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CALIBRATION COEFFICIENT OF A HEAT-FLOW DSC
Part II. Optimal calibration procedure

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One-point (Mettler) and many-point (Netzsch) heat flow calibration of a DSC is discussed. It is shown that the two types of calibration are the alternative extremes between quick but rough procedure and time-consuming but accurate one. One-point calibration compares a 'typical' function $k(T)$ at the melting point of indium with the measured value for particular DSC and multiplies $k(T)$ by a scaling factor. Many-point calibration is based on general mathematical procedure, namely fitting a set of experimental values of sensitivity to a polynomial. The polynomial coefficients are evaluated by the method of least squares.

Based on the relationship between the sensitivity of a thermocouple and calibration coefficient of a DSC sensor made from it, two-point heat flow calibration is suggested. This is an optimal calibration procedure, for the relationship contains only two unknown coefficients. An example of how to perform the two-point calibration with Netzsch-Proteus Software is described in the Appendix.

Keywords: *DSC sensor, heat-flow calibration, Mettler–Toledo, Netzsch, thermocouple*

Introduction

In the previous paper it was shown that the calibration coefficient of a heat-flow DSC, $k(T)$, is a function of temperature that differs from the sensitivity of a thermocouple, $\varepsilon(T)$, which the sensor is made from, by the factor depending on heat transfer by heat conductivity and radiation [1]:

$$k(T) = \varepsilon(T)\frac{1}{A + BT^3} \tag{1}$$

Here, A and B are the coefficients depending on heat conductivity and radiation, respectively. These cannot be derived exactly from a design of the calorimeter and usually are evaluated after a calibration.

Calibration is compulsory for all heat flux DSCs. It consists of two parts, experimental and mathematical. First, the sensitivity is measured at several points (temperatures, T_i) yielding experimental values K_i. Then, the values K_i are fitted to the hypothetical 'true' function $k(T_\mathrm{i})$ as correct as possible.

The experimental part of a sensitivity calibration is a routine procedure. Every company that manufactures a DSC provides it with an operational instruction describing of how to proceed the calibration experiments. In essence, all the instructions contain the same recommendations. Regarding the mathematical treating of the experimental results, there is no conventional way to derive the fitting function $k(T)$. In the recommendation of the GEFTA working group 'Calibration of Scanning Calorimeters' this is not discussed, but in the 'Example of caloric calibrations' the authors used a square function, the fitting parabola [2]. Each company-manufacturer uses its own function. For example, the calibration of a Mettler DSC is proceeded after a measurement of a single substance melting, namely indium. On the contrary, the calibration function for a Netzsch DSC can be evaluated only after the measurements of at least five various substances, not specified. It is not evident for a user of a DSC which calibration procedure, one-point or many-point, is better for his particular purpose and why these procedures differ so drastically.

The objectives of this work were to analyze the advantages and disadvantages of existing calibration procedures and to develop the optimum scheme of the sensitivity calibration.

Mathematical background

A smooth function without discontinuity and singularity can be expanded to a series near point x_0

$$f(x) = f(x_0) + \sum \frac{f^{\mathrm{n}}(x - x_0)}{n!}(x - x_0)^{\mathrm{n}} \tag{2}$$

where $f^n(x–x_0)$ is the n-th derivative. If the functional relation is not known exactly, one can use a polynomial of x with unknown coefficients a_i instead

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$$p(x)=a_0+a_1x+a_2x^2+a_3x^3+... \qquad (3)$$

The polynomial fits function $f(x)$ if its coefficients are evaluated by solving the set of linear equations

$$\begin{aligned} a_0 + a_1x_1 + a_2x_1^2 + a_3x_1^3 + ... + a_kx_1^k &= F_1 \\ a_0 + a_1x_2 + a_2x_2^2 + a_3x_2^3 + ... + a_kx_2^k &= F_2 \\ a_0 + a_1x_m + a_2x_m^2 + a_3x_m^3 + ... + a_kx_m^k &= F_m \end{aligned} \qquad (4)$$

where F_i are the values of the function $f(x)$ at points x_i: $f(x_1) = F_1$, $f(x_2)=F_2$, …, $f(x_m)=F_m$, etc. The equations are linear because they can be rewrite in the evident linear form

$$\begin{aligned} & a_0 + a_1x + a_2x^2 + a_3x^3 + ... + a_kx^k \\ & = a_0 + a_1y_1 + a_2y_2 + a_3y_3 + ... + a_ky_k \end{aligned} \quad . \qquad (5)$$

On the right-hand side, there is the linear equation with $k+1$ coefficients and k variables. All the variables are different. They relate with one another by the ratio $y_{k+1}/y_k=x$, but this is a particular case.

The equation set (4) has an indefinite number of solutions if $m<k+1$ and has a unique solution if $m=k+1$ with polynomial $p(x)$ passing exactly through the points F_i. If the values F_i were measured in an experiment, these contain an experimental error. Fitted exactly to the experimental points, the polynomial will be twisting and not quite close to the true function $f(x)$ between the points x_i. An example of such a curve is shown in Fig. 1 where the 4th-order polynomial is fitted to five experimental points. This makes evident that the unique solution is not a good solution to the problem of fitting unknown function with a polynomial.

In treating experimental results, another case is considered more suitable when the number of the values F_i is greater than the number of coefficients a_i ($m>k+1$). The equation set (4) is overdeterminated and single exact solution does not exist. Approximate result (unique again) of such a set can be received as an analytical solution. The coefficients a_0, a_1, ..., etc., are expressed in terms of sums $\sum_i x_i^j$ and $\sum_i x_i^j F_i$. An example of such a solution is also shown in Fig. 1: a quadratic polynomial with three coefficients was evaluated after the same five points. The curve passes by the experimental points but fits the true function better than the polynomial with five coefficients.

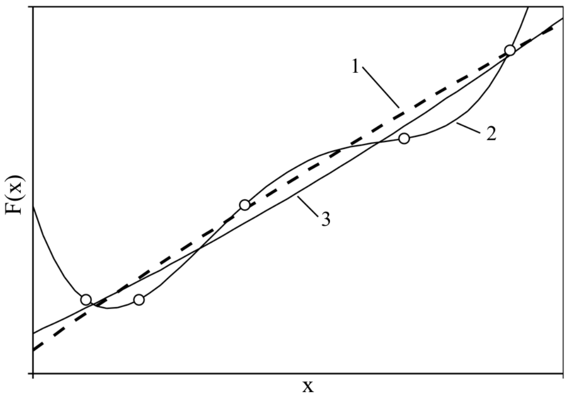

Fig. 1 Fitting experimental points to a polynomial: 1 – dashed line is a ‘true’ function; 2 – the polynomial with five coefficients, the exact solution; 3 – the polynomial with three coefficients, the method of least squares. Open circles are the points measured with an experimental error

The mathematics of fitting is described in detail in [3] (for students) and [4] (for scientists).

Many-point calibration (by Netzsch)

In the Netzsch–Proteus Software, an experimental value of the calibration coefficient $k^*(T)$ at the particular temperature (T_m, melting point) is defined as a ratio of the experimental peak area to the enthalpy of melting (Appendix). After the measurements of several reference materials with different melting points we receive a set of values $k^*(T_i)$. The fitting formula in the Netzsch–Proteus Software contains six coefficients a_i:

$$k^*(T) = (a_2 + a_3z + a_4z^2 + a_5z^3)\ \exp\,(-z^2) \qquad (6)$$

where

$$z = \frac{T - a_0}{a_1} \qquad (7)$$

All the six coefficients are evaluated only if the number of experimental values $K_i=k^*(T_i)$ is greater than seven. If the number of experimental values is six, the number of the coefficients is five. For five experimental values, the number of the coefficients evaluated is four. If the number of experimental values is four or less, the program fails to evaluate the calibration polynomial. At a glance, the many-point calibration procedure in the Netzsch–Proteus Software agrees with case $m>k+1$ described in the previous paragraph. But this is not quite right. If formulae (6) and (7) are combined in a single expression, the resulting equation is not linear. Each coefficient a_2 to a_5 in the sum (6) is multiplied by the exponent containing, in turn, coefficients a_0 and a_1. Moreover, the power of the exponent contains the ratio of coefficients a_0 and a_1. The set of such an equation cannot be solved by the least squares procedure. No analytical solution to the set exists as well. Usually, a numerical solution is received after iteration procedure [4]. But the iteration technique needs the number of experimental points (m) to exceed the number of the coefficients ($k+1$) significantly (several times). If not, the solution converges slowly and the function calculated 'twists' around the experimental points like the polynomial with $m=k+1$ in Fig. 1.

Fortunately, this is not the case in the Netzsch–Proteus Software. The coefficients in Eqs (6) and (7) are defined separately. First, the values of a_0 and a_1 in (7) are calculated. These are used for the scaling of temperature in (6): a_0 is the temperature of the experimental point with the greatest value of K_i. The value of a_1 depends on the greatest difference between the temperature of the maximum value of K_i and the temperature of the rest experimental points. The exact equation for the calculation of a_1 is not known to us but this is chosen in such a way that variable z in formula (6) ranges within the limits about –0.5 to 0.5. Then the coefficients are calculated after conventional method of least squares: four coefficients a_2–a_5 for seven or greater experimental points, three coefficients for six points, and two coefficients for five points.

The advantage of such a calibration is a high accuracy attainable over the temperature range at will. The greater is the number of experimental values of the calibration coefficient in a temperature range of interest, the greater is the number of coefficients in the fitting polynomial, and the better is the fitting of unknown 'true' calibration function $k^*(T)$.

The disadvantage is the labor-consuming schedule. We have to measure at least five different reference substances even if we plan to measure heat effects in a short temperature range. The manufacturer himself does not complete the calibration schedule when provides a new equipment with a calibration file evaluated after six experimental points from melting point of mercury (–38.8°C) to the phase transition in CsCl (476°C) with five coefficients a_0–a_4. And what is more, the manufacturer recommends to repeat the calibration at least every 2 months.

One-point calibration (by Mettler)

The calibration program of DSC-30 (Mettler) needs a single value 'E' calculated automatically after the measurement of indium melting. The value must be inserted into the file of DSC configuration. To improve the 'calibration coefficient', one should use an average value after several runs.

The manufacturer does not provide a user with the information about mathematical operations in the calibration program. One can suppose that a 'typical' calibration function is stored in a memory of the computer processing experimental data. The following analysis of the program operation will be based on the analytical function (1) derived from the general design of a DSC.

There are three factors in the function $k(T)$: thermocouple (ε), heat conductivity (A), and radiation (B). They can be combined into two coefficients:

$$k(T)=\frac{\varepsilon(T)}{A}\frac{1}{1+(B/A)T^3}=\varepsilon^*(T)\frac{1}{1+DT^3} \qquad (8)$$

where $\varepsilon*(T)$ depends on the relationship between the sensitivity of a thermocouple and heat conductivity, and D depends on the relationship between heat conductivity and radiation.

Technical (thermophysical) parameters of stock-produced calorimeters are similar but not identical. Calibration functions of individual calorimeters differ from one another and from the 'typical' function $k(T)$. Several examples of the function are shown in Fig. 2a. The variants differ from one another by 10% in $\varepsilon^*(T)$ and D values. The first step of the one-point calibration by Mettler, namely the measurement of indium melting, yields a value of the calibration coefficient at 156.6°C which has to be compared with that of 'typical' calibration function. Then the calibration program calculates a factor to multiply the whole calibration curve of the particular calorimeter to fit it to the 'typical' calibration function. Such a correction decreases the difference between the calibration functions of dif-

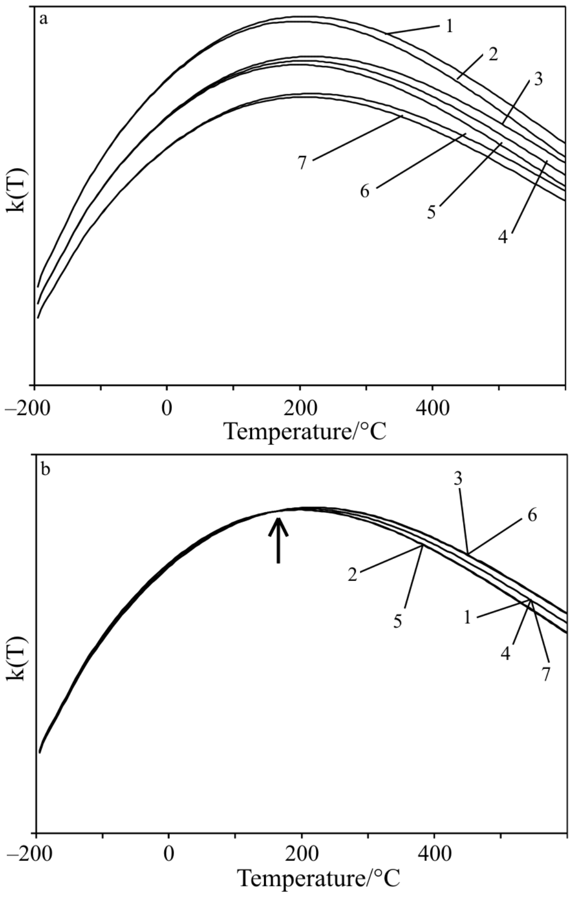

Fig. 2 Calibration functions a – before and – b after one-point calibration. Seven lines represent the variants of the function for particular DSC with varying thermophysical parameters, $\varepsilon^*(T)$ and D. The variants are listed in Table 1

Table 1 Changes in calibration function caused by the changes in factors $\varepsilon^*(T)$ and D of formula (8) before and after one-point calibration by Mettler. Variant 4 is the 'typical' calibration function

No.	Factors		Before calibration			After calibration	
	$\times\varepsilon^*(T)$	$\times D$	–100°C	156.6°C	600°C	–100°C	600°C
1	1.1	1.0	+11.1	+11.1	+11.1	0.0	0.0
2	1.1	1.1	+11.0	+10.2	+6.2	+0.8	–3.7
3	1.0	0.9	0.1	0.8	4.3	–0.7	+3.4
4	1.0	1.0	0.0	0.0	0.0	0.0	0.0
5	1.0	1.1	–0.1	–0.8	–4.0	+0.7	–3.3
6	0.9	1.1	–9.0	–8.5	–5.6	–0.6	+3.1
7	0.9	1.0	–9.1	–9.1	–9.1	0.0	0.0

ferent calorimeters (Fig. 2b). The variations in $\varepsilon^*(T)$ and D values affecting the difference in $k(T)$ values are listed in Table 1. The discrepancy between corrected and 'typical' functions $k(T)$ remains significant even after the calibration by Mettler: up to 0.8% at –100°C and 3.7% at +600°C.

Equation (8) allows us to recognize the reason of the rest discrepancy and explain why it is asymmetric with respect to temperature. At low temperatures ($1 << DT^3$) all the discrepancies in the calibration functions are caused by the variation in $\varepsilon^*(T)$, i.e., sensitivity of a thermocouple and heat conductivity. These factors can be corrected after the multiplication of the whole function $k(T)$ by a constant. At high temperatures the term DT^3 becomes greater and affects the calibration coefficient. If the D value differs from that in 'typical' $k(T)$ function, the discrepancy cannot be corrected by multiplying a constant. This is the reason why the corrected curves differ from one another at temperatures above 200°C in Fig. 2b.

The problem was discussed by Schubnell, a specialist of Mettler–Toledo [5]. He showed that an error in the enthalpy of melting of several substances can be as high as ±3% in a temperature range between –100 and +160°C. Schubnell supposed that the reason of the errors is the difference in heat transfer conditions within the samples. But this is not quite right because there is the trend in the errors: the far is the temperature from 156.6°C, the greater is the discrepancy. A peculiarity in the heat transfer conditions of a particular substance produces an error only in the enthalpy of that substance. But the trend derived from the measurements of several substances is evidently caused by an inherent imperfection of the calibration procedure, not by a peculiarity of a particular substance. Probably, the DSC model he used has the calibration function differing significantly from the 'typical' $k(T)$ function, namely in the conditions of the heat transfer by radiation. In our calculations (Table 1) 10% difference in the D value produces 0.8% discrepancy at –100°C. One can assume that the difference in the D value of the Schubnell's DSC was about 40%. One more remark. The difference in the calibration function develops much more at temperatures above 200°C. One can expect that similar experiments with Schubnell's DSC at high temperatures can produce much higher discrepancy, as high as 40% at 600°C.

To solve the problem of the discrepancy in the enthalpies of melting of reference substances measured with a calibrated (!) DSC, Schubnell suggests to change the calibration equation. Instead of $E_{\mathrm{in}}E_{\mathrm{rel}}(T)$, where E_{in} is a constant and $E_{\mathrm{rel}}(T)$ describes the temperature dependence of the caloric sensitivity as defined by the manufacturer, he proposed $E_{\mathrm{in}}[E_{\mathrm{rel}}(T)+\mathrm{d}E(T)]$, where $\mathrm{d}E(T)$ is a second-order polynomial that may be added by the user for calibration purpose. Thus, the improvement in the calibration by Mettler is in the increase of the number of coefficients in a fitting polynomial like the many-point calibration by Netzsch. It means that the user has to measure several (at least three or four) substances in addition to indium.

The advantage of the one-point calibration by Mettler is the rapid operation. After only one measurement of indium melting we have the calibration function for the whole temperature range where DSC operates.

The disadvantage is the incorrectness in the calibration function that cannot be corrected within the bounds of the one-point procedure.

Optimal calibration procedure

Having the analytical Eq. (1) for the calibration coefficient of a DSC, we can develop optimal procedure for the sensitivity calibration. There are one function, $\varepsilon(T)$, and two constants, A and B, in the equation

$$k(T)=\varepsilon(T)\frac{1}{A+BT^3}$$

Strictly speaking, the problem of fitting $\varepsilon(T)$ is out of the scope of routine DSC calibration. The manufacturers of DSCs chose the material of a thermocouple for the sensor after careful investigations and tests of it. They know function ε(T) in detail and it is reasonable that a user of the DSC will be provided with the whole information on ε(T). For example, in the Netzsch–Proteus Software this problem was solved by excluding the function ε(T) from the equation for the calibration coefficient

$$k^*(T) = \frac{k(T)}{\varepsilon(T)} = \frac{1}{A + BT^3}$$

Two constants in the formula can be derived from the values of $k^*(T)$ at two different temperatures. It is evident for the inverse equation

$$\frac{1}{k^*(T)} = A + BT^3$$

which is identical to the equation of a straight line

$$y=a+bx.$$

The coefficients a and b can be derived from two points, $y_1(x_1)$ and $y_2(x_2)$, that the line passes through. To proceed the calculation, one need to solve a set of two equations with two variables:

$$\begin{cases} a + bx_1 = y_1 \\ a + bx_2 = y_2 \end{cases} \sim \begin{cases} A + BT_1^3 = \dfrac{1}{K_1} \\ A + BT_2^3 = \dfrac{1}{K_2} \end{cases}$$

Exact solution instead of the least squares method can be used for K_i values with experimental errors, for straight line does not deflect from true line like a curve of a high-order polynomial. The calibration is described in detail in the Appendix.

Conclusions

Sensitivity calibration of a DSC by Netzsch differs from that by Mettler in the number of experimental points needed and in accuracy. Sensitivity of a thermocouple ε(T) is excluded from the calibration coefficient in the Netzsch–Proteus Software. Many-point calibration by Netzsch allows a user to fit unknown function $k^*(T)$ to a polynomial of a scaled temperature variable. The polynomial fits the calibration function well but needs much labor to measure at least five experimental points several times. In the calibration by Mettler, the whole calibration function is tabulated and stored inside the computer program as ‘typical’ function. Single measurement of indium melting allows the program to compare the calibration function of a particular DSC with ‘typical’ one at 156.6°C. Multiplying the ‘typical’ function by a constant, the program makes it equal to the experimental one at the point and uses it in the whole temperature range where the DSC operates. Equal at 156.6°C, the calibration functions diverge from one another when moving off that point. The discrepancy can rise as high as tens per cent. To solve the problem, Mettler advises a user to introduce his own additional polynomial into the calibration function. This transforms one-point calibration into many-point one.

Based on the relationship between the calibration coefficient of a DSC and the sensitivity of a thermocouple which the sensor is made from, two-point calibration is developed. This is an optimal procedure, for the measurements of only two reference substances melting at the ends of the temperature range of interest allow one to evaluate the calibration function over the whole temperature range. The procedure was tested for DSC-204 and found to fit heat capacity of corundum better than 1% [1].

Appendix

Most calorimetric experiments in the Research and Educational Center of the Novosibirsk State University are carried out above ambient temperature [6, 7]. DSC results are combined with the low-temperature adiabatic calorimetry [8]. We need the calibration of DSC-204 to be valid at a temperature range of 100–450°C. The calorimeter was checked to obey the relationship

$$\frac{1}{k^*(T)} = A + BT^3$$

with accuracy better than 1% [1].

1. Two points of the calibration are In (T_m=156.6°C, ΔH_m=28.6 J mol^{-1}) and Zn (T_m=419.5°C, ΔH_m=107.5 J mol^{-1}). The measurements of these metals melting yield the enthalpies (ΔH_{exp}) 109.9 and 306.6 μV s mg^{-1}, respectively.
2. The calibration coefficient is the ratio $\Delta H_{exp}/\Delta H_m$: $k^*(T_m)$=3.8427 for In and $k^*(T_m)$=2.8521 for Zn.
3. Melting points of indium and zinc are 429.75 and 692.65 K, respectively.
4. Evaluation of coefficients A and B:

$$B = \frac{\dfrac{1}{k^*(429.75)} - \dfrac{1}{k^*(692.65)}}{429.75^3 - 692.65^3} = \frac{0.26024 - 0.35062}{79368405 - 332308550} = 3.5733 \cdot 10^{-10}$$

$$A = \frac{1}{k^*(429.75)} - 429.75^3 B = 0.26021 - 79368405 \cdot 3.5748 \cdot 10^{-10} = 0.23188$$

5. Choosing 5 additional points of the calibration (at will): T=200, 250, 300, 350 and 400°C=473.15, 523.15, 573.15, 623.15 and 673.15 K.
6. Evaluation of $1/k^*(T)$ for the additional points:

$$\frac{1}{k^*(T)} = A + BT^3$$

Table 2 Data for the evaluation of a calibration file on DSC sensitivity in the Netzsch–Proteus Software. Two-point procedure

Substance	Temperature/ °C	Enthalpy/ J g^{-1}	Peak area/ μV s mg^{-1}	Sensitivity exp./ μV mW^{-1}	Mathematical weighting	Sensitivity calc. /μV mW^{-1}
Indium	156.6	–28.6	–109.900	3.843	10.0	3.843
A	200.0	–1.0	–3.708	3.708	1.0	3.709
B	250.0	–1.0	–3.533	3.533	1.0	3.533
C	300.0	–1.0	–3.343	3.343	1.0	3.342
D	350.0	–1.0	–3.141	3.141	1.0	3.142
E	400.0	–1.0	–2.934	2.934	1.0	2.934
Zn	419.5	–107.5	–306.600	2.852	0.8	2.852

These are 0.26973, 0.28304, 0.29915, 0.31834 and 0.34087. The $k^*(T)$ values are 3.7075, 3.5331, 3.3428, 3.1413 and 2.9337.

Now we have the complete set of the basic data to start the calibration program of the Netzsch–Proteus Software.

7 The program suggests us to fill in the table with the data. Delete all default rows but indium and zinc, and insert five new rows in between with dummy substances A, B, C, D and E (Table 2).

8 Fill in the columns ‘Temp.’, ‘Enthalpy’ and ‘Peak Area’ and press the button ‘Calculate’ of the right panel of the program window. The rest columns ‘Sensit.Exp’, ‘Mathem. Weighting’ and ‘Sensit.Calc’. will be filled in automatically.

The difference between ‘experimental’ and ‘calculated’ sensitivity is within the error of round-off, i.e., the last digit in a value can vary by ±1.

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