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STANDARDIZATION IN THERMAL ANALYSIS

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The present state of the certification of the reference materials for thermal analysis is considered. Six sets of reference materials for temperature calibration, resulting from the research work of the ICTA Standardization Committee, are discussed.

Since adequate standards are needed for instrument calibration as well as for the comparability of the results obtained with different instruments and in different laboratories, research work dealing with standards for thermal analysis involves a very important methodological problem and is carried out by many national and international organizations, such as the ISO, ASTM, ICTA and SAMA, as well as by individual investigators and individual laboratories.

As concerns this research work on thermal analysis standards, only the International Test Programs organized by the ICTA have so far resulted in the certification of the standards. These Programs, their principles, requirements and results have been described in detail earlier [1–16].

The present state of thermal analysis standardization is illustrated in Table 1. There are 6 sets of certified reference materials for the calibration of temperature scales. Most of them are standards to be applied in DTA or DSC in 5 temperature ranges; however, one of them is a set of reference materials of temperature calibration in thermogravimetry.

It should be emphasized that all these reference materials have been certified for measurements under dynamic temperature conditions, and that the certificates deal only with definite batches of materials, not with these materials generally. This remark also applies to the ferromagnetic reference materials certified for calibration of temperature scales in TG, because of the influence of the variations in composition of these materials from batch to batch on their magnetic transition temperatures.

Certified reference materials for the glass transition temperature

The glass transition of polystyrene has been used for the calibration of temperature about 100° in DTA and DSC. The temperature of the glass transition is considered very important for the characterization of polymers as it is the temperature of change

Table 1 NBS–ICTA Certified Reference Materials

Number of NBS–ICTA set of reference materials	Application	Number of reference materials in set	Temperature range of calibration
GM 754	DTA, DSC	1	about 100°
GM 757	DTA, DSC	4	below 350 K
GM 758	DTA, DSC	5	125–435°
GM 759	DTA, DSC	5	295–675°
GM 760	DTA, DSC	5	570–940°
GM 761	TG	5	250–760°

in physical properties due to the increased mobility of some part of the macromolecule. The heat capacity also changes at this temperature, and this phenomenon is recorded in DTA and DSC curves.

The reference material based on the glass transition has been tested and certified as a result of the Fourth ICTA International Program; 24 laboratories in 11 countries, using 8 kinds of apparatuses, participated in the work. Finally, the polystyrene PS 2 from the Polymer Supply and Characterization Centre of the Rubber and Plastics Research Association, U. K., was chosen and certified as reference material GM 754. The DTA effect of its glass transition is shown in Fig. 1.

The results of the Fourth ITP indicated that the measured point T_a (initial deflection) should be rejected as not reproducible enough and rather subjectively defined. The next two measured points, T_b and T_c, have been determined at 104.4° and 107.5°, respectively, as unweighted mean values from interlaboratory results.

Certified reference material for temperature calibration below 350 K

This set resulted from the Third ICTA International Test Program based on examinations performed in 14 laboratories in 7 countries, using 9 different kinds of instruments.

The set contains 4 organic compounds defining 5 measured temperature values, as shown in Table 2. Analysis of the interlaboratory data demonstrated the reproduci-

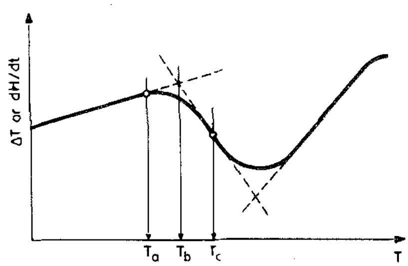

Fig. 1 Measured points T_a, T_b and T_c in the DTA or DSC curve for the glass transition (according to Certificate GM 754)

Table 2 Mean values of laboratory data in degrees Kelvin of the reference materials below 350 K (according to Certificate NBS–ICTA GM 757)

Reference material	Transition	Onset temperature	Peak temperature
1,2-Dichloroethane	melting	237.3	241.6
Cyclohexane	phase transition	187.1	190.9
	melting	278.0	280.2
Phenyl ether	melting	298.6	301.9
o-Terphenyl	melting	328.2	331.1

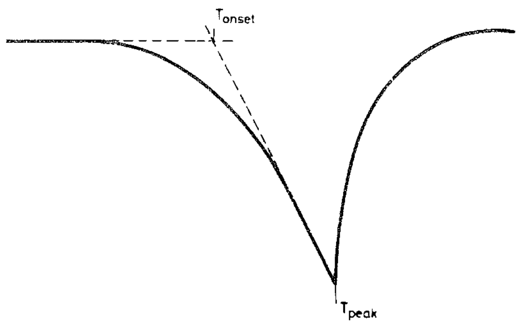

Fig. 2 Representative DTA peak showing defined points accepted in the Third International Test Program (according to Certificate GM 757)

bility of two measured points for calibration purposes: onset and peak temperature (Fig. 2). Variation has also been revealed in these values, depending on the apparatus design. The use of the reference materials allows a comparison of different instruments and the reconcilement of the differences in temperatures measured on other materials.

Certified reference materials for the temperature range 125–940°

This wide temperature range is covered by 3 sets of reference materials issued as a result of the Second International Test Programs. They consist jointly of 10 materials, ranked in 3 sets, corresponding to the following temperature ranges: 125–435°, 295–675° and 570–940°. Eight of these materials define the Solid I ⇌ Solid II first-order phase transitions, while two indicate melting points. Table 3 presents the mean values obtained from analysis of the experimental results received from 34 laboratories in 12 countries. Statistical analysis of these results was performed by considering instrumental parameters such as sample holder configuration and construction, the characteristics of the ΔT thermocouple, the characteristics and location of the T thermocouple, the method of temperature measurement, etc., and experimental conditions such as sample weight, dilution, gas flow characteristics, heating rate, etc.

Table 3 Transition temperature data on reference materials for calibration of temperature scales in the temperature range 125–940° (according to Certificates NBS–ICTA GM 758–760)

Number of NBS–ICTA set	Reference material	DTA mean values, °C	
		Extrapolated onset temperature	Peak temperature
GM 758	KNO_3	128	135
GM 758	In	154	159
GM 758	Sn	230	237
GM 758, GM 759	$KClO_4$	299	309
GM 758, GM 759	Ag_2SO_4	424	433
GM 759, GM 760	SiO_2	571	574
GM 759, GM 760	K_2SO_4	582	588
GM 759, GM 760	K_2CrO_4	655	673
GM 760	$BaCO_3$	808	819
GM 760	$SrCO_3$	928	938

The us of some materials of these sets is connected with special requirements, e.g. heating in situ up to 150–160° in the case of KNO_3, and special sample holders for materials defining temperature points by melting (In, Sn).

Temperature standards for thermogravimetry

Attempts to establish temperature standards for TG were begun in 1966. First a set of 9 inorganic and organic compounds was considered, then the thermal decomposition processes of carbonates and oxalates were examined, but the conclusions from these experiments were negative. In 1969 Norem, O'Neil and Gray proposed the use of ferromagnetic materials as the reference materials for temperature calibration in TG, based on the Curie point [12]. The investigations of magnetic materials by the ICTA Standardization Committee started in 1971 [7]. It was found that the temperature point of magnetic transition measured in the TG curve is not the exact Curie point; it was called the "magnetic reference point".

The problem of the choice and testing of materials suitable for use as magnetic reference materials was the subject of the Fifth and the Sixth International Test Programs. Finally, the Sixth ITP resulted in the certifying of the following 5 reference materials: nickel and 4 magnetic alloys (Permanorm 3, Mumetal, Permanorm 5, Trafoperm) produced by Vakuumschmeltze GmbH, FRD (Table 4). In a magnetic field these materials show easily detectable apparent weight changes in temperature ranges in which thermally-induced disorder or structural change eliminates or drastically reduces their magnetic properties (Fig, 3). When exposed to temperature changes, each of these materials shows a corresponding change in its magnetic properties at the reproductible temperature, recorded in the TG curve. At the same time, the

Table 4 Temperature ranges, mean temperatures and standard deviations for ferromagnetic reference materials (according to Certificate NBS–ICTA GM 761)

Reference material		Temperature range, °C	Mean temperature, °C	Standard deviation
	T_1	242–263	253.3	5.3
Permanorm 3	T_2	250–270	259.1	5.2
	T_3	255–278	266.4	6.2
	T_1	343–360	351.4	4.8
Nickel	T_2	344–361	352.9	5.3
	T_3	345–363	354.4	5.4
	T_1	363–392	377.4	6.3
Mumetal	T_2	366–395	381.6	7.0
	T_3	370–398	385.9	7.2
	T_1	435–463	451.1	6.7
Permanorm 5	T_2	438–466	455.0	7.1
	T_3	441–470	459.3	7.3
	T_1	728–767	749.5	10.9
Trafoperm	T_2	731–769	752.1	10.9
	T_3	733–771	754.3	11.0

temperature determined with a temperature sensor is compared with that recorded during TG, to detect any possible systematic error.

ICTA research work in progress on reference materials

Work on purity reference materials, enthalpy reference materials and an inorganic, high-temperature (above 1000°) glass transition reference materials has recently been started by the ICTA Standardization Committee. The substitution of some of the expensive or difficult materials in the original sets of DTA CRMs (e.g. silver sulphate and quartz) by cheaper or more readily obtainable materials is also being considered.

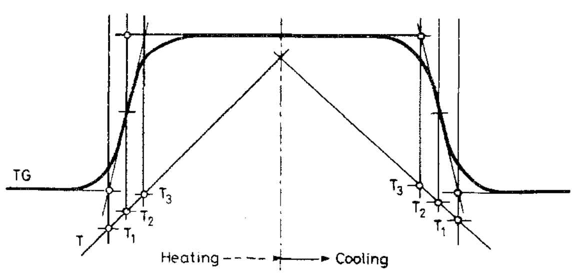

Fig. 3 Defined points in the thermogravimetric temperature calibration curve (accoring to Certificate GM 761)

Other subjects of standardization

The recommendations of reporting practices as well as the nomenclature recommendations also belong among the problems of standardization of thermal analysis. Both are of great significance for the appropriate development of thermal analysis methodology and for correct practice as the means of making possible interlaboratory comparability.

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Zusammenfassung — Die gegenwärtige Lage der Attestierung von Referenzmaterialien für die thermische Analyse wird erörtert. Sechs Sets von Referenzmaterialien, die vom ICTA-Standardisierungskomitee zur Temperaturkalibrierung in Vorschlag gebracht wurden, werden diskutiert.

Резюме — Рассматривается современное состояние проверки реперных материалов для термического анализа. Обсуждено шесть наборов стандартных веществ для калибровки температуры, исследование которых проведено стандартизационным комитетом ИСТА.