rate that the apparatus can sustain, and which is claimed to be 100°C min^{-1}. Therefore, we should have $\beta_{max}\leq$100°C min^{-1}. However, the system should also have a maximum sustainable acceleration. A qualitative argument may be as follows: since linear propagation of a heat wave in a homogeneous medium is expected to have an attenuation length proportional to the period, above a critical frequency, the power needed to achieve the same temperature modulation should roughly scale with the modulation amplitude and the square of the frequency i.e., with the acceleration. If the temperature profile of an MTDSC experiment is given by:

$$T_{mod} = T_o + \beta t + A_T\sin(\omega t)$$

with $\omega=2\pi/P$ its maximum acceleration is:

$$a_{max} = \left| A_T\left(\frac{2\pi}{P}\right)^2 \right| \qquad (7)$$

To evaluate the limiting acceleration we set $\langle\beta\rangle$=3°C min^{-1}; A_T=3.00°C; P=40 s and obtain β_{max}=31.27°C min^{-1}, a_{max}=266.48°C min^{-2}. However, from a run with these parameters we recorded $\Delta\beta\cong$40.2°C min^{-1}, (rather than the expected, $\Delta\beta_{calc}$=56.55°C min^{-1}) and $A_T\cong$2.1°C rather than 3.00°C. The corresponding acceleration of this experiment may be assumed to be the maximum obtainable acceleration $a_{max}\cong$187°C min^{-2}. Such a value is confirmed by another determination a_{max} performed with the same modulation as before, but a higher average heating rate ($\langle\beta\rangle$=5°C min^{-1} rather than 3°C min^{-1}), which yielded $a_{max}\cong$184°C min^{-2}.

It is now clear why at P=40 s we obtained $\Delta\beta/2=0.71A_\beta$ (see above); the apparatus could not attain the desired modulation conditions. On the other hand, the agreement between $\Delta\beta$ and A_β is good when $\langle\beta\rangle$=3÷5°C min^{-1}; A_T=3.00°C; P=60 s, and the expected acceleration of 118.4°C min^{-2} is below the limit.

Proposed criteria for the correct selection of experimental parameters

It was seen that there are instances where it is difficult or impossible for the instrument to follow the selected modulation conditions, and which are not specified as such by the manufacturer. Our measurements suggest that a condition to have a good agreement between selected and realized modulation is that $\Delta\beta$ is not too low with respect to $\langle\beta\rangle$. A reasonable condition may be:

$$\Delta\beta \geq 2\langle\beta\rangle$$

which corresponds to:

$$A_T \geq \langle\beta\rangle\frac{P}{2\pi} \tag{8}$$

This relationship gives the lowest limit of the suggested range of A_T values as a function of $\langle\beta\rangle$ and P. The highest A_T may be obtained from the maximum sustainable acceleration, but, conservatively, we prefer not to exceed an acceleration of 100°C min^{-2}. Thus:

$$A_T \leq \frac{100P^2}{4\pi^2} \tag{9}$$

From (8) and (9) the suggested A_T range is:

$$\langle\beta\rangle\frac{P}{2\pi} \leq A_T \leq \frac{100P^2}{4\pi^2} \tag{10}$$

Equation (10) constitutes a guide to optimize the experimental parameters: it includes the condition $\beta_{min} \geq 0$ (indicated by manufacturer). The ranges of the suggested A_T values (°C) for different combinations of $\langle\beta\rangle$ (°C min^{-1}) and P (s) are reported in Table 7. Here $\beta_{max,max}$ is the maximum allowed value of β_{max} given by Eq. (5). The minimum heating rate under these conditions will be $\beta_{max,max} - \Delta\beta_{max}$. When the minimum A_T value is selected ($A_{T,min}$), the corresponding minimum and maximum heating rates are respectively zero and 2 $\langle\beta\rangle$.

Check of the criteria for the selection of modulation parameters

A meaningful check is possible only for P=40 s and P=80 s when the number of data points is sufficiently high and representative.

P=40 s

Two of the measurements have A_T values that are 1/18 (A_T=0.030; $\langle\beta\rangle$=5) or 1/11 (A_T=0.030; $\langle\beta\rangle$=3) of the minimum suggested value. The corresponding K_{cp} values are appreciably different from the others (Table 1). Two measurements have A_T values that are 2.6 times greater (A_T=3.00; $\langle\beta\rangle$=3 and A_T=3.00; $\langle\beta\rangle$=5) than the maximum suggested ones. The corresponding K_{cp} values are strongly anomalous (Table 1). If the measurements with A_T values out of suggested range are disregarded, mean K_{cp} values with much lower standard deviations (up to five times) are obtained.

Table 7 Suggested ranges of A_T values and corresponding heating rates as a function of (<β>) and P

P	⟨β⟩	$A_{T,max}$	$A_{T,min}$	$\beta_{max,max}$	$\Delta\beta_{max}$
20	1	0.281	0.053	6.30	10.61
20	2		0.106	7.30	
20	3		0.159	8.30	
20	4		0.212	9.30	
20	5		0.265	10.30	
30	1	0.633	0.081	8.96	15.91
30	2		0.159	9.96	
30	3		0.239	10.96	
30	4		0.318	11.96	
30	5		0.398	12.96	
40	1	1.126	0.106	11.61	21.22
40	2		0.212	12.61	
40	3		0.318	13.61	
40	4		0.424	14.61	
40	5		0.530	15.61	
50	1	1.759	0.133	14.26	26.53
50	2		0.265	15.26	
50	3		0.398	16.26	
50	4		0.531	17.26	
50	5		0.663	18.26	
60	1	2.533	0.159	16.91	31.83
60	2		0.318	17.91	
60	3		0.477	18.91	
60	4		0.637	19.91	
60	5		0.796	20.91	
70	1	3.448	0.186	19.57	37.14
70	2		0.371	20.57	
70	3		0.557	21.57	
70	4		0.743	22.57	
70	5		0.928	23.57	

Table 7 Continued

P	$\langle\beta\rangle$	$A_{T,max}$	$A_{T,min}$	$\beta_{max,max}$	$\Delta\beta_{max}$
80	1	4.503	0.212	22.22	42.44
80	2		0.424	23.22	
80	3		0.637	24.22	
80	4		0.849	25.22	
80	5		1.061	26.22	
90	1	5.699	0.239	24.87	47.75
90	2		0.477	25.87	
90	3		0.716	26.87	
90	4		0.955	27.87	
90	5		1.194	28.87	
100	1	7.036	0.265	27.52	53.05
100	2		0.530	28.52	
100	3		0.796	29.52	
100	4		1.061	30.52	
100	5		1.326	31.52	

P=80 s

Three measurements have A_T values (A_T=0.159, 0.186, 0.030) lower than the suggested minimum value. However, in two of them the selected A_T is near the suggested minimum ($A_{T,min}$=0.212). It seems that in these cases the K_{cp} values are not appreciably affected. In the third measurement, the selected A_T=0.030 is 1/21 of the minimum suggested value. In this case, K_{cp} is appreciably different (Table 1).

To complete the check, a new series of measurements was performed on the same sapphire sample. The pertinent data are reported in Table 8. First we note that, particularly for high P values and at the lower T, $A_{T,exp}$ values are appreciably lower than the selected ones (A_T). However, due to the excellent correlation between A_φ and A_β, this does not have a great effect on K_{cp}. Note however that the differences between average K_{cp} values of Table 8 and the corresponding of Table 1 are one order of magnitude larger than the typical standard errors (Table 5). We believe that, between the two sets of measurements the working conditions of the apparatus have changed. Work is in progress to identify the reason of the change.

An important point is that, for all P values, the difference between the selected and experimental values of A_T are higher when $A_T<A_{T,min}$ and lower when $A_{T,min}\leq A_T\leq A_{T,max}$. Furthermore, for $A_T<A_{T,min}$ and $A_{T,min}\leq A_T\leq A_{T,max}$, the differences between the expected and the experimental A_T values increase with increasing P. This confirms that, when P increases, it is more and more difficult for the apparatus to follow the selected modulation conditions.

Table 8 Check of the criteria for parameters selection

P/ s	$\langle\beta\rangle$*	$A_{T,min}$/ °C	A_T/ °C	T=166.85°C				T=196.85°C			
				$A_{T,exp}$/°C	$(A_T-A_{T,exp}/A_T)100$	$K_{cp,Am}$	$K_{cp,\Delta}$	$A_{T,exp}$/°C	$(A_T-A_{T,exp}/A_T)100$	$K_{cp,Am}$	$K_{cp,\Delta}$
30	2	0.159	0.080	0.07850	1.87	1.802	1.727	0.07883	1.46	1.778	1.704
30	2	0.159	0.080	0.07883	1.46	1.788	1.730	0.07883	1.46	1.765	1.694
30	2	0.159	0.080	0.07883	1.46	1.774	1.680	0.07933	0.84	1.765	1.665
30	1	0.080	0.080	0.07986	0.17	1.772	1.703	0.07950	0.62	1.760	1.654
30	2	0.159	0.557	0.5520	0.90	1.785	1.697	0.5555	0.27	1.776	1.693
40	2	0.212	0.106	0.1018	3.96	1.499	1.463	0.1050	0.94	1.503	1.457
40	2	0.212	0.106	0.1015	4.24	1.504	1.472	0.1050	0.94	1.500	1.471
40	2	0.212	0.743	0.7288	1.91	1.501	1.462	0.7402	0.38	1.498	1.460
60	2	0.318	0.159	0.1350	15.09	1.280	1.288	0.1565	1.57	1.288	1.276
60	2	0.318	1.114	1.068	4.13	1.287	1.273	1.103	0.99	1.290	1.275
70	2	0.371	0.186	0.1524	18.06	1.251	1.237	0.1827	1.77	1.244	1.239
70	2	0.371	1.300	1.256	3.38	1.241	1.229	1.286	1.08	1.245	1.233
90	2	0.477	0.239	0.1717	28.16	1.198	1.186	0.2340	2.09	1.193	1.193
90	2	0.477	1.671	1.554	7.00	1.192	1.182	1.647	1.59	1.195	1.187
90	2	0.477	0.239	0.1800	24.69	1.203	1.207	0.2352	1.44	1.207	1.202
100	2	0.531	0.265	0.2039	23.06	1.180	1.168	0.2600	1.89	1.180	1.190
100	2	0.531	0.265	0.1697	35.96	1.186	1.188	0.2568	3.09	1.182	1.185
100	2	0.531	1.857	1.660	10.61	1.176	1.169	1.827	1.61	1.180	1.175
100	2	0.531	1.857	1.688	9.10	1.190	1.178	1.826	1.67	1.193	1.186

* in °C min^{-1}

Concluding remarks

It has been shown that the influence of the experimental parameters $\langle\beta\rangle$ and A_T on K_{cp} is quite small. With P=40 s, $\langle\beta\rangle$ was changed of 1 order of magnitude while A_T was changed of 2 orders of magnitude: the standard deviations of the K_{cp} values were around 2% of the mean values. Also for P=80 s $\langle\beta\rangle$ and A_T were changed in a wide range and the standard deviations of the K_{cp} were below 2% of the mean values.

The relationship $\Delta\varphi$–$\Delta\beta$ was carefully checked in different experimental conditions and it was found that very accurate calibration constants may be obtained only if the modulation period is maintained constant.

The agreement between nominal and observed parameters is sometimes unsatisfactory. This may be related with a selection of experimental parameters, and a criterion for a correct selection is proposed. However, even if the system does not comply with the programmed modulation, errors in the determination of the calibration constant tend to cancel out at least to a large extent.

It is somewhat disturbing to speak in terms of a calibration constant (K_{cp}) which has a substantial dependence from (at least) one of the experimental parameters (P). In our opinion the true parameter affecting K_{cp} is not P but the phase lag between the β and φ waves which is proportional to P in case of a constant delay and it is influenced also by the algorithm controlling the heating power. Work is in progress to thoroughly analyze the relationship between period and phase lag.

Legend

Symbol	Unit	Meaning
c_p^*	J K^{-1}	heat capacity
A_T	K	temperature amplitude
P	s	modulation period
c_p	J K^{-1} g^{-1}	specific heat
K_{cp}	dimensionless	heat capacity cal. constant
A_φ	W	amplitude of modulated heat flow
A_β	K s^{-1}	amplitude of modulated heating rate
β_{max}	K s^{-1}	maximum heating rate within a period
β_{min}	K s^{-1}	minimum heating rate within a period
φ_{max}	W	maximum heat flow rate within a period
φ_{min}	W	minimum heat flow rate within a period
$\langle\beta\rangle$	K s^{-1}	underlying heating rate
$\beta_{max,max}$	K s^{-1}	maximum value of β_{max} allowed by Eq. (5)
$K_{cp,Am}$	dimensionless	heat capacity cal. constant calculated according to Eq. (2)
$K_{cp,\Delta}$	dimensionless	heat capacity cal. constant calculated according to Eq. (4)

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