

## An investigation of the ICTA certified reference materials for DTA as potential standards for the temperature calibration of thermomechanical analysis equipment <sup>α</sup>

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### Abstract

A preliminary study has been carried out to investigate the potential of the International Confederation for Thermal Analysis (ICTA) certified reference materials (CRMs) for DTA for the temperature calibration of thermomechanical analysis equipment. A thermomechanical analysis apparatus (TMA) operating over the range ambient to 1000 °C was calibrated using the melting points of pure metals and then used to characterise the dimensional changes associated with the solid–solid transitions of the ICTA DTA CRMs. The results have been compared with those obtained using a calibrated DTA apparatus and the materials which appear most suitable for TMA calibration have been identified.

### INTRODUCTION

The usual method for carrying out the temperature calibration of thermomechanical analysis equipment is to use the melting points of pure metals [1]. As has been discussed recently in connection with the calibration of DTA equipment [2], the International Confederation for Thermal Analysis (ICTA) certified reference materials (CRMs) for DTA offer an alternative method for temperature calibration on a routine basis. In particular they are easier to handle at high temperatures, as they do not react with platinum or other metallic crucibles and are not susceptible to oxidation.

It was therefore decided to determine whether the solid–solid transitions given by the ICTA CRMs for DTA, contained within sets GM 758,

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GM 759 and GM 760 [3], provided well-defined dimensional changes suitable for temperature calibration purposes.

#### EXPERIMENTAL

All the experiments were carried out on a Stanton Redcroft TMA 792 thermomechanical analyser, which operates over the temperature range ambient to 1000 °C. The metal samples were contained in 6 mm diameter inconel crucibles, 2 mm in height, which had been oxidised in air at 1000 °C to provide a non-reactive coating. The samples were covered with an oxidised inconel disc to avoid contamination of the TMA probe. For the ICTA CRMs, platinum crucibles, 6 mm in diameter and 4 mm in height, were used with a platinum disc on top of the sample.

A flat-tipped quartz probe, with a diameter of 5 mm, was used for all experiments. Sample temperatures were measured by an inconel-sheathed mineral-insulated chromel–alumel thermocouple adjacent to the sample crucible. The arrangement of the measuring system is shown schematically

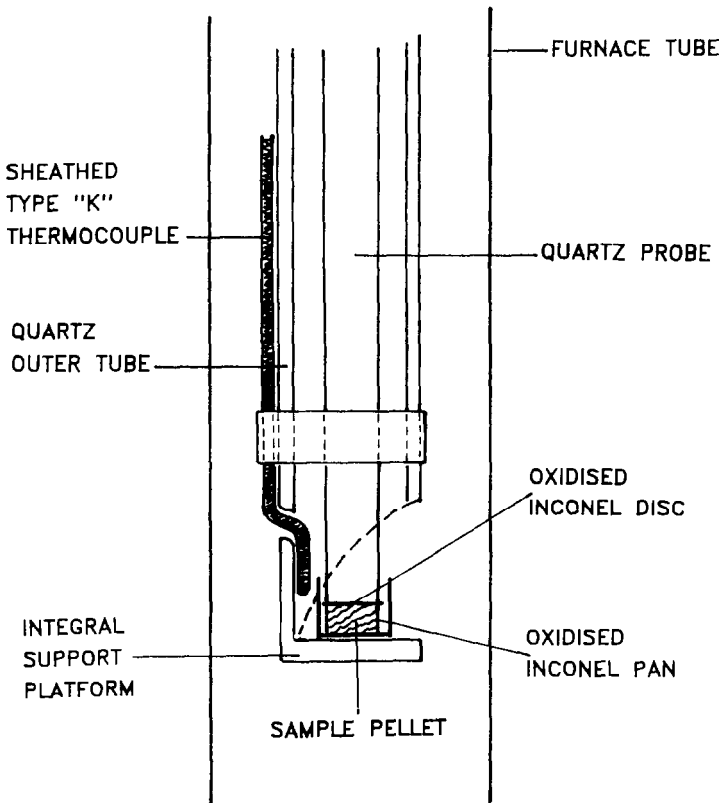


Fig. 1. Schematic of TMA measuring assembly.

in Fig. 1. Temperature measurements were made by taking the direct thermocouple output, referred to an ice junction, to a potentiometric recorder (Servogor Model SE 460). This was used on the 1 mV 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 better than  $0.1^{\circ}\text{C}$ . The same recorder was used to display the TMA trace and extrapolated onset temperatures were determined manually.

The initial calibration of the system using pure metals (minimum purity 99.99%, Goodfellow Metals and Ventron Alpha Products) was carried out using 20 mg samples of the materials as supplied in the form of finely divided powders. A heating rate of  $3^{\circ}\text{C min}^{-1}$  and a probe load of 20 g were used. All the runs were carried out in an atmosphere of nitrogen at a flow rate of  $50\text{ ml min}^{-1}$ .

For the ICTA CRMs, 50 mg samples were taken. These were evenly settled into the platinum crucible, the lid applied and the system pressed with a external load of 1 tonne. Measurements were made with a probe load of 10 g at a heating rate of  $3^{\circ}\text{C min}^{-1}$  in a nitrogen atmosphere. At least two runs were carried out on each material.

## RESULTS AND DISCUSSION

### *Calibration experiments using pure metals*

The mean values obtained for the extrapolated onset temperatures for fusion of the pure metal samples were subtracted from the equilibrium values for the melting points reported by Rossini [4], to give the temperature correction values. The errors in the measured values ranged from

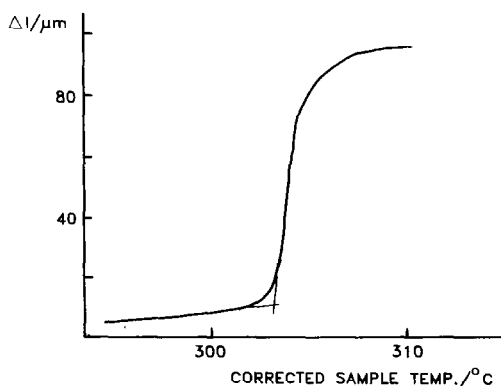


Fig. 2. TMA curve for potassium perchlorate: sample weight, 50 mg; heating rate,  $3^{\circ}\text{C min}^{-1}$ ; atmosphere, nitrogen.

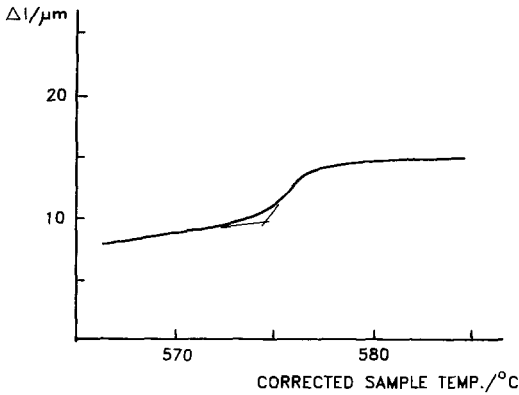


Fig. 3. TMA curve for quartz: sample weight, 50 mg; heating rate,  $3^{\circ}\text{C min}^{-1}$ ; atmosphere, nitrogen.

$-3^{\circ}\text{C}$  (In) to  $-21^{\circ}\text{C}$  (Ag). The need for temperature calibration procedures for TMA is thus clearly emphasised.

#### *Measurements on the ICTA CRMs for DTA*

The TMA experiments on the ICTA materials gave curves which showed different characteristics in the region of the solid–solid phase transitions.

Potassium perchlorate, quartz and potassium sulphate gave well-defined expansions during the phase change; these are illustrated in Figs. 2–4.

In the case of potassium chromate (Fig. 5), the sample also expanded during the phase change, but this expansion was superimposed on an overall contraction due to the sample sintering. The transition was nevertheless well defined.

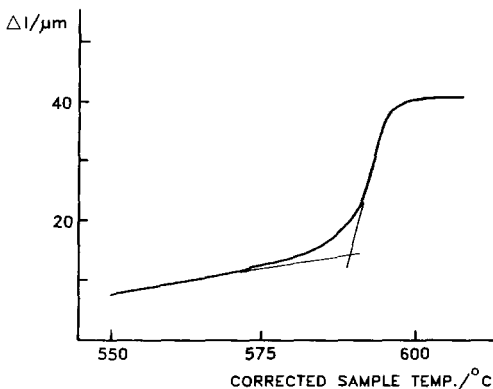


Fig. 4. TMA curve for potassium sulphate: sample weight, 50 mg; heating rate,  $3^{\circ}\text{C min}^{-1}$ ; atmosphere, nitrogen.

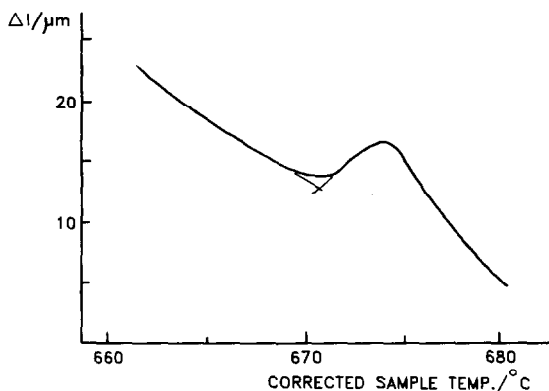


Fig. 5. TMA curve for potassium chromate: sample weight, 50 mg; heating rate,  $3^{\circ}\text{C min}^{-1}$ ; atmosphere, nitrogen.

For barium carbonate, the change due to the phase change was masked by the contraction due to sintering of the sample and could only be observed as a change in the rate of contraction (Fig. 6). Reheating the sintered sample, however, produced a well-defined expansion (Fig. 7).

The results for potassium nitrate showed some variability in the contraction observed during the phase change and in some cases this was not well defined. Further measurements were therefore not carried out in this preliminary programme. Similarly the study of silver sulphate was not continued after initial experiments had shown that the transition was poorly resolved at low heating rates.

The extrapolated onset temperatures for the selected materials, determined using the constructions given in the figures, are shown in Table 1,

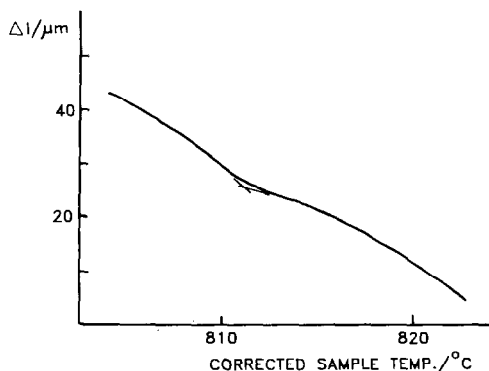


Fig. 6. TMA curve for barium carbonate (first heating): sample weight, 50 mg; heating rate,  $3^{\circ}\text{C min}^{-1}$ ; atmosphere, nitrogen.

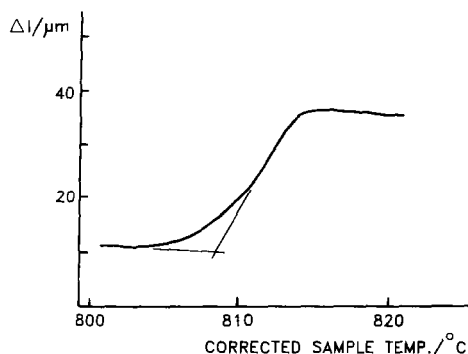


Fig. 7. TMA curve for barium carbonate (second heating).

together with the values from the ICTA programme and those measured using a calibrated DTA apparatus [2].

It can be seen from Table 1, that the extrapolated onset temperatures obtained from the TMA curves show good precision. In addition the temperatures are in reasonable agreement with the extrapolated onset temperatures determined by DTA.

From these preliminary experiments, a number of the CRMs appear to offer considerable potential as temperature calibrants for TMA equipment. As discussed previously in connection with the calibration of DTA equipment [2], the use of metals is preferred for initial calibration, but the ICTA CRMs can be used advantageously for monitoring the calibration on a regular basis. In the case of TMA, the use of metals needs more care than in DTA because in some cases sample deformation before melting can cause uncertainty in the determination of the extrapolated onset temperature. This problem is not experienced with the inorganic ICTA CRMs.

Further work now needs to be carried out to investigate the effect of sample form and weight, probe type and load, and the heating rate on the measured transition temperatures for the selected materials.

TABLE 1

Extrapolated onset temperatures for ICTA CRMs for DTA

Materials	Extrapolated onset temperatures (°C)		
	TMA	ICTA [3]	DTA [2]
KClO <sub>4</sub>	303.0 ± 0.5	299 ± 6	300.8 ± 0.3
SiO <sub>2</sub>	574.4 ± 0.5	571 ± 5	573.3 ± 0.4
K <sub>2</sub> SO <sub>4</sub>	588.6 ± 0.5	582 ± 7	585.3 ± 0.1
K <sub>2</sub> CrO <sub>4</sub>	671.2 ± 0.6	665 ± 7	669.0 ± 0.1
BaCO <sub>3</sub>	808.6 ± 0.7 <sup>a</sup>	808 ± 8	807.4 ± 0.4

<sup>a</sup> Second heating.

## CONCLUSIONS

Preliminary studies on the ICTA CRMs for DTA have indicated that several of the materials show potential for the routine temperature calibration of TMA equipment. Reproducible TMA transitions have been given by potassium perchlorate, quartz, potassium sulphate, potassium chromate and also by barium carbonate when a preliminary heating cycle had been carried out. The extrapolated onset values obtained by TMA were in reasonable agreement with those measured by DTA.

## REFERENCES

- 1 ASTM Standard E831-86, 1990 Annual Book of ASTM Standards, 14.02, p. 553.
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