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STUDIES ON ICTA REFERENCE MATERIALS USING SIMULTANEOUS TG-DTA

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SUMMARY

A simultaneous TG-DTA apparatus has been used to determine accurate values for the ICTA Magnetic Reference Standards. The apparatus, which enables sample temperature to be measured directly, was first calibrated using the melting points of pure metals. Extrapolated onset temperatures were also determined for the ICTA DTA Certified Reference Materials.

INTRODUCTION

In recent years there has been an increasing recognition of the need for reliable methods for the accurate temperature calibration of conventional thermobalances, where the temperature sensor is not in direct contact with the sample. The ICTA Certified Reference Materials for Thermogravimetry, distributed by the National Bureau of Standards as set GM-761, comprise four alloys and one metal which undergo a loss of ferromagnetism at a characteristic temperature (ref.1). When heated in a thermobalance in a magnetic field, the materials show an apparent weight change in the region of this characteristic temperature. A summary of the values obtained for these materials in the ICTA International Test Programme, involving data from 18 laboratories is reproduced in Table 1. The temperature points T_1, T_2 and T_3 represent the extrapolated onset, mid-point, and extrapolated offset, respectively, as defined in the ICTA protocol (ref.1).

The deviations shown represent the consistency that can be achieved by experienced workers using the same samples and different equipment.The spread of results emphasises the need for these reference materials to enable inter-laboratory comparisons between instruments to be made. The uncertainty in the values for these transitions however has limited their use for accurate temperature calibration of thermobalances.

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TABLE 1
ICTA Test Programme Mean Values for CRM's for Thermogravimetry.

	T_1	T_2	T_3 /°C
PERMANORM 3	253.3 ± 5.3	259.1 ± 5.2	266.4 ± 6.2
NICKEL	351.4 ± 4.8	352.9 ± 5.3	354.4 ± 5.4
MUMETAL	377.4 ± 6.3	381.6 ± 7.0	385.9 ± 7.2
PERMANORM 5	451.1 ± 6.7	455.0 ± 7.1	459.3 ± 7.3
TRAFOPERM	749.5 ± 10.9	752.1 ± 10.9	754.3 ± 11.0

In the present work, we have used simultaneous TG-DTA to determine accurate values for the transitions of these materials under normal operating conditions. In this technique the sample temperature is measured directly, thus eliminating the uncertainty in temperature measurement associated with conventional thermobalances. Since the DTA signal is measured simultaneously, the sample thermocouple can be calibrated directly using the melting points of pure metals.

The calibrated instrument was also used to determine extrapolated onset temperatures for the ICTA CRM's for DTA, Sets GM 758,GM 759 and GM 760 (ref.2) to enable their use as working standards for high temperature DTA and DSC calibration. These sets between them contain 8 inorganic salts with well defined solid-solid transitions covering the temperature range from 130°C to 930°C, and the metals indium and tin. The latter were not included in the present study since the instrument was calibrated with metals. The value of the solid-solid transitions for high temperature calibration is that they may be run in platinum and other metallic crucibles.

EXPERIMENTAL

All the experiments were carried out on a simultaneous TG-DTA instrument (Stanton Redcroft model STA-781), which features a precious metal plate-type thermocouple DTA head suspended from an electronic microbalance (ref.3). The samples were contained in alumina or platinum crucibles, 6mm diameter and 4mm in height, in direct contact with the plate-type thermocouples. For studies on the magnetic materials, horseshoe magnets were mounted on the case of the water-cooled furnace, below the DTA head, as shown in Fig.1. Precise temperature measurements were made by taking the direct thermocouple output, referred to an ice junction, to a potentiometric recorder (Servogor Model SE460). This was used exclusively on the 1mV range and calibrated regularly with a precision voltage source (Time Electronics Model 2003N) which was also used to offset the thermocouple output to read on scale. Measurement precision was estimated to be ± 0.2°C. The same recorder displayed either TG or DTA traces, and weight loss and peak parameters were determined manually.

The calibration of the thermocouples using pure metals (minimum purity 99.99%, ex Goodfellow Metals and Ventron Alfa Products) was carried out on 20 mg samples in alumina crucibles. Measurements at a series of heating rates on the fusion peaks of indium and gold showed no effective difference in the extrapolated onset temperatures for runs at 0.5 and 3°C min^{-1}, and the latter heating rate was therefore used for the thermocouple calibration.

The five ICTA TG reference materials, in the form of 4mm diameter discs, weighing between 9 and 20 mg, were measured at least in duplicate, at heating rates of 3 and 10°C min^{-1}, using alumina crucibles. A balance range of 2 mg full scale was used and the field strength was adjusted so that deflections of between 0.15 and 0.25 mg were obtained depending on the sample being studied.

The ICTA DTA reference materials were examined at 3°C min^{-1} using sample weights of approximately 20 mg in platinum crucibles. All the above runs were made in high purity argon flowing at 50 cm^3 min^{-1}.

RESULTS AND DISCUSSION

Calibration experiments using metals.

The values for the extrapolated onset temperatures for the metals run at 3°C min^{-1} for the two TG-DTA heads used in this work programme are given in Table 2, together with the equilibrium values (ref.4).

TABLE 2

Calibration of the STA-781 Simultaneous TG-DTA Unit Using Pure Metals

Metal	T extrapolated onset/°C		Equilibrium
	Head 1	Head 2	Value/°C
INDIUM	156.6 ± 0.2	156.6 ± 0.1	156.63
TIN	231.8 ± 0.1	-	231.97
ZINC	419.0 ± 0.1	418.9 ± 0.1	419.58
ALUMINIUM	659.8 ± 0.1	-	660.37
SILVER	-	960.7 ± 0.1	961.93
GOLD	1063.8 ± 0.5	1063.2 ± 0.2	1064.43

These results, which showed good precision, were used to provide corrections to the measured temperatures for the ICTA samples.

Results on the ICTA CRM'S for Thermogravimetry.

The results for the magnetic reference materials are given in Table 3. Typical curves are displayed in Fig.2, for nickel and Permanorm 5.

TABLE 3

Measured Values for ICTA CRM's for Thermogravimetry

Material		Temperatures/°C 3°C min^{-1}	10°C min^{-1}
	T_1	257.3 ± 0.6	258.2 ± 0.1
PERMANORM 3	T_2	261.2 ± 1.1	262.0 ± 0.7
	T_3	265.3 ± 1.3	266.3 ± 1.5
	T_1	356.4 ± 0.2	357.3 ± 0.3
NICKEL	T_2	357.1 ± 0.3	358.0 ± 0.4
	T_3	357.8 ± 0.4	358.8 ± 0.4
	T_1	382.4 ± 0.6	383.4 ± 0.2
MUMETAL	T_2	387.7 ± 1.8	387.4 ± 1.8
	T_3	393.2 ± 4.3	391.5 ± 3.1
	T_1	455.2 ± 0.3	457.1 ± 1.4
PERMANORM 5	T_2	458.3 ± 0.2	460.0 ± 2.2
	T_3	461.4 ± 0.4	463.3 ± 3.2
	T_1	745.2 ± 0.0	745.5 ± 0.1
TRAFOPERM	T_2	745.9 ± 0.2	746.2 ± 0.1
	T_3	746.4 ± 0.2	746.7 ± 0.0

The results on the whole show good reproducibility and, in agreement with the observations of Blaine (ref.5), do not show a marked dependence on heating rate. The curves for Mumetal showed considerable variation in peak shape and in view of the proximity of this transition to the well behaved nickel transition, it is suggested that Mumetal should be omitted from calibration procedures.

Although T_3 has been traditionally used as the favoured point in the magnetic calibration of thermobalances (ref.6) since it lies nearest to

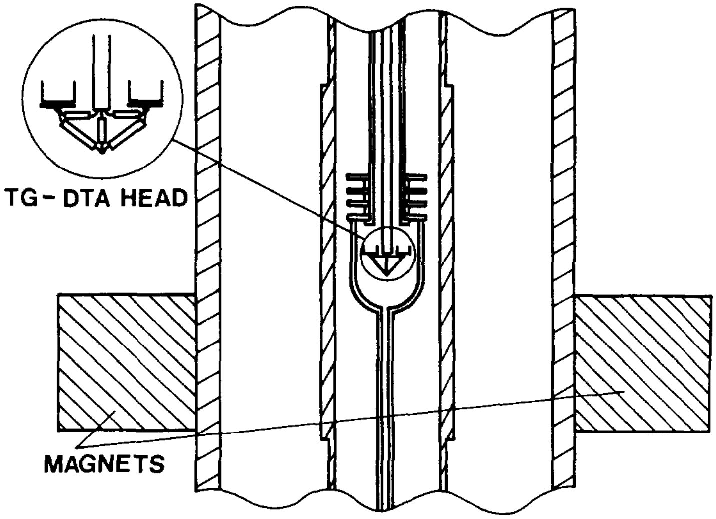

Fig.1. Cross-section of STA 781 head and furnace assembly.

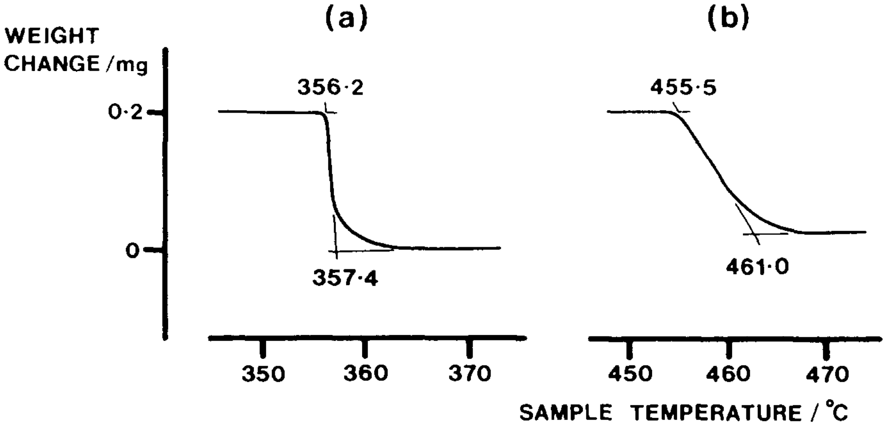

Fig.2. TG curves for (a) nickel (21.8 mg) and (b) Permanorm 5 (9.6 mg) 3°C min^{-1}, argon 50 cm^3 min^{-1}.

the theoretical Curie point (the point where ferromagnetism disappears completely) it is clearly is some distance from the Curie temperature, its value depending mainly on the rate of change of weight. The present work shows that better reproducibility is given by the T_1 construction (this corresponds to the extrapolated onset method widely used in DTA and DSC) and this may be preferable for accurate temperature work.

An initial limited study on the effect of magnetic field strength on the measured values for the transition temperatures, was carried out on nickel and Permanorm 5 using different magnet configurations giving deflections of 0.03 and 9% of the sample weight, in addition to the deflection of about 1% used in the main work programme.

For nickel, the three sets of measured temperatures at the different field strengths agreed within 1°C. In the case of Permanorm 5, a reduction of approximately 3°C was observed on changing from the lowest to the highest field strength for all three sets of temperatures. The reduction from the lowest to the normal field strength was less than 1°C in all cases. It would therefore appear that provided the ICTA recommendation that the minimum magnetic field strength required to obtain a measurable deflection is followed, the results should not be markedly dependent on field strength, where modern high sensitivity thermobalances are being used. Before commencing calibration work however, this should be verified for the experimental arrangement being used.

Comparison of the results with earlier work on the ICTA CRM's.for TG.

The T_3 values from the present study (using the values obtained at 10°C min^{-1}) are compared with those of the ICTA test programme (ref.1) in Table 4. The table also lists results obtained by Blaine (ref.5) using a thermobalance calibrated by the "dropping-weight" method (ref.7) and Garn's values, which represent estimates of the Curie points determined on a specially designed (non-thermogravimetric) apparatus.(ref.8).

The values for the present work fall well within the limits given by the ICTA programme. Overall the results are in reasonable accord, except for Garn's value for nickel which is somewhat high, and Blaine's values for Mumetal and Permanorm 5, which are exceptionally high and low respectively. Garn noted that, because of the tailing of the weight curve for nickel in the region of the Curie point, there would be a much greater difference between the Curie temperature and the T_3 value for this metal than for the three alloys that he tested. It is interesting to note that using his purpose-built apparatus Garn showed two transitions for Mumetal. The first in the region of 388°C, corresponding to T_3, was attributed to a discontinuity between two levels of ferromagnetism and the second, in the region of 404°C, to the end of all ferromagnetism. The value obtained by Blaine appears close to this latter value.

Table 4 Comparison of T_3 Values for ICTA CRM's for Thermogravimetry

MATERIALS	PRESENT WORK	GARN[1]	BLAINE[2]	ICTA MEAN VALUE
PERMANORM 3	266.3 ± 1.5	267	259.6 ± 3.7	266.4 ± 6.2
NICKEL	358.8 ± 0.4	364	361.2 ± 1.3	354.4 ± 5.4
MUMETAL	391.5 ± 3.1	388	403.0 ± 2.5	385.9 ± 7.2
PERMANORM 5	463.3 ± 3.2	457	431.3 ± 1.6	459.3 ± 7.3
TRAFOPERM	746.7 ± 0.0	-	756.2 ± 1.9	754.3 ±11.0

Measurements on ICTA CRM's for DTA.

The extrapolated onset temperatures for the eight ICTA DTA reference materials with solid-solid transitions are compared with those from the ICTA test programme (ref.2) in Table 5.

TABLE 5

Extrapolated Onset Temperatures for ICTA CRM's for DTA

Materials	Present Work	ICTA Values	Equilibrium Values/°C
KNO_3	129.8 ± 0.1	128 ± 5	127.7
$KClO_4$	300.8 ± 0.3	299 ± 6	299.9
Ag_2SO_4	427.2 ± 0.5	424 ± 7	430
SiO_2	573.3 ± 0.4	571 ± 5	573
K_2SO_4	585.3 ± 0.1	582 ± 7	583
K_2CrO_4	669.0 ± 0.1	665 ± 7	665
$BaCO_3$	807.4 ± 0.4	808 ± 8	810
$SrCO_3$	932.1 ± 0.4	928 ± 7	925

The measured extrapolated onset temperatures show good precision and a number of the reference materials, selected to cover a wide temperature span, are used in our laboratory for routinely checking the temperature calibration of high temperature DTA and DSC equipment, under normal operating conditions. If the determined values fall outside pre-set limits, then a clear indication is given of the need for head re-calibration using pure metals.

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REFERENCES

1. P.D.Garn, O.Menis and H.G.Wiedemann, J.Therm.Anal.,20 (1981) 185.
2. H.G.McAdie in: H.G.Wiedemann (Ed.), Thermal Analysis, Vol.1, Birkhauser Verlag, 1972, 591.
3. E.L.Charsley, J.Joannou, A.C.F.Kamp, M.R.Ottaway and J.P.Redfern in: H.G.Wiedemann (Ed.), Thermal Analysis, Vol.1, Birkhauser Verlag 1980, 237.
4. F.D.Rossini, Pure and Appl.Chem., 22 (1970) 557.
5. R.G.Blaine and P.G.Fair, Thermochim. Acta, 67 (1983) 233.
6. S.D.Norem, M.J.O'Neill and A.P.Gray, Thermochim. Acta, 1 (1970) 29.
7. A.R.McGhie, J.Chiu, P.G.Fair and R.L.Blaine, Thermochim. Acta, 67 (1983) 241.
8. P.D.Garn and A.A.Alamolhoda in: J.F.Johnson and P.S.Gill (Eds.), Analytical Calorimetry, Plenum Press, 1984, 33.