ELSEVIER

Thermochimica Acta 347 (2000) 9–13

thermochimica acta

www.elsevier.com/locate/tca

Temperature, heat and heat flow rate calibration of differential scanning calorimeters

E. Gmelin[a,*], S.M. Sarge[b]

[a]Max-Planck-Institut für Festkörperforschung, Heisenbergstraße 1, D-70569 Stuttgart, Germany
[b]Physikalisch-Technische Bundesanstalt, Bundesallee 100, D-38116 Braunschweig, Germany

Received 2 August 1999

Abstract

This contribution discusses basic problems and fundamental requirements for a universally applicable, unified and metrologically correct calibration of differential scanning calorimeters (DSC). The essential features of previously published recommendations of the German Society for Thermal Analysis (GEFTA) [see Höhne et al., Thermochim. Acta 160 (1990) 1–12; Cammenga et al., Thermochim. Acta 219 (1993) 333–343; Sarge et al., Thermochim. Acta 247 (1994) 129–168; J. Thermal Anal. 49 (1997) 1125–1134] developed for a correct and instrument-independent calibration of temperature, heat and heat flow rate of DSC, are outlined. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Differential scanning calorimeters; Calibration of DSC; Calibration of temperature; Heat calibration; Heat flow rate calibration

1. Introduction

Calibration means the set of operations that establish, under specific conditions, the relationship between values of a quantity indicated by a measuring instrument or measuring system *and* the corresponding values realised by standards [5].

Differential scanning calorimeters (DSCs) provide a widely used and rapid method to determine, as thermometers, temperatures of phase transition or chemical reaction, or, as calorimeters, heat capacities or enthalpies of transition or chemical reaction in the temperature range from about 100 to 1800 K [6–10]. However, the quality of measurements is influenced by instrumental, sample and operator-related parameters, and critically depends on the accuracy of the temperature and caloric calibration of the instrument.

DSC instruments are no absolute measuring devices, the measurements are not made in thermal equilibrium and, therefore, the *relative* data obtained must be related to absolute thermodynamic values by calibration [11]. The dynamic working principle of the various instruments is complex and theoretically not yet fully understood in every detail. The calibration factors for heat and heat flow rate calibration differ and are, in the first place, dependent on temperature, sample mass and heat flow rate. In addition, the result may depend on numerous boundary conditions, e.g. parameter setting, emissivity and thermal resistance of the sample, sample geometry, etc. The accuracy of DSC experiments is also intimately correlated with the individual knowledge, skill and working style of the operator [11–13]. Finally, the reliability of the cali-

---

[*] Corresponding author. Fax: +49-711-689-1010.
E-mail addresses: gmelin@servix.mpi-stuttgart.mpg.de (E. Gmelin), stefan.sarge@ptb.de (S.M. Sarge).

PII: S0040-6031(99)00424-4

bration performed depends on the degree to which cell asymmetry can be corrected. For these reasons, a lack of confidence in the accuracy of DSC data has been expressed in many papers (for more references, see Ref. [11]).

Calibration of these instruments is necessary for several reasons:

- to convert the indicated relative scales (temperature and caloric scales) to an absolute scale;
- to establish the traceability of the measured values to SI units; and
- to assess the uncertainty of measurement.

In principle, three requirements must be fulfilled to obtain correct and reliable DSC data and to guarantee the comparability of published data:

- a reliable instrument of high reproducibility and sufficiently high resolution;
- high-precision certified reference materials, traceable to international standards; and
- metrologically sound and instrument-independent procedures which are directly based on equilibrium thermodynamics, i.e. ITS-90 and traceable heat and heat flow rate standards.

The first requirement can be easily fulfilled: Suitable DSC instrumentation is commercially available today from several manufacturers.

The second requirement poses a problem: a close examination of the literature reveals serious lack of high-precision and/or certified reference materials, in particular, heat capacity and enthalpy values based on thermal equilibrium data, i.e. adiabatic or drop calorimetry. In Ref. [3], the best-known materials are given together with their thermophysical data and their uncertainties [11]. Recommended reference substances (for thermal analysis) were critically reviewed by Marsh [14] and recently by Sabbah [15] and Stølen and Grønvold [16]. Very few suppliers, e.g. the Laboratory of the Government Chemist (UK) or the National Institute of Standards and Technology (USA) provide certified reference materials, but usually they cover only a limited range of temperatures.

The third requirement cannot be met either, since no unified and *instrument-independent* calibration procedure exists. The different procedures described by either ASTM, ISO, various manufacturers, or the procedures established by the users' own expertise, as a result of the dynamic behaviour of DSCs, generally yield different results since the procedures in use are arbitrary from the thermodynamics point of view. As a consequence, the experimental data from different laboratories cannot be compared.

2. Scope and application of the GEFTA recommendations

2.1. Prerequisites for a correct and reliable calibration

It is mainly for the third requirement that the German Society for Thermal Analysis (GEFTA), some years ago started their work to develop correct, reliable, high-precision and instrument-independent calibration procedures for DSCs. From the very beginning, calibration procedure and reference materials were treated separately in three recommendations which describe temperature, heat and heat flow rate calibrations [1–3]:

- The procedure should ensure traceability, uniformity and intercomparability of measurements performed in the heating or cooling mode, in different laboratories with different experimental equipment.
- The list of reference materials should be open to new well-documented or certified substances, especially with respect to the temperature range.

The basic concepts of each calibration procedure which was adopted by GEFTA are the following:

- reproducibility,
- highest possible precision, based on the best scientific knowledge;
- relation of the measured quantities to internationally recognised primary standards, i.e. International Temperature Scale ITS-90, and to thermodynamic equilibrium values;
- independence of instrument type;
- application in both, the heating and the cooling mode;
- practicability;
- experimental conditions for calibration and sample measurement should be as similar as possible; any asymmetry of heat flow, temperature gradients and measuring effects must be avoided;

- identification of experimental parameters and elimination of their influences; in particular, the procedure must indicate in detail how to establish reproducible environmental conditions and how to test for non-linearities;
- prescription of all steps of the calibration process,
- well-defined data treatment algorithms; and
- discussion of systematic and statistical uncertainties.

Calibration substances should, as far as possible, fulfil the following requirements:

For temperature calibration:

- represent a fixed point of ITS-90;
- have a transition point unequivocally defined from the viewpoint of thermodynamics;
- display no measurable overheating;
- possess a high rate of transition;
- show no measurable influence of the grain size on the transition temperature;
- must be available in sufficiently high purity;
- should not react with the crucible material or purge gas;
- must be stable over a long period of time; and
- should be recognised as physiologically safe.

For heat calibration, the following additional requirements are valid:

- the material must exhibit a well-defined first-order phase transition,
- the heat of transition should be known from at least two independent adiabatic calorimetric measurements;
- the change of the heat capacity during phase transition should be small; and
- the best value of heat of transition must be available.

For heat flow calibration, the following additional requirements are valid:

- no transition must take place in the temperature range applied; and
- reliable fitting polynomials must be available.

2.2. The GEFTA calibration procedure

The recommendations have been published in three papers [1–3]. They describe the procedures and evaluation methods, state calibration materials and their characteristic data, provide guidance for handling the samples and indicate how to eliminate dependences on sample and instrument parameters. Another publication gives a condensed summary of the three previous papers and can serve as a laboratory guide for metrologically correct DSC calibration [4].

2.2.1. Temperature calibration [1–2]

The procedure for temperature calibration establishes, in particular, the link of the measured temperature, i.e. the temperature indicated by the instrument to the International Temperature Scale of 1990 (ITS-90) by recommending the use of fixed point materials of the ITS-90.

In the GEFTA procedure, the thermodynamic equilibrium temperature is approached by the determination of the extrapolated peak onset temperature, measured at different heating and cooling rates, and by extrapolation to zero heating rate [1].

The recommended calibration substances (cyclopentane, water, gallium, indium, tin, lead, zinc, lithium sulphate, aluminium, silver and gold) cover the temperature range from 120 to 1350 K and usually refer to materials that define fixed points of the ITS-90. The annex to the recommendation also contains examples of temperature calibrations and describes in detail the handling of the calibration substances as well as the compatibility of the calibration substances with the crucible materials [2].

2.2.2. Caloric calibration [3]

Although the unit of energy is defined by the SI through electric quantities, only a few calorimeters allow the heat and heat flow rate to be directly calibrated by means of a built-in or an additional electric heater in the place of the sample. Therefore, the application of certified reference materials is necessary. As a consequence, for both types of calibration — heat and heat flow rate calibrations — a distinction must be made between calibration by means of electrical power/energy and by means of heats of transition/heat capacities.

Heat and heat flow rate calibration procedures and calibration substances are described in a comprehensive overview [3] which primarily refers to the relevant documents taken into account (nomenclature, international regulations, etc. [17–20]. Secondly, it defines the various quantities used to describe the measuring curves. Thirdly, it describes the procedures and calibration materials; fourthly, it gives numerous and detailed examples of the different types of calibration, and, finally, in the annexure, it considers the different experimental conditions to be taken into account, e.g. base-line interpolation, sample temperature lag, weighing regulations and important thermodynamic fundamentals. The paper also justifies why the certain calibration materials can be recommended and why others cannot.

The materials recommended for heat calibration (cyclopentane, gallium, indium, tin, bismuth, lithium sulphate and aluminium) cover the range from 120 to 930 K and are, to a great extent, identical with the substances recommended for temperature calibration. Thus, when the enthalpies of transition of the temperature calibration materials have been determined by precision calorimetry (adiabatic or drop calorimetry), the same measurement can be used to calibrate the heat and temperature scales.

The materials recommended for heat flow rate calibration, performed by means of precisely measured heat capacities, are corundum (α-Al_2O_3) in the range from 70 to 2250 K and copper in the range from 20 to 320 K. The relevant polynomials and coefficients used to represent the specific heat capacities of corundum and copper are also given [3–4].

2.3. Application of the GEFTA calibration

A calibration is recommended whenever a new instrument is taken into operation, even if it has been calibrated by the manufacturer, or whenever essential components (e.g. sensors, electronic components) are replaced or modified (e.g. cleaning of the measuring system by burning out). Calibration is also recommended whenever irreproducibility or non-linearity in the results are observed, due, for example, to mass dependence, influence of purge gas pressure, thermal emissivity of the sample, positioning of the sample crucible in the calorimeter, etc. Many of the possible influencing parameters, their importance for the accuracy of a measurement, the long-term stability of the instrument and many other observations to be taken into account when DSC experiments are performed have been discussed in detail in Ref. [3]. It is a matter of fact that the higher the required precision the longer the time to be invested for a calibration. Performing the calibration as recommended by GEFTA in full length is rather time-consuming, but it is the only way to achieve the lowest possible uncertainty. We also recommend that inexperienced users of DSC instruments work in strict accordance with the full calibration procedure in order to gain an insight into the characteristics of their DSC and to learn about the variation and interdependence of the individual parameters (calibration factors for heat and heat flow, dependence on temperature range, scanning rate, mass, purge gas pressure, etc.). However, complete calibration is not always necessary! For routine work, it is sufficient to carry out a simplified procedure for checking and updating the calibration, for example, test of the stability of baseline, and to perform calibrations at selected values only. It is the responsibility of the operator to shorten the recommended procedure, to simplify the measurement, to reduce the number of measurements according to his own requirements; however, additional uncertainties will then have to be reckoned with.

According to the general intention, all GEFTA procedures are applicable to cooling calibrations, too. However, for the temperature calibration in the cooling mode appropriate substances other than those for the heating mode are required, which could not yet be specified . GEFTA work today is concentrated on a number of liquid crystals which seem to fulfilthe aforementioned requirements for calibration materials. It is intended to publish a fourth recommendation in regard to calibrations in the cooling mode in 1999.

Acknowledgements

The authors express their sincere thanks to the other members of the GEFTA working group ‘Calibration of Dynamic Calorimeters’, Prof. H.K. Cammenga, W. Eysel, Prof. W. Hemminger and G.W.H. Höhne, for fruitful discussions and involvement in drawing up the recommendations.

References

[1] G.W.H. Höhne, H.K. Cammenga, W. Eysel, E. Gmelin, W. Hemminger, The temperature calibration of scanning calorimeters, Thermochim. Acta 160 (1990) 1–12.

[2] H.K. Cammenga, W. Eysel, E. Gmelin, W. Hemminger, G.W.H. Höhne, S.M. Sarge, The temperature calibration of scanning calorimeters. Part 2. Calibration substances, Thermochim. Acta 219 (1993) 333 –343.

[3] S.M. Sarge, E. Gmelin, G.W.H. Höhne, H.K. Cammenga, W. Hemminger, W. Eysel, The caloric calibration of scanning calorimeters, Thermochim. Acta 247 (1994) 129 – 168.

[4] S.M. Sarge, W. Hemminger, E. Gmelin, G.W.H. Höhne, H.K. Cammenga, W. Eysel, Metrologically based procedures for the temperature, heat and heat flow rate calibration of DSC, J. Thermal Anal. 49 (1997) 1125–1134.

[5] International Vocabulary of Basic and General Terms in Metrology, DIN Deutsches Institut für Normung e. V., 2nd Edition, Beuth, Berlin, 1994.

[6] W. Hemminger, G. Höhne, Calorimetry. Fundamentals and Practice, Chemie, Weinheim, 1984.

[7] B. Wunderlich, Thermal Analysis, Academic Press, Boston, 1990.

[8] W.F. Hemminger, H.K. Cammenga, Methoden der Thermischen Analyse, Springer, Berlin, 1989.

[9] M.J. Richardson, E.L. Charsley, Calibration and standardisation in DSC, in: M.E. Brown (Ed.), Handbook of Thermal Analysis and Calorimetry, vol. 1, Principles and Practice, Elsevier, Amsterdam, 1998, pp. 547–575.

[10] P.J. Haines, M. Reading, F.W. Wilburn, Differential thermal analysis and differential scanning calorimetry, in: M.E. Brown (Ed.), Handbook of Thermal Analysis and Calorimetry, vol. 1, Principles and Practice, Elsevier, Amsterdam, 1998, pp. 279–361.

[11] E. Gmelin, S.M. Sarge, Calibration of differential scanning calorimeters, Pure Appl. Chem. 67 (1995) 1783–1800.

[12] J.E. Callanan, S.A. Sullivan, Development of standard operating procedures for differential scanning calorimeters, Rev. Sci. Instr. 57 (1986) 2584–2592.

[13] G.W.H. Höhne, E. Glöggler, Some peculiarities of the DSC-2/-7 (Perkin–Elmer) and their influence on accuracy and precision of the measurements, Thermochim. Acta 151 (1989) 295–304.

[14] K.N. Marsh (Ed.), Recommended Reference Materials for the Realization of Physicochemical Properties, Blackwell Scientific Publications, Oxford, 1987.

[15] R. Sabbah, An Xu-wu, J.S. Chickos, M.L. Planas Leitão, M.V. Roux, L.A. Torres, Reference materials for calorimetry and differential thermal analysis, Thermochim. Acta 331 (1999) 93–204.

[16] S. Stølen, F. Grønvold, Critical assessment of the enthalpy of fusion of available and potential metal enthalpy standards for use at moderate to high temperatures, Thermochim. Acta 327 (1999) 1–32.

[17] J.O. Hill (Ed.), For Better Thermal Analysis and Calorimetry, 3rd Edition, International Confederation for Thermal Analysis, 1991.

[18] I. Mills, T. Cvitaš, K. Homann, N. Kallay, K. Kuchitsu (Eds.), Quantities, Units and Symbols in Physical Chemistry, 2nd Edition, Blackwell Scientific Publications, Oxford, 1993.

[19] H. Preston-Thomas, The International Temperature Scale of 1990 (ITS-90), Metrologia 27 (1990) 3–10.

[20] H. Preston-Thomas, The International Temperature Scale of 1990 (ITS-90), Metrologia 27 (1990) 107.