Thermochimica Acta, 67 (1983) 233–240
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

ESTIMATE OF THE "TRUE" MAGNETIC TRANSITION TEMPERATURES FOR THE ICTA REFERENCE MATERIALS GM761

ROGER L. BLAINE and PAUL G. FAIR
DuPont Company, Clinical and Instrument Systems Division, Wilmington, DE 19898 (U.S.A.)
(Received 1 March 1983)

ABSTRACT

New estimates were determined for the "true" magnetic transition temperatures of the ICTA Certified Magnetic Reference Materials GM761, using a six-point calibration method traceable to the standards of the International Practical Temperature Scale of 1968. These new estimate values have a pooled standard deviation of $\pm 2.0°C$, making them acceptable as temperature calibration materials for thermogravimetric apparatus.

INTRODUCTION

One of the most common methods of temperature calibration for thermogravimetric apparatus (TGA) uses the magnetic transition of ferromagnetic materials [1,2]. In this procedure, a magnetic material is placed in the TGA as the test specimen. A magnetic field is imposed on the material creating an apparent weight loss or gain as measured by the TGA. When the material is heated, the magnetic properties disappear over a narrow temperature range (i.e. the material becomes paramagnetic). The point at which the magnetic properties completely disappear, defined as the Curie temperature, is used as a point of temperature calibration. This approach has found wide appeal because of its ease of use and because it requires no instrument modification; however the technique is not without its difficulties. The most serious deficiency is the lack of readily available standard materials of known transition temperatures.

Under the auspices of the International Confederation for Thermal Analysis (ICTA), a set of magnetic reference materials has been selected and extensively tested by a number of laboratories. These well-tested materials are now commercially available from the United States National Bureau of Standards (Washington, DC 20234) as ICTA Certified Reference Materials for Thermogravimetry GM761. The specifically stated purpose for these reference materials is to permit correlation of results among instruments [3–5]. Because of their well-documented nature and reliable availability,

0040-6031/83/$03.00

however, the materials could serve as temperature calibration materials if their "true" magnetic transition temperatures (rather than experimental mean values) were known. It is the purpose of this report to provide such temperature values.

In this work, a commercial TGA was precisely temperature calibrated using the weight drop method of McGhie et al. [6]. The magnetic transitions of the ICTA Reference Materials were then determined and corrected for the instrument calibration. The precision of these new magnetic transition values was then calculated as a combination of the precision of their experimental determination and the precision of the calibration curve.

EXPERIMENTAL

All work was carried out using a DuPont 1090 Thermal Analyzer and 951 Thermogravimetric Analyzer. Transition temperatures were objectively determined using the General Analysis Utility program. A heating rate of 10°C min^{-1} under a 50 ml min^{-1} nitrogen purge gas was used throughout, unless otherwise noted.

The indium, lead, zinc, aluminum and silver temperature calibration samples were obtained from A.D. Mackay (Darien, CT 06820) as 0.25 mm or smaller wire of 99.99 + % purity. The gold sample, of similar diameter and purity, was obtained from Alfa Products (Danvers, MA01923). The melting temperatures of these six materials are all primary or secondary temperature standards for the International Practical Temperature scale and are known to better than 100th of a degree [7].

The Permanorm 3, Nickel, Mumetal, Permanorm 5 and Trafoperm magnetic transition samples were obtained from the United States National Bureau of Standards (Washington, DC 20234) as ICTA Certified Reference Materials GM761. They are supplied as thin metal sheets (0.1–0.2 mm in thickness) from which specimens of suitable size were cut with heavy-duty scissors.

TEMPERATURE CALIBRATION

The apparatus was initially calibrated at room temperature using the procedure described in the instrument operator's manual. This involves the adjustment of the "cold junction compensator" on the apparatus at room temperature equilibrium so that the instrument correctly indicates that temperature.

A more detailed temperature calibration was then carried out by the weight drop method of McGhie et al. [6]. In this method, fusible metal links are used to suspend a 50 mg platinum weight from a quartz support inside

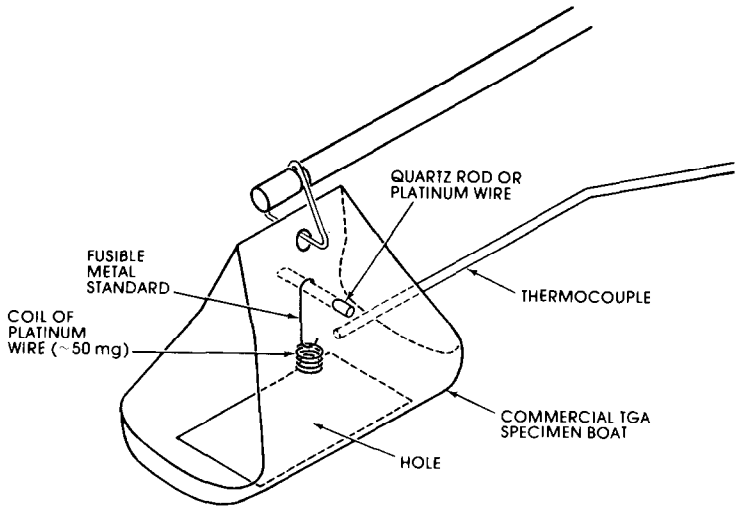

Fig. 1. Fusible link calibration. Dropping weight schematic.

the TGA sample boat (see Fig. 1). When heated through the melting temperature of the fusible link, the weight drops through a hole in the bottom of the sample boat. A sharp weight loss is thus produced on the thermal curve such as that shown in Fig. 2. The observed melting temperature may then be determined objectively using the "Onset Temperature" feature of the General Analysis Utility program. The observed melting

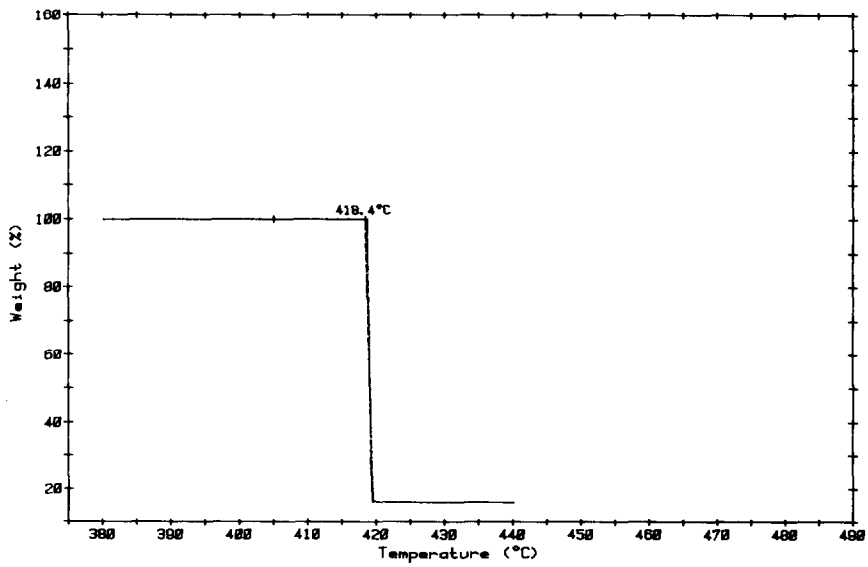

Fig. 2. Weight drop thermal curve.

TABLE 1

Dropping weight calibration data

Material	Obsd. temp. (°C)	Corrected temp. (°C)	Lit. temp. (°C)	Deviation from Lit. value (°C)
Indium	159.90 ± 0.97	154.20	156.63	−2.43
Lead	333.02 ± 0.91	331.05	327.50	3.55
Zinc	418.78 ± 1.08	419.68	419.58	0.10
Aluminum	652.23 ± 1.32	659.09	660.37	−1.28
Silver	945.90 ± 0.52	960.25	961.93	−1.68
Gold	1048.70 ± 0.87	1065.67	1064.43	1.24

temperatures for each of the six calibration metals (indium, lead, zinc, aluminum, silver, and gold) were recorded a minimum of three times. Mean values were calculated and are presented in Table 1 along with their respective standard deviations. The precision for each calibration material is quite consistent and shows no trend as a function of temperature. The pooled standard deviation for all determinations is ± 1.0°C.

The 23 individual experimental results were then compared with their respective literature values using the linear regression program of a Texas Instruments (Dallas, TX) model TI-59 calculator [7]. A straight-line slope of 0.9751 ± 0.0015 and an intercept of 9.53 ± 0.93°C were obtained. This calibration curve may be used to "correct" the observed temperature. Corrected temperatures, and their deviations from literature values, are also presented in Table 1. The data for lead at 327°C appears to be an outlier but could not be eliminated based upon the "95% confidence" test. Even with the data for lead included, the average variance of these mean values about the line is ± 2.0°C.

This best-fit linear calibration information may be entered into the 1090 Thermal Analyzer so that the future transition temperature data is collected. In this case, however, the temperature correction procedure was carried out manually external to the 1090 Thermal Analyzer so that the precision of the best-fit calibration line might be combined with the precision of the experimental determination of the magnetic transition temperatures.

MAGNETIC TRANSITION MATERIALS

The magnetic transitions of the GM761 reference materials were prepared by cutting strips from the sheet sample approximately 2 mm in width and 1 cm in length. These strips were then bent to form an inverted "V" and placed over the quartz support rod in the TGA boat. A small (less than 10%) apparent weight loss of the specimen was created by placing one of several

small "hobby" magnets on top of the TGA furnace directly over the test specimen. Some matching of magnets to sample was needed since the reference materials have differing magnetic susceptibilities and tended to "jump" out of the pan if too large a magnetic field is applied. This selection process was facilitated by the "Display Axis" key on the DuPont 1090 Thermal Analyzer reading specimen weight % directly on the instrument's display.

The specimens were then temperature programmed through their magnetic transition region and their apparent weight gain recorded. Using the "Onset temperature" feature of the General Analysis Utility program, the extrapolated endpoint of the magnetic transition was objectively measured as illustrated in Fig. 3. This corresponds with "T_3" reported by Garn et al. [3] for these materials and approximates the Curie temperature of the material (Curie temperature is defined as "the temperature below which the substance ceases to be paramagnetic").

The results of these series of tests are presented in Table 2. The precision of the experimental measurements vary from a low of $\pm 0.81°C$ for Nickel to a high of $\pm 3.2°C$ for Permanorm 3. This experimental precision is directly related to the temperature range of the magnetic transition. The narrowest magnetic transition temperature range of these five materials is Nickel with 3.0°C while the widest is Permanorm 3 with 13.1°C [3]. This experimental precision appears to be a nearly constant 23% of the reported transition ranges. Recognizing that differences in experimental precision exist, a pooled standard deviation of $\pm 2.0°C$ may, nonetheless, be calculated. This value is somewhat better than the intralaboratory mean standard deviation of $\pm 3.6°C$

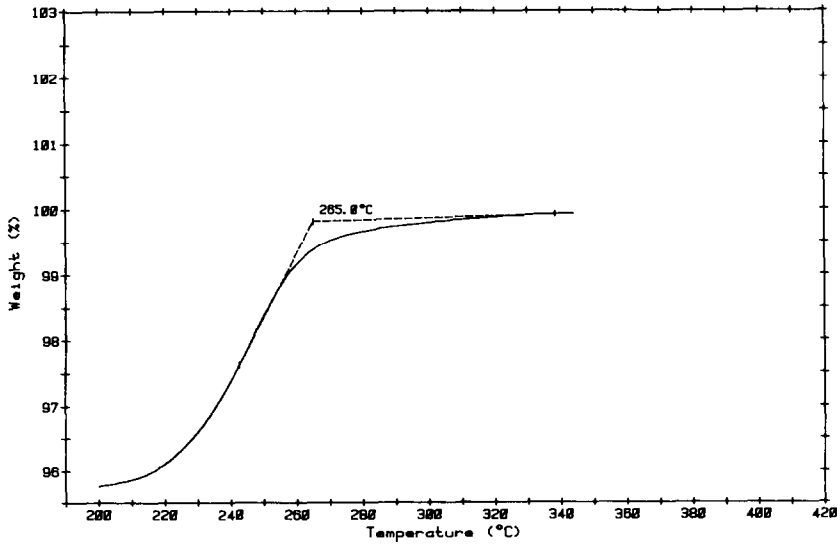

Fig. 3. Measurement of the extrapolated endpoint of the magnetic transition.

TABLE 2

Observed magnetic transition data

Material	No. of determinations	Mean temp. (°C)	S.D. (°C)
Permanorm 3	4	262.6	±3.2
Nickel	3	361.73	±0.81
Mumetal	3	402.5	±2.3
Permanorm 5	3	430.1	±1.1
Trafoperm	4	746.9	±1.2

and substantially better than the average precision ±7.7°C reported by Garn et al. [3] for the interlaboratory results on these materials. These experimental results were then corrected, using the linear calibration curve obtained above, producing an estimation of their true magnetic transition temperatures. These values are reported in table 3 along with estimations of individual precision based upon the individual experimental precision and the precision of the calibration curve calculated by the method of propagation of uncertainties [8].

These results are graphically compared, in Fig. 4, with the previously reported interlaboratory mean values for these materials reported by Garn et al. [3]. The abcsissa of this figure represents this estimation of the true magnetic transition values. The ordinate displays the deviation between these newly estimated values and the interlaboratory mean values. The imprecision of the interlaboratory values are indicated as bars on either side of the mean value.

Figure 4 shows that for three of the reference materials (Permanorm 3, Nickel and Trafoperm), the interlaboratory mean values lie within their 95% confidence level of this estimation of their true transition temperature values. For Mumetal and Permanorm 5, however, the interlaboratory mean values lie well outside this 95% confidence limit. This discrepancy between reported

TABLE 3

New estimates of magnetic transition temperatures

Material	Transition temp. (°C)		Deviation (°C)
	Experimental	Lit. (5)	
Permanorm 3	259.6±3.7	266.4± 6.2	−6.8
Nickel	361.2±1.3	354.4± 5.4	6.8
Mumetal	403.0±2.5	385.9± 7.2	17.1
Permanorm 5	431.3±1.6	459.3± 7.3	−28.0
Trafoperm	756.2±1.9	754.3±11.0	2.2

true values is particularly troublesome since the transition temperatures for Nickel, Mumetal and Permanorm 5 all lie within 80°C of each other. It would seem that confusion might rightly accrue to the user who attempeted

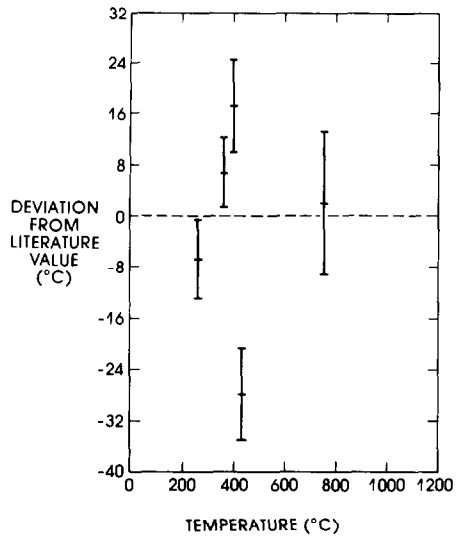

Fig. 4. Comparison of the magnetic transition temperatures obtained with the interlaboratory mean values reported by Garn et al. [3].

to use these three materials even for their stated comparison purposes. Conflicts of this nature are reported by Elder [9].

The interlaboratory results of Garn et al. [3] were collected at the heating rate of 1–2°C min^{-1}, while the present data were collected at 10°C min^{-1}. To test the effect of heating rate on observed transition temperatures, Nickel and Trafoperm specimens were tested in duplicate at four heating rates between 2.5 and 20°C min^{-1}. Average values for each heating rate were compared to that obtained at 10°C min^{-1}. Calculated deviation values are tabulated in Table 4 along with the pooled standard deviation for all eight determinations. When compared to the imprecision of each measurement, there appears to be no effect of heating rate on the observed transition

TABLE 4

Effect of heating rate deviation from observed temperature at 10°C min^{-1}

Material	Heating rate (°C min^{-1})				σ Pooled
	2.5	5	10	20	
Nickel	−0.9	−0.7		−0.4	±0.3
Trafoperm	0.4	−0.3		0.2	±0.6

temperature over at least one decade of heating rate change. This is in agreement with a similar observation for melting point standards [6].

CONCLUSION

New, "true" values are determined for the extrapolated endpoint of the ICTA Certified Magnetic Transition materials. The precision of these new values varies with the transition temperature range of each particular material but has a pooled standard deviation of $\pm 2°C$. This permits their use as secondary TGA temperature calibration materials over the temperature range 200–800°C. These materials must, however, be considered secondary temperature calibration materials compared with the more precise and larger temperature range of melting temperature standards [6].

REFERENCES

1 S.D. Norem, M.J. O'Neill and A.P. Gray, in H.G. McAdie (Ed.), Proc. 3rd Toronto Symp. Therm. Anal., 1969, Chemical Institute of Canada, 1969, p. 221.
2 S.D. Norem, M.J. O'Neill and A.P. Gray, Thermochim. Acta, 1 (1970) 20.
3 P.D. Garn, O. Menis and H.G. Wiedemann, J. Therm. Anal., 20 (1981) 185.
4 P.D. Garn, Thermochim. Acta, 55 (1982) 121.
5 ASTM Method E914.
6 A. McGhie, J. Chiu, P.G. Fair and R.L. Blaine, Thermochim. Acta, 67 (1983) 241.
7 F.D. Rossini, Pure Appl. Chem., 22 (1972) 557.
8 D.C. Baird, Experimentation, Prentice-Hall, Englewood Cliffs, NJ, 1962.
9 J.P. Elder, Thermochim. Acta, 52 (1982) 235.