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ON THE QUANTITATIVE RELIABILITY OF HEAT FLUX DSC

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In an attempt to explain how the calibration factor of a heat flux DSC cell depends both on the standard utilized and on the experimental variables, a study has been undertaken of the entire DSC trace.

This report deals with the second half of the peak and shows that, other experimental conditons being fixed, the peak area increases with increasing heating rate.

This accounts for the observed decrease in the calibration factors with increasing heating rate.

In previous work concerning the calibration of a heat flux DSC cell [1], it was shown that, contrary to what is usually believed, the calibration factor depends on the standard utilized as well as on the experimental variables (e.g. heating rate).

To understand both the reasons for and the modes of such a relationship, a study has been undertaken of the entire DSC trace. The first results of this study, concerning the baseline and the first part of the peak (as far as the peak maximum), have already been published [2].

The second part of the study is now reported, dealing with the second half of the peak. It will be shown that, other experimental conditions being fixed, the area of the second half of the peak increases with increasing heating rate, leading to lower calibration constant values. An explanation of why different calibration factors can be obtained with different standards will be given in a later paper [3], in which a relationship will be proposed for the dependence of the measured signal on the physico-chemical properties of the sample.

It was shown in [2] that, at the beginning of a DSC run, a temperature difference arises between the sample and reference holders as a consequence of the differences in the thermal capacities of the sample and reference systems. During sample melting, this temperature difference increases with a rate of change depending both on the experimental variables and on the instrumental constants ([2], Eg. 19).

When sample melting is over, the following relationship must be fulfilled (see [2] for symbols and definitions);

$$(\mathrm{d}Q/\mathrm{d}t)_{\mathrm{SaF}} = C_{\mathrm{PS1}} \frac{\mathrm{d}T_{\mathrm{SaF}}}{\mathrm{d}t} = \frac{T_{\mathrm{ShaF}} - T_{\mathrm{SaF}}}{R_3 + R_4} \tag{1}$$

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where:

$(\mathrm{d}Q/\mathrm{d}t)\mathrm{SaF}$ = heat flux on the sample system when melting is over (i.e. during the return of the peak to the baseline);

C_{PSl} = heat capacity of the sample system when all the sample is melted;

T_{SaF} and T_{ShaF} = sample system and sample holder temperatures during the return of the peak to the baseline.

It was shown in [2] that the differential heat flux on the sample holder is determined by the temperature difference between the reference and sample holders. As the same temperature difference produces the same differential heat flux, the heat fluxes on sample and reference holders can be related in the same way, no matter whether the temperature difference is increasing (first half of the peak) or decreasing (second half of the peak).

Then, taking into account Eqs 6, 11 and 12 in [2], we can write:

$$(\mathrm{d}Q/\mathrm{d}t)_{\mathrm{SaF}}\cdot\frac{C_{\mathrm{PSh}}+C_{\mathrm{PS}}}{C_{\mathrm{PS}}}=\beta\,(C_{\mathrm{PR}}+C_{\mathrm{PRh}})-\frac{T_{\mathrm{RhaF}}-T_{\mathrm{ShaF}}}{R_2}+ \\ +\beta\,(C_{\mathrm{PS}}-C_{\mathrm{PR}})+\frac{T_{\mathrm{RhaF}}-T_{\mathrm{ShaF}}}{R} \qquad (2)$$

From Eqs (1) and (2), and taking into account that [2] $1/R=1/R_1+1/R_2$ and that $C_{\mathrm{PSh}}=C_{\mathrm{PRh}}$ (the cell is symmetrical), we get:

$$\mathrm{d}T_{\mathrm{SaF}}/\mathrm{d}t=C_{\mathrm{PS}}/C_{\mathrm{PSl}}\cdot[\beta+(T_{\mathrm{RhaF}}-T_{\mathrm{ShaF}})/R_1(C_{\mathrm{PS}}+C_{\mathrm{PSh}})] \qquad (3)$$

From Eqs (1) and (3):

$$T_{\mathrm{SaF}}=T_{\mathrm{ShaF}}\cdot\frac{R_1\,(C_{\mathrm{PS}}+C_{\mathrm{PSh}})+(R_3+R_4)\,C_{\mathrm{PS}}}{R_1\,(C_{\mathrm{PS}}+C_{\mathrm{PSh}})}-T_{\mathrm{RhaF}}\cdot \\ \cdot\frac{C_{\mathrm{PS}}\,(R_3+R_4)}{R_1\,(C_{\mathrm{PS}}+C_{\mathrm{PSh}})}-\beta\,C_{\mathrm{PS}}\,(R_3+R_4) \qquad (4)$$

Differentiating Eq. (4) with respect to time and solving for $\mathrm{d}(T_{\mathrm{ShaF}}-T_{\mathrm{SaF}})/\mathrm{d}t$, we obtain:

$$\mathrm{d}(T_{\mathrm{ShaF}}-T_{\mathrm{SaF}})/\mathrm{d}t=\frac{(R_3+R_4)\,C_{\mathrm{PS}}}{R_1\,(C_{\mathrm{PS}}+C_{\mathrm{PSh}})}[\mathrm{d}(T_{\mathrm{RhaF}}-T_{\mathrm{ShaF}})/\mathrm{d}t] \qquad (5)$$

Putting $(T_{\mathrm{RhaF}}-T_{\mathrm{ShaF}})=\Delta T$, from Eqs (5) and (3):

$$\mathrm{d}T_{\mathrm{ShaF}}/\mathrm{d}t=\beta(C_{\mathrm{PS}}/C_{\mathrm{PS1}})+\Delta T\frac{C_{\mathrm{PS}}}{R_1\,C_{\mathrm{PS1}}(C_{\mathrm{PS}}+C_{\mathrm{PSh}})}+\frac{C_{\mathrm{PS}}(R_3+R_4)}{R_1(C_{\mathrm{PS}}+C_{\mathrm{PSh}})}\cdot \mathrm{d}\Delta T/\mathrm{d}t \tag{6}$$

The dependence of the reference holder temperature on time can be obtained from Eq. 15 in [2] as:

$$\mathrm{d}T_{\mathrm{RhaF}}/\mathrm{d}t=\beta-\frac{T_{\mathrm{RhaF}}-T_{\mathrm{ShaF}}}{R_2\,(C_{\mathrm{PR}}+C_{\mathrm{PRh}})} \tag{7}$$

By subtracting (6) from (7):

$$\mathrm{d}\Delta T/\mathrm{d}T=\beta-\frac{\Delta T}{R_2(C_{\mathrm{PR}}+C_{\mathrm{PRh}})}-\beta\,(C_{\mathrm{PS}}/C_{\mathrm{PS1}})-\frac{\Delta T\,C_{\mathrm{PS}}}{R_1C_{\mathrm{PS1}}(C_{\mathrm{PS}}+C_{\mathrm{PSh}})}-\frac{C_{\mathrm{PS}}(R_3+R_4)}{R_1(C_{\mathrm{PS}}+C_{\mathrm{PSh}})}(\mathrm{d}\Delta T/\mathrm{d}t) \tag{8}$$

and if $C_{\mathrm{PS}}\cong C_{\mathrm{PS1}}$:

$$(\mathrm{d}\Delta T/\Delta T)=-\frac{R_1C_{\mathrm{PS1}}\,(C_{\mathrm{PS}}+C_{\mathrm{PSh}})+R_2C_{\mathrm{PS}}(C_{\mathrm{PR}}+C_{\mathrm{PRh}})}{R_2\,(C_{\mathrm{PR}}+C_{\mathrm{PRh}})C_{\mathrm{PS1}}\,[R_1\,(C_{\mathrm{PS}}+C_{\mathrm{PSh}})+C_{\mathrm{PS}}\,(R_3+R_4)]}\cdot\mathrm{d}t \tag{9}$$

By integrating Eq. (9) between the limits $\Delta T_{\max}$, ΔT and $t_{\max}$, t:

$$\Delta T(t)=\Delta T_{\max}\exp\left\{-\frac{R_1C_{\mathrm{PS1}}(C_{\mathrm{PS}}+C_{\mathrm{PSh}})+R_2C_{\mathrm{PS}}(C_{\mathrm{PR}}+C_{\mathrm{PRh}})}{R_2(C_{\mathrm{PR}}+C_{\mathrm{PRh}})C_{\mathrm{PS1}}[R_1(C_{\mathrm{PS}}+C_{\mathrm{PSh}})+C_{\mathrm{PS}}(R_3+R_4)]}\cdot(t-t_{\max})\right\} \tag{10}$$

Equation (10) holds only for $t\geqslant t_{\max}$ and shows the law that governs the return of the peak to the baseline. Here ΔT is measured on a relative scale and a $\Delta T(t)=0$ means that the baseline after the peak is at the same level as it was before the peak. This can be seen with the aid of Eq. (8). When in fact the peak is over, $\mathrm{d}\Delta T/\mathrm{d}T=0$ and from Eq. (8) one obtains:

$$0=\beta-\frac{\Delta T}{R_2(C_{\mathrm{PR}}+C_{\mathrm{PRh}})}-\beta\,(C_{\mathrm{PS}}/C_{\mathrm{PS1}})-\frac{\Delta T\,C_{\mathrm{PS}}}{R_1C_{\mathrm{PS1}}(C_{\mathrm{PS}}+C_{\mathrm{PSh}})} \tag{8'}$$

If $C_{PS} = C_{PS1}$ it follows from Eq. (8') that $\Delta T = 0$, i.e. the baseline after the peak is at the same level as it was before the peak. In this case, $\Delta T_{fin} = \Delta T_{in}$ and, as shown in Eq. 9 [2]:

$$\Delta T_{fin} = \Delta T_{in} = \beta (C_{PS} - C_{PR}) R$$

Substituting this ΔT value into Eq. (10) and solving for $(t_{fin} - t_{max})$, we obtain:

$$(t_{fin} - t_{max}) = \frac{R_2(C_{PR} + C_{PRh})C_{PS1}[R_1(C_{PS} + C_{PSh}) + C_{PS}(R_3+R_4)]}{R_1 C_{PS1}(C_{PS} + C_{PSh}) + R_2 C_{PS}(C_{PR} + C_{PRh})} \cdot \ln \frac{\Delta T_{max}}{\beta(C_{PS} - C_{PR})R} \tag{11}$$

Equation (11) gives the time necessary for the measured signal to return to the baseline in the case $C_{PS} = C_{PS1}$. The time necessary for the peak to return when $C_{PS} \neq C_{PS}$ can be calculated by adding the initial ΔT value (see Eq. 9 in [2]) to the ΔT value calculated from Eq. (8').

Although the equation obtained in this case is slightly different from Eq. (11), it is important to note that it shows the same type of dependence of $(t_{fin} - t_{max})$ on β.

Some comments are now necessary on Eqs (3), (6) and (11). While Eq. (3) gives the rate of change of the sample temperature during the peak return, Eq. (6) gives the rate of change of the sample holder temperature. As ΔT diminishes during the peak return, it has a negative derivative with respect to time. It then follows that the rate of change of the sample holder temperature (Eq. (6)) is less than the rate of change of the sample temperature (Eq. (3)), and that the two rates will be equal when $\mathrm{d}T/\mathrm{d}t = 0$, that is when the peak is over and the baseline has again been reached. This is just that would be expected if it is taken into account that, differently from the sample holder temperature, the sample temperature remains constant during melting [2].

As concerns Eq. (11), our interest is to see how β affects $(t_{fin} - t_{max})$. To do this, a knowledge of the dependence of ΔT_{max} on β is in turn necessary. It will be shown later [3] that ΔT_{max} varies as $\beta^{1/2}$ With this information, it can be seen from Eq. (11) that $(t_{fin} - t_{max})$ varies as $\ln(\text{constant}/\beta^{1/2})$. Thus, the product ΔT_{max} $(t_{fin} - t_{max})$, which is proportional to the area of the second half of the peak, varies as $\beta^{1/2} \ln(\text{contant}/\beta^{1/2})$; this means that the area of the second half of the peak increases with increasing β.

On the other hand, it can be seen from Eqs 19 and 20 in [2] that the more the experimental signal value approaches the limiting signal value, the less the peak slope becomes, as does the area of the first half of the peak. Now, as ΔT_{lim} increases with β more rapidly than ΔT_{max}, it may be concluded that the area of the first half of the peak too increases with increasing heating rate.

Thus, with increasing heating rate, lower calibration factors are obtained, owing to the fact that, other conditions being constant, the peak areas are greater than those obtained at lower heating rates. Table 1 reports the calibration factors obtained for In, Sn, Pb and Zn at heating rates of 100, 10 and 1 deg min^{-1}.

Table 1 – Calibration factors obtained with different standards

Heating rate, deg/min	In	Sn	Pb	Zn
1.0	1.244	1.217	1.336	1.334
10.0	1.201	1.208	1.315	1.330
100.0	1.186	1.184	1.235	1.249

The calibration factors are dimensionless.

The decrease in the calibration factors at the higher heating rates is evident and agrees with our predictions.

One more thing should be noted in Table 1: the differences between the calibration factors obtained with different standards depend on the heating rate. To explain this interesting behaviour, the role that the physico-chemical properties of the sample in heat flux differential scanning calorimetry must be discussed, which will be done in the following paper [3].

References

1 A. Marini, V. Berbenni, V. Massarotti, G. Flor and G. Campari-Viganò, Thermochim. Acta, 85 (1985) 279.

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Zusammenfassung – Die gesamte DSC-Kurve wurde untersucht, um zu klären, wie der Eichfaktor einer Wärmefluss-DSC vom verwendeten Eichstandard und von den Versuchsbedingungen abhängt. Der vorliegende Teil behandelt den zweiten Abschnitt eines DSC-peaks (vom Maximum an). Es wird gezeigt, dass bei Konstanthalten aller anderen Versuchsbedingungen die peak-Flächen mit steigender Aufheizgeschwindigkeit zunehmen. Das wird als Ursache für die beobachtete Verringerung des Eichfaktors mit steigender Aufheizgeschwindigkeit angesehen.

РЕЗЮМЕ — Для установления зависимости калибровочного коэффициента теплового потока в ячейке ДСК от стандартных и экспериментальных переменных параметров, изучена полная запись ДСК измерений. Первая часть проведенного исследования уже была опубликована. Настоящее сообщение касается второй половины пика и показано, что при каком-либо фиксированном экспериментальном условии, площадь пика увеличивается с увеличением скорости нагревания. Этим объясняется наблюдаемое уменьшение калибровочного коэффициента с увеличением скорости нагрева.