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Calibration as an aspect of quality assurance in differential scanning calorimetry (DSC) measurements ☆

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Abstract

Quality assurance will be instrumental to the economic survival of companies in the Single European Market. Test laboratories will have to prove and demonstrate their qualifications. As DSC's services are frequently enlisted for quality assurance tasks in the industrial production process, the requirements of the relevant quality assurance standards must also be applicable to DSC. The European Standard EN 45001 defines general criteria for the operation of test laboratories. For example, a calibration program for instruments must be available. For the temperature calibration of DSCs a recommendation prepared by the German Society for Thermal Analysis (GEFTA) is available and will be presented. Recommendations for caloric calibration are also mentioned.

Keywords: Calibration; DSC; EN 45001; GEFTA; Quality assurance

1. Introduction

The realization of the Single European Market and the interdependence in world trade require that the quality of measurement results by which products are characterized be proved. The ISO 9000 series of international standard contains the basic standards for quality management and quality assurance (adopted as European Standards EN 29000 and following). The formal organizational require-

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ments are put in a concrete form; EN 45001 lays down general criteria for the operation of testing laboratories and will play an important role in the future. It will no longer be sufficient to be technically and scientifically competent; this competence must be documented and made transparent to others. Before Differential Scanning Calorimetry (DSC) is dealt with in more detail, it appears to be advisable to make some general remarks on the quality assurance in the TA testing laboratory (TA stands for Thermal Analysis).

TA methods are used for quality assurance in many ways — for the inspection of the raw mterials, as an accompanying measure in manufacture and for the control of the finished products. To enable the TA methods to be of use for quality assurance, they must be subject to the requirements of the relevant standards. To ensure the comparability of various testing laboratories, the EN 45001 standard lays down general requirements as to

Organization
Premises
Equipment
Working procedures
Qualification of personnel
Establishment and maintenance of the quality manual

All these general requirements of EN 45001 are to be met not only by laboratories testing products with TA methods and establishing a test report on behalf of third parties, but also by the companies' own quality system which is based on TA methods.

Some of the requirements which particularly apply to TA will be briefly described in the following.

The personnel must be appropriately trained and have the technical knowledge and experience required.

The premises must be such that neither the test results are falsified nor the accuracy of measurement adversely affected. For measurements with TA equipment this means that the influence of changing ambient conditions on the measurement results is quantified.

Equipment, i.e. instruments, must be identified and maintenance instructions must be available. Records for test and measuring facilities must document, for example, the maintenance work carried out. Instruments must be calibrated according to an established program. This program must be such that the measurements performed are traced to national or international measurement standards. Should this not be possible, the accuracy of the test results must be proved (e.g. within the scope of intercomparisons).

The requirements of the ISO 9000 and EN 45000 series have been devised for the quality assurance of all kinds of products, including the services rendered by testing laboratories. Pure research work is not covered but it would be absurd to apply standards that are less strict to research where the calibration, determination of uncertainties, verification of test procedures, traceability of reference materials, etc., are concerned. This means that the new quality assurance requirements cover all

areas in which TA or calorimetry is applied, and they basically stand for only the self-evident rules of reliable measurement.

2. Calibration of DSCs

The aspects referred to will be described in more detail for the example of DSCs. Differential scanning calorimeters are used in many ways for testing substances, for example, in the area of polymers. Test results often have economic effects such as in incoming inspection, in-plant control or final inspection of the finished product.

Of the various requirements of EN 45001 only the calibration of DSCs will be briefly dealt with here; other important measures such as (a) the calibration of balances, flowmeters, digital voltmeters and other auxiliary equipment, (b) the preparation of samples and crucibles for measurement (very important, for example, for heat capacity determination), will not be discussed.

A DSC is used to determine characteristic temperatures, heat flow rates as a function of temperature, and heat. A DSC must therefore be calibrated for temperature, heat flow rate and heat. This is chiefly done using calibration substances.

The requirement of EN 45001 for calibration substances is graded. Calibration substances whose properties can be traced to national or international standards have the highest rank, whereas calibration substances whose properties have been determined within the scope of an intercomparison rank lower. It is the objective of traceability to ensure reliable statements on uncertainties of measurement.

2.1. Temperature calibration

In all DSCs, the temperature to be assigned to the sample is measured with thermocouples or special resistance thermometers. As the temperature sensors are integrated in the measuring system and cannot be arranged in the place of the sample (which implies that in dynamic operation there is a temperature difference between the place of the sensor and the place of the sample) these sensors must be calibrated in situ by a substance which, at a certain temperature, produces a caloric effect when used as sample (e.g. it will melt).

The hierarchy of potential temperature calibration substances is as follows:

(a) Fixed-point materials of the International Temperature Scale of 1990 (ITS-90) (which serve to establish the temperature scale) whose transition temperatures are not affected by uncertainties (absolute values).

(b) Substances which are compared (in national metrology institutes or accredited testing laboratories) with national or international standards (values with a verified uncertainty).

(c) Substances whose values have been measured in various suitable instruments calibrated against (a) or (b) (e.g. DTA, DSC) within the scope of intercomparisons (best-value estimates).

Calibration materials are suitable for calibrating DSCs only if they meet some additional conditions [1]:

Thermodynamically defined transition
Compatibility with the crucibal material
High transition rate
Available in high purity
No secondary reaction (gas, light)
Not hygroscopic, volatile, etc.

Substances can be sampled using these criteria and identified as potential calibration substances.

Substances for DSC temperature calibration (not complete) [1] are shown in Table 1. Regarding the temperature calibration of DSCs, there are still gaps on the temperature scale. It is the task of the standardization working groups to fill these.

Calibration substances are not, however, sufficient; the calibration procedure must also comply with the metrological requirements. Two aspects are to be taken into account.

(a) Thermodynamically defined transition temperatures are always equilibrium temperatures. DSC measurements are dynamic; therefore DSC calibration results must be extrapolated to equilibrium conditions to ensure a temperature calibration which is independent of the heating rate used.

(b) For the curve of DSC measurement results, the characteristic temperature is to be selected which can be best assigned to a transition temperature.

On the basis of these requirements, the German Society for Thermal Analysis (GEFTA) has suggested a procedure which ensures a correct temperature calibration which is as accurate as possible and independent of the instrument type, i.e. a procedure which allows the indicated temperature to be correlated with the true sample temperature [2]. The central elements of the procedure are as follows:

(a) Use of the extrapolated onset temperature T_e of the transition peak (calibration substance) to establish the instrument temperature scale.

Table 1
Substances for DSC temperature calibration [1]

Fixed-point materials with solid–liquid transition		
Water	0.00°C ± 10 mK	(IPTS-68 converted to ITS-90)
Gallium	29.7646°C	(ITS-90)
Indium	156.5985°C	(ITS-90)
Tin	231.928°C	(ITS-90)
Lead	327.46°C ± 10 mK	(IPTS-68 converted to ITS-90)
Zinc	419.527°C	(ITS-90)
Aluminium	660.323°C	(ITS-90)
Silver	961.78°C	(ITS-90)
Gold	1064.18°C	(ITS-90)
Substance traceable to national standards (solid–solid transition)		
Li_2SO_4	578.28°C ± 250 mK	

(b) Measurement of the function $T_e(\beta)$ and extrapolation to zero heating rate at which the temperature difference between the place of the sample and the place of the sensor disappears, which allows $T_e(\beta = 0)$ and the equilibrium transition temperature to be directly compared.

Following the calibration procedure, the correct determination of the transition temperature of a first-order transition means determination of $T_e(\beta)$ and extrapolation to $\beta = 0$ in order to obtain the equilibrium value.

2.2. Caloric calibration (heat flow rate, heat)

For this, too, calibration substances and calibration procedures are to be developed. Fixed-point materials for directly realizing the heat flow rate or the heat do not exist; metrological tracing is to electrical units.

Electrical heat flow rate and heat calibration thus have the highest rank in the hierarchy, but in general reference materials are used for caloric calibration.

The electrical caloric calibration procedure is as follows: installation of an electric heating element (ohmic resistor) at the place of the sample, determination of the electric heating power (energy) by current, voltage (and time) measurement. All these quantities can be measured much more precisely than is required by the repeatability error of DSC measurements (approx. 1%).

The problems encountered are,

(a) Heating elements cannot be installed in all DSC types.

(b) The uncertainty of calibration is determined by the uncertainty of the conduction corrections (Joule effect in the supply lines, heat leaks along the supply lines, uncertainty of the correction 10–20%).

The advantages of electrical calibration are,

(a) Heat flow rate and heat can be realized in any amount.

(b) The effect can be turned off (realization of the base line).

(c) Continuous calibration with respect to temperature is possible.

The hierarchy of the substances for heat flow rate and for heat calibration is as follows:

(a) Primary calibration substances: determination of the heat capacity C_p or the heat of transition Q_{trs} by adiabatic calorimetry, i.e. by direct comparison with electrical power/energy (uncertainty: $\geq 0.1\%$). The problem is that only a small number of substances have been precisely measured by several institutions.

(b) Secondary calibration substances: determination of C_p of Q_{trs} by means of electrically calibrated precision calorimeters (e.g. drop calorimeters, ice calorimeters).

(c) Tertiary calibration substances: determination of C_p of Q_{trs} with a DSC, which in turn has been calibrated against primary calibration substances.

Heat flow rate calibration

Substances recommended for DSC heat flow rate calibration are [3],

(a) Primary substances with well-known specific heat capacity (sapphire (α-Al_2O_3) in the temperature range of 70–2250 K (uncertainty about 0.1%) and copper in the temperature range 97.5–320 K (uncertainty about 0.1%)).

(b) No recommendation has been made for secondary substances and tertiary substances because they show uncertainties that are not substantially smaller than the repeatability error of DSC measurements.

The GEFTA has submitted a proposal for the calibration procedure which essentially consists of construction of an initial line (isothermic, initial temperature) and an extrapolated final line (isothermic, final temperature) and the bringing into coincidence of the initial and final lines of the blank and calibration measurement [3].

The uncertainty of calibration is to be thoroughly estimated, with the repeatability errors included (for heat flux DSC: approx. 1–2%). The uncertainty of calibration is the smallest possible systematic uncertainty with which heat flow rates, i.e. also unknown heat capacities, can be determined.

Precise C_p measurements and heat flow rate measurements ($<1\%$) with DSCs are almost impossible. The effects of changing heat resistances in the measuring system and the amount of the temperature gradient in the sample are insufficiently known and too hard to determine.

Heat calibration

A certain heat is assigned to the peak area. An obvious problem is the determination of the peak area (integration limits, base line). Here, too, electrical calibration would be the best solution providing it is feasible.

Calibration is generally carried out with substances showing a thermodynamically defined first-order transition (possibly also suitable for temperature calibration). The problem is that independent measurements by means of adiabatic calorimetry have been carried out for only a small number of substances that are able to serve as primary calibration substances (e.g. In, Sn). Even secondary calibration substances (measurement of the transition heat with precision calorimeters which are electrically calibrated) are very scarce (e.g. Bi), so tertiary calibration substance have to be investigated in order to perform a best-value estimation on a broad basis of experimental results. All the recommended calibration substances [3] regrettably show uncertainties in Q_{trs}, which are of the same order as the repeatability error of the area determination with DSC (approx. 0.5%).

3. Conclusions

The application of EN 45001 to thermoanalytical measurements, e.g. DSC measurements, among other things, compels test laboratories to use certified

calibration materials which can, if possible, be traced to national or international standards. This requirement is and can be best complied with for temperature calibration for which a number of fixed-point materials of the ITS-90 are available and other substances can be linked up with the ITS-90.

Both for heat flow rate and heat calibration there is a striking lack of substances precisely and fundamentally measured (i.e. with adiabatic calorimeters). Where several independent measurements have been carried out, some of the stated ranges of uncertainty do not overlap.

Not only calibration substances but also calibration procedures are essential for a best possible DSC calibration.

In future national and international TA associations must also deal with these problems within the scope of working groups in order to meet the requirements of EN 45001, i.e. in order to achieve uniformity of measurement in this area.

References

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