Calibration of a DSC: its importance for the traceability and uncertainty of thermal measurements

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Abstract

A differential scanning calorimeter was calibrated by Joule effect and by measuring the temperature of fusion of several pure (99.999%) metals. Repeatability and reproducibility tests were performed to access the accuracy of the instrument, the stability of the calibration constant and the correction to the temperatures of fusion was obtained experimentally.

The results demonstrate that this calorimeter is capable of producing data of enthalpies of fusion with an uncertainty of 1.5%, temperatures of fusion between 0.1 and 0.2 K, and heat capacities with an uncertainty of 1.5%, all at a 95% confidence level.

In order to calculate the uncertainty of the measurements performed, a discussion about the traceability in thermal measurements and its key elements (relation to 'stated references', unbroken chain of comparisons and stated uncertainties of those references) is done. A possible structure of the traceability chain in DSC and DTA measurements is presented. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Calibration; Differential scanning calorimetry; Heat capacity; Traceability; Uncertainty

1. Introduction

The determination of thermal properties of solids and liquids is a very important factor for a variety of technological applications that involve heat transfer and flow at high temperatures. In addition, they can help in the formulation of liquid equations of state, to the understanding of the solids structure and their behaviour, and in the indirect calculation of related properties, sometimes difficult to obtain experimentally.

Calorimetry is a universal method for the study of the physical and chemical transformations in a system where heat changes occur. Heat capacity is one of the key pieces of information for the design of chemical plants, for separation operations, and for chemical reactors. Particularly, in liquid-phase chemical reactions, C_P data are necessary to establish the energy requirements for heating and cooling reactants and products, in distillation to establish the heat and mass balances occurring in the columns, and for heat exchangers design.

In high temperature applications, namely, in the metallurgical field, the existing data for thermal properties is far from being satisfactory. For example, the

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melting point of indium is a ITS90 fixed point but the molten indium physical properties are not known with a small uncertainty, as it should be aimed for a high quality reference material. The existing data for the heat capacity of liquid indium, in the temperature range 430–1000 K is also far from being satisfactory [1]. There are two data sets available [2,3] reaching a difference of up to 25%, between them although Grønvold [2] states an accuracy of 0.3%, and a correlation [4]. Reasons for these discrepancies can also be attributed to a deficient operation and design of the calorimeters, although this last author used an adiabatic-shield calorimeter. The same behaviour is found for other metals used in fixed points of ITS 90 realisation, as tin and zinc. Effects of a bad accountability of heat flows and sample temperature measurement have been found in other systems to produce big errors in the values reported for heat capacity. This is especially true for high temperature calorimetric measurements.

Uncertainty calculations for DSC measurements (and in consequence for DSC/DTA measurements) have been a subject of some controversy and are discussed in several accompanying papers [5]. A recent monograph [6] deals with this problem, trying to demonstrate that DSC can perform thermal properties measurements (transition and melting enthalpies and temperatures, heat capacity, etc.) with low uncertainty, if the calibration of the instruments is performed carefully.

However, the calibration of the instrument, herein called instrumental calibration, has some times to be accompanied by what the chemists usually call analytical calibration, e.g. the use of reference materials. This is especially true when the equipment is not able to perform the calibration of the enthalpy by Joule effect[1]. These two aspects of calibration are not separable and they are fundamental for the measurement traceability to 'stated references' (ideally the SI units) and for its uncertainty evaluation.

In this paper we present a brief description of a DSC calibration. The readers can find further details in reference [7]. Discussion about the traceability chain is also presented [8].

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[1] Not many DSC and DTA equipments have this possibility.

2. The traceability concept

The definition of traceability can be found in The International Vocabulary of Basic and General Terms in Metrology (VIM) [9].

From a metrological point of view, traceability is at the heart of measurement and provides the basis for valid measurements that can be compared. Physical and chemical measurements can be considered to be traceable to the corresponding SI unit, to a standard or to a reference method. The key elements of the traceability concept are the relation to stated references, the existence of an unbroken chain of comparisons and the calculation of uncertainties.

2.1. Related to stated references

These may be reference methods, reference materials or, in the strict meteorological sense, the preferred references are the International System (SI) units. In the case of calorimetric measurements the SI units are the joule, the mole, the kilogram and the kelvin.

2.2. Unbroken chain of comparisons

Traceability requires an 'unbroken chain of comparisons' between a measurement and the 'stated references', that means that appropriate links in the traceability chain must be established.

In the case of physical measurement a comprehensive international system of metrology exists, providing a readily available means of tracing measurements to SI. The links in chemical traceability chains are less well understood. Consequently, structured measurement systems are not in place or at best only partly. Probably, this is because in the minds of many chemists traceability to an artefact (as with the kg) is seen as the goal [8]. In fact, for SI traceability, this is rather the exception than the rule as most of the SI units today are linked to a measurement procedure.

In a first step, the measured needs to be defined as correctly as possible as a function of the measurement parameters (the working equation, corresponding, if possible, to a known modelling for the experimental measurement). In a second step, the quality of that expression (how correct is the description of the measurement — departures from all the idealisations involved in the description of the real situation), and

the magnitude of the uncertainty of the measurement parameters needs to be assessed.

One way of considering the links in a generic way is as follows: SI units e.g., kg, mol, etc.; international standards e.g., atomic masses; pure chemical reference materials; primary methods; primary matrix reference materials; secondary methods and reference materials; and working methods and reference materials. The purity of pure chemical reference materials must be high and the uncertainty known.

A hierarchy of methods can be established such that a primary method [10] is used to validate or calibrate a secondary method which, in turn, can be directly linked to a working level method. Whereas the primary method will often be expensive and time consuming, a typical working level method will be simple but much more uncertain. The CCQM also adopted a statement on the meaning of traceability in measurements in chemistry. Strictly, traceability to the SI in measurements of the amount of substance — or of any other quantity — requires that the measurements be made using a primary method of measurement, which is correctly applied and stated with an evaluated uncertainty. There may be other, indirect ways of establishing traceability to the SI, beyond those covered by primary methods of measurements, and these are under study by the CCQM. These other indirect methods may include combinations of methods that are not established as primary, but have calculated uncertainties where the evaluation requires a study of the links to national or international measurement standards of each SI unit and includes an estimate of the uncertainty of the method, or comparison with reference materials of the same or similar substance or mixture, which themselves are linked to the SI through a chain of other comparisons, culminating in a measurement using a primary method.

2.3. Stated uncertainties

Measurement uncertainty is emerging as the preferred means and operationally defined way of stating the level of confidence that can be attached to a measurement and offers advantages over other more vague terms such as precision, trueness, etc. It is a synonym of the word accuracy, used for decades by physical chemists. It encompasses both random and systematic effects and represents a band within which the true value of a measurement can be expected to lie, with a stated confidence level.

A general strategy for the estimation of measurement uncertainty has been published by ISO in 1993 [11] and an interpretation that includes four worked examples has been published by EURACHEM in 1995 [12][2] and is currently under revision.

2.4. Reference materials

The highest levels of reference materials are primary reference materials (PRMs) [13]. Reference materials higher up in the traceability structure, that follow a certification procedure, are certified reference materials (CRMs)[3].

An important distinction must be made between a PRM and a RM (reference material) whose characteristics are defined by the so-called consensus method. This is based on the average of a number of measurements made by one or more methods that are not primary. In the absence of primary methods of measurement, and only then, there is no alternative to the consensus approach [14].

3. Experimental

A differential scanning calorimeter (TG-DSC111, from Setaram, France) was used. This calorimeter is a heat flux DSC, operating on the Tian–Calvet principle, and using a cylinder type measuring system composed by two sintered alumina cylindrical tubes set parallel and symmetrically in the heating furnace. The sensing part in this calorimeter is the central portion of the alumina cylinders, which are surrounded by thermocouple-carrying heat-flux transducers (thermopiles) wrapped around the central part of the tubes. The heat flow can be measured by the temperature changes in these transducers. Further details of the instrument can be obtained in the manufacturer manual and in ref. [15].

The calorimetric block temperature can be varied at a programmed rate; the difference between the heat

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[2] A revision of this document is underway an a new version is expected after July 1999.

[3] The designation in the US is Standard Reference Material, (SRM).

Table 1
Values of the calibration constant for different calibrations[a]

T (°C)	Calib 1 (0)	Calib 2 (15)	Calib 3 (16)	Calib 4 (22)	Calib 5 (28)	Calib 6 (32)	$\bar{K}$ (μV/mW)	σ_K (%)
−100	4.10	4.22	3.32	4.10	4.25	4.45	4.07	9.6
−50	5.19	5.26	4.69	5.19	5.35	5.44	5.19	5.0
0	6.06	6.11	5.77	6.07	6.23	6.25	6.08	2.8
100	7.25	7.31	7.22	7.27	7.41	7.38	7.28	1.0
150	7.62	7.70	7.67	7.65	7.78	7.75	7.70	0.8
200	7.87	7.98	7.97	7.92	8.03	8.00	7.96	0.7
250	8.03	8.16	8.15	8.08	8.19	8.15	8.13	0.7
300	8.10	8.26	8.24	8.16	8.27	8.22	8.21	0.8
350	8.11	8.29	8.25	8.16	8.28	8.23	8.22	0.9
400	8.07	8.25	8.20	8.12	8.23	8.18	8.18	0.8
450	7.98	8.18	8.11	8.02	8.13	8.09	8.09	0.9
500	7.87	8.06	7.98	7.89	7.99	7.98	7.96	0.9
550	7.72	7.92	7.83	7.73	7.80	7.85	7.81	1.0
600	7.56	7.76	7.66	7.54	7.55	7.72	7.63	1.2
650	7.37	7.59	7.46	7.33	7.25	7.59	7.43	1.9
700	7.16	7.41	7.24	7.10	6.88	7.49	7.21	3.1
750	6.93	7.24	6.99	6.85	6.43	7.41	6.98	4.9
800	6.66	7.06	6.70	6.57	5.88	7.37	6.71	7.5

[a] The values in brackets mean months elapsed since the first calibration.

fluxes from the block into the sample and the reference are recorded as a function of the sample temperature or of the time elapsed since the beginning of the temperature scan.

The heat fluxes and temperature calibrations were performed in the following way:

1. A resistive probe was placed in the sample holder, and a known heat flow was dissipated by Joule effect, using a constant power source, P, during a pre-programmed time interval t_i, giving rise to a dissipated energy $(Q_P)_{real}$:

$$(Q_P)_{real} = P \, t_i \tag{1}$$

2. If W is the instantaneous power detected, the total energy detected during the time interval $\Delta t = t_2 - t_1$ by the calorimeter is $(Q_P)_{meas}$:

$$(Q_P)_{meas} = \int_{t_1}^{t_2} W \, dt \tag{2}$$

3. If there were no heat losses to the environment, these two signals should be equal. In fact ratio of the two energies is the calibration constant, K, which is a function of temperature:

$$K = \frac{(Q_P)_{meas}}{(Q_P)_{real}} \tag{3}$$

4. It was assumed at this state that the power dissipate in the resistive probe was exact, which has to be verified. In fact, the complete traceability of this calibration needs the measurement of the current that flows in the probe and its resistance, which is currently under implementation in the calibration unit.

5. The temperature of the calibration was assigned to the average of the temperatures measured at times t_1 and t_2.

6. The calibration K was determined between — 100 and 800°C in intervals of 50°C. A polynomial of 4th order in temperature was fitted to the data obtained for the temperature range of the instrument. The calibration of the calorimeter was initially considered to be necessary every 6 months, a fact determined by the quality system of our accredited laboratory. However, work showed that sometimes it was convenient to make it more often. Table 1 shows the values of the different calibrations, the average value of K, and the root mean square deviation σ_K in %, for six calibrations done in a period of 32 months[4]. The dependence of all the six values on

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[4] The variation of K with time is not systematic, a fact that also justifies a tighten control, decreasing the time between consecutive calibrations.
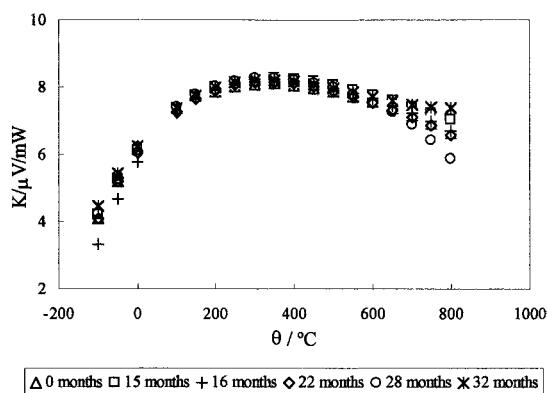
Fig. 1. The calibration constant K obtained for different calibrations.

temperature is shown in Fig. 1[5]. The variation in K did not exceed 1% between 100 and 550°C.

7. For sub-ambient temperatures, the fluctuation is larger (9.6% at −100°C) because, the refrigerating fluid is cold nitrogen gas and the temperature control is not very accurate. Above 600°C the root mean square deviation also increases to 7.5% at 800°C.

8. For the moment, this value is taken as a superior limit of the uncertainty in the calibration constant. We believe that the uncertainty in K for each calibration is much smaller, of the order of $\frac{1}{4}$ of these values. The absolute measurement of the current flow, the resistance of the probe and the time of the heat dissipation have to be measured accurately, and, therefore, the uncertainty in $(Q_P)_{meas}$ estimated.

9. The melting temperatures of Hg, In, Sn, Pb (LGC, UK certified reference materials) were used to calibrate the temperature indicated by the instrument. The heat of fusion of these metals was used to assess the calibration uncertainty due to the Joule effect[6]. As described in a previous paper [7],

the difference ΔT_{corr} between the temperature of the melting point of the standard, T_s, and the temperature measured by the calorimeter, T_{exp}, can be fitted as a function of temperature and scanning rate β [15]. Table 2 shows results obtained with In and Sn. It can be seen that the deviation in the temperature measurement can be as large as 0.2 K from the accepted value [16], although the difference of the average temperature is smaller than 0.1 K.

10. The calibration in temperature can be done in a different way [6], by extrapolating the measured temperature for zero scanning rate. This behaviour is shown on Figs. 2 and 3 and the corresponding values for the melting point of In and Sn are also shown in Table 2. The deviation from the accepted value is 0.09 and −0.08 K, respectively, which means that the error in the temperature measurement can be decreased to 0.1 K.

The uncertainty of the enthalpy change measurements can also be calculated from Table 2. As the measurements where performed in different times (during 32 months) the reproducibility can be calculated from the root mean square deviation of seven samples (In) and six samples (Sn), equal to 1.1 and 1.0%, respectively. The uncertainty at a 95% confidence level ($k=2$) is 1.5%. Some determinations of the enthalpy of fusion of Hg and Pb showed also uncer-

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[5] Formally, the calibration constant is dimensionless, as it is the ration between two energies. However, to obtain the value of the energy measured by thermopile (the heat flux sensor), it is necessary to calibrate it, which is not done in the commercial equipments. In the Setaram system it has units of μV/mW, as it is obtained directly from the variation of the e.m.f of the thermopiles, divided by the energy dissipated in the probe during the time interval chosen for the calibration.

[6] This is in fact a decrease in the traceability tree, but necessary until the measurements discussed in point 4 are made.
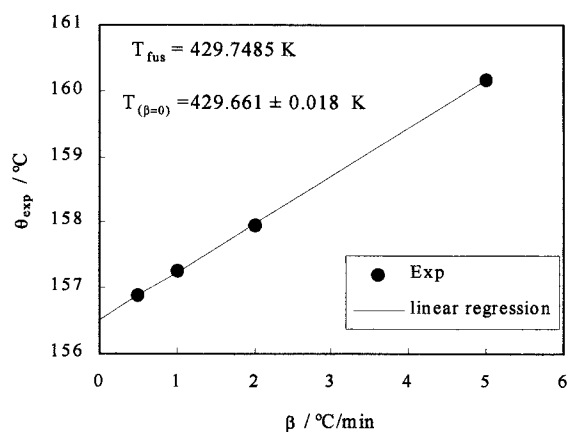

Fig. 2. The variation of the measured melting temperature of In with the scanning rate. The indent shows the value extrapolated to zero scanning rate, with the respective uncertainty.

Table 2
Comparison between the temperatures and enthalpies of fusion of indium (LGC 2601) and tin (LGC 2609) measured and reported by the certificates for enthalpy[a]

T_{std} (K)	T_{exp} (K)	ΔT_{corr} (K)	$(\Delta_f H)_{std}$ (J mol^{-1})	$(\Delta_f H)_{exp}$ (J mol^{-1})	$(\Delta_f H)_{std} - (\Delta_f H)_{exp}$ (J mol^{-1})
In	429.76	−0.01	3296±9	3220	76
	429.55	0.20		3308	−12
429.7485 [16]	429.64	0.11		3238	58
	429.63	0.11		3254	42
	429.85	−0.10		3285	11
	429.66	0.09		3232	64
	429.65	0.10		3210	86
Average	429.68	0.07		3249±35	47
Extrapolation to $\beta=0$	429.66±0.02	0.09			
Sn	505.16	−0.08	7187±4	7028	159
	504.88	0.20		7098	89
505.078 [16]	505.38	−0.30		7053	134
	504.80	0.28		6983	204
	504.82	0.26		7198	−11
	505.01	0.07		7088	99
Average	505.01	0.07		7083±74	104
Extrapolation to $\beta=0$	505.16±0.15	−0.08			

[a] The value reported for the melting temperature (K) of indium is 429.76±0.02 and for tin 505.07±0.02.

tainty smaller than 2%, but the number of runs were not enough to obtain a significant statistics. No systematic differences between the measured enthalpy of fusion for the different metals and the certified values
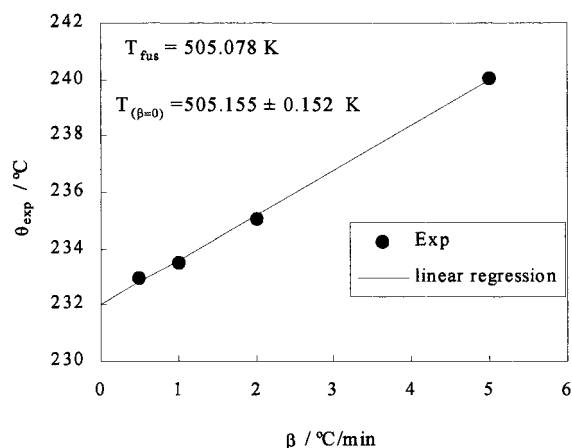

Fig. 3. The variation of the measured melting temperature of Sn with the scanning rate. The indent shows the value extrapolated to zero scanning rate, with the respective uncertainty.

were found, as expected for heat flow rate calibrations using heat capacity standards [6].

The determination of heat capacity with this calorimeter is based on the definition of C_P and was described in ref. [7]. Experimental measurements obtained for sapphire (NIST SRM 720), water and toluene, in the temperature range 300–400 K[7] showed an absolute uncertainty better than 1.5%. This result is commensurate with the uncertainty obtained for enthalpy and temperature measurements. Details of the uncertainty calculations can be found in [7].

4. Traceability in DSC measurements

From the definitions of Section 2 and the work described in Section 3, we can suggest the traceability chain presented in Table 3. The instrumental calibration is the calibration of the calorimetric signal by Joule effect and, in an ultimate effort, the calibration of the heat flux sensor — the thermopile. This last one

[7] Extension of the measurements to 850 K will be made in a near future.

Table 3
Structure of the traceability chain in DSC and DTA

		H	T
	Basic units for measurement	J, mol, kg, K	
	Intensive units	J/mol, J/kg, J/(mol/K)	
Metrological Value / Uncertainty	Primary standard or primary Reference material	Joule effect probe — V, I, t (0.1–0.5%)	ITS 90 reference points (0.001 K)
	Secondary standard	Joule effect probe — V, I, t (0.5–1%)	standard platinum resistance thermometers thermocouples (0.001-0.1 K)
	Certified reference material	enthalpy of fusion of pure compounds (0.3–1.5%)	temperature of fusion of pure compounds (0.01–0.3 K)
	Reference materials	enthalpy of fusion and transition of pure compounds (1–3%)	temperature of fusion of pure compounds (0.1–3 K)

can be avoided if the e.m.f. values are sufficient, by software design. However, the functioning of the thermopiles as a temperature variation detector or the thermopile used as the thermometer should be calibrated periodically. This is rather difficult in most of the commercial equipment, but must be enforced, in order to have the traceability of the temperature measurements to the kelvin. The use of the melting points of very pure metals, namely those used as ITS90 reference points, can be an alternative of closer metrological value.

In most of the applications of DSC in industry the analytical calibration is the only one used, via CRMs and the RMs. These are commonly used also for the enthalpy calibration in most of the commercial equipments, to avoid the instrumental calibration. However, this must be avoided in high quality work, as the uncertainty of the enthalpies of fusion of the metals (and organic compounds) is big.

As a final comment, we can say that our DSC is an excellent instrument that, if operated carefully and accordingly to its theory of operation, can produce very accurate results. It is not very far of being considered a primary instrument. In fact, its mode of operation can be completely described and understood (some effort still left, mainly in the solution of the complete heat transfer phenomena during the scanning of temperature); a complete uncertainty statement can be written down in terms of SI units and if the thermopiles are calibrated, its results can be accepted without reference to a standard of the quantity being measured.

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