

## **A REVIEW OF THE WORK OF THE GERMAN SOCIETY FOR THERMAL ANALYSIS (GEFTA) ON STANDARDIZATION**

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Working groups of the German Society for Thermal Analysis (GEFTA) are active in the fields of calibration of dynamic calorimeters (DSC), calibration of dilatometers, evaluation of DSC curves and standard samples for dynamic mechanical analysis (DMA). Two papers on the temperature calibration of DSC instruments have been published, which recommend a calibration procedure and calibration materials. Another recommendation on caloric calibration is in preparation. Certified calibration samples for dilatometers are available for the temperature range  $-190^{\circ}$  to  $700^{\circ}\text{C}$ .

**Keyword:** GEFTA

### **Introduction**

The German Society for Thermal Analysis (Gesellschaft für Thermische Analyse e. V.) has at present ca. 200 personal members and 25 company members, e.g. manufacturers of thermal analysis equipment. In 1986 GEFTA established Working Groups (WGs) in the fields of

- Dynamic Calorimetry (DSC)
- Thermogravimetry (TG)
- Dilatometry

with the aim to improve the calibration of DSC instruments, thermobalances and dilatometers. To reach this goal, up-to-date recommendations on calibration procedures and calibration substances have been worked out for DSC, and a certified calibration material for dilatometry is on sale (the work on TG has not yet started).

In 1990 two more WGs were established.

- Calorimetry
- Thermal Analysis for Polymers

The task of the Calorimetry Group is to identify general problems in the field of evaluating the measured curves of DSCs, in particular deconvolution of

measured curves, correct determination of true characteristic temperatures etc. The WG on Thermal Analysis for Polymers aims to create standards for dynamic mechanical analysis of polymers and rubber products which are mainly used in the automobile industry.

In principle, GEFTA restricts its activities only to recommending procedures and substances; with the exception of calibration samples for dilatometry no certified reference material is kept in stock (this material is certified and distributed by the Physikalisch-Technische Bundesanstalt). GEFTA, as a scientific society, cannot act as a certifying institution and distributor of reference materials.

### **Certified reference material for dilatometry**

To calibrate dilatometers (measurement of linear thermal expansion) GEFTA initiated in collaboration with PTB (Physikalisch-Technische Bundesanstalt) the procurement of specially tempered quartz glass rods (made of natural quartz) with a diameter of 6 mm and a length of 25 or 50 mm. Additionally, three special rods out of the same melt were prepared for measuring the thermal expansion coefficient of the material fundamentally (absolutely) by means of laser interferometry.

The material is certified between  $-190^{\circ}$  and  $700^{\circ}\text{C}$ , and the thermal expansion coefficient given by a polynomial shows a standard deviation of 0.3%. Roughly one-third of the 200 certified samples are still in stock at PTB.

In 1988 GEFTA contacted a manufacturer of sapphire with the aim to buy – and to have certified by the PTB – standard samples for an extended temperature range, up to  $1500^{\circ}\text{C}$ . The intention was to cut some hundreds of samples, together with rods of a special geometry, for the fundamental determination of the thermal expansion coefficient out of one big crystal (up to 50 kg) to ensure homogeneity and uniform purity of all the samples. Regrettably, GEFTA did not succeed in bringing together enough orders for rods such that a reasonable price per sample could be fixed.

### **Calibration of dynamic calorimeters (DSCs)**

Calibration must be performed with regard to temperature and heat flow rate/heat. The task has been to develop recommendations on procedures and substances, which allow a correct calibration of DSCs irrespective of the instrument type.

The recommendations for temperature calibration are published in *Thermochim. Acta* [1, 2].

The main steps in temperature calibration procedure are:

– Defining the measured temperature  $T_m$  as the extrapolated peak onset temperature  $T_e$  and reading it from the curve

- Measuring the dependence of  $T_c$  on the heating rate
- Extrapolating  $T_c$  to zero heating rate to get a quasi-equilibrium value
- Defining the true temperature by means of the transformation temperatures of fixed point materials of the International Temperature Scale of 1990 (ITS-90) or of materials directly compared with fixed point materials
- Comparing the extrapolated  $T_c$  with the ITS-90 temperatures to obtain a calibration table/polynomial.

This procedure gives a calibration with the smallest possible uncertainty. For routine work a simplified procedure is recommended. Twelve materials (nine of them fixed-point materials) are recommended for temperature calibration.

Procedures for caloric calibration, i.e. heat flow rate and heat calibration, have been finalised and will be published soon. As calibration material for the heat flow rate calibration GEFTA is going to recommend in the first place sapphire which shows the best known values for heat capacity. For heat calibration, i.e. peak area calibration, among others, indium, tin and bismuth will be recommended, but a serious lack of adiabatic measurements of heats of fusion of these and other materials is evident. Thus the uncertainty of the heat calibration by means of heat of fusion samples is of the same order of magnitude as the repeatability of the instruments. A far better situation exists where an electric calibration is possible because the uncertainty of the measurement of electric power and heat – even taking the wire corrections into consideration – is substantially smaller than the DSC repeatability.

#### *Working Group on Calorimetry*

To identify problems and needs in the field of standardization, an inventory of calorimeters in use was performed. It was found that 50 GEFTA members use a total of ca. 120 calorimeters (among them are: ca. 70 DSC, 11 Flow, 10 Reaction, 9 Bomb, 7 Adiabatic, 5 Solution, 3 Gas).

Initially, work is focused on the desmearing (deconvolution) of DSC curves by means of standard procedures to get more accurate information on the sample behaviour inside the DSC, i.e. to eliminate the time lag and the distortion caused by the measuring system and recorded in the curve. This true information is needed, e.g. for a kinetic evaluation of the DSC curve.

#### *Working Group on Thermal Analysis for Polymeric Materials*

There is an urgent need for standard reference samples which can be used to calibrate equipment for dynamic mechanical analysis. Many industries have an interest in precisely measuring viscoelastic properties of polymeric materials and rubber products. Here GEFTA is still at a very early stage because the various analyzers need calibration samples of widely differing geometry.

*Cooperation with institutions*

There is a close collaboration between GEFTA and the Physikalisch-Technische Bundesanstalt (PTB), the metrological state institute in Germany, especially in the field of DSC calibration and calibration materials for dilatometry. Members of GEFTA are involved in the development of national standards which is the task of the German Organisation for Standardization (DIN, Deutsches Institut für Normung). Up to now we have five standards for different areas of Thermal Analysis. There is of course an interaction between the work done in the GEFTA working groups and the requirements used as a basis in the standards.

**References**

- 1 G. W. H. Höhne, H. K. Cammenga, W. Eysel, E. Gmelin and W. Hemminger, *Thermochim. Acta*, 160 (1990) 1.
- 2 H. K. Cammenga, W. Eysel, E. Gmelin, W. Hemminger, G. W. H. Höhne and S. M. Sarge, *Thermochim. Acta*, (submitted).

**Zusammenfassung** — Arbeitsgruppen der Deutschen Gesellschaft für thermische Analyse e.V. (GEFTA) sind auf dem Gebiet der Kalibrierung von dynamischen Kalorimetern (DSC) und von Dilatometern sowie der Auswertung von DSC-Kurven und Standardproben für die DMA tätig. Es erschienen zwei Arbeiten über die Temperaturkalibrierung von DSC-Geräten, in der Kalibriermethoden und Kalibriersubstanzen empfohlen wurden. Weitere Empfehlungen für die kalorische Kalibrierung sind in Arbeit. Erhältlich sind zertifizierte Kalibrierproben für Dilatometer für das Temperaturintervall  $-190^{\circ}$  bis  $700^{\circ}\text{C}$ .