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Note

Feasibility study on the determination of accurate temperature values for the ICTA certified reference materials: potassium chromate

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The International Confederation for Thermal Analysis (ICTA) has marketed Certified Reference Materials for thermal analysis since 1971 [1] through the National Bureau of Standards and now the National Institute of Standards and Technology. It is unlikely that these reference materials are now used in the way originally intended, i.e. to facilitate inter-laboratory comparisons by means of common standards. For present day temperature calibration requirements the certificate values lack both precision and accuracy because they were obtained using a variety of equipment, often without the possibility of accurate calibration.

The purpose of the present work is to establish the feasibility of using the ICTA materials for accurate temperature calibration of differential thermal analysers and differential scanning calorimeters. Temperature calibration is often treated in a cavalier fashion, the more so with modern equipment, which produces printouts of temperatures, usually to two decimal places. However, obtaining temperatures with a precision of a few tenths of a degree is demanding, both of the equipment and the experimental protocol. As a first step we have chosen to examine the suitability of ICTA potassium chromate for accurate temperature calibration. The temperature of the solid state phase transition has been compared with that of the melting of aluminium. The temperatures are sufficiently close to allow a single point calibration of the equipment.

We have used a range of thermal analysers from a differential thermal analyser with bead-type thermocouples to power compensated and heat

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TABLE 1

Equipment [a]

Laboratory	Instrument	Description
Thermal Analysis Consultancy	Du Pont 9900 DSC	Heat flux DSC constantan plate
	STA 1500, Stanton-Redcroft	Simultaneous TG/DTA, independent Pt/Pt–13%Rh disc thermocouples
	DTA 673, Stanton-Redcroft	Pt/Pt–13%Rh bead thermocouples in an alumina block
University of Leeds	STA 1500H, PL Thermal Sciences	Similar to STA 1500 above but fitted with Pt/Pt–13%Rh heat flux DSC plate
	DTA 673, Stanton-Redcroft	As above
NPL	Perkin-Elmer DSC 2	Power compensated DSC

[a] The measurements using the Perkin-Elmer DSC were carried out using platinum crucibles with the samples supported on a mica disc.

flux differential scanning calorimeters. The details are shown in Table 1. The aluminium was in the form of wire (99.999% pure, Goodfellows Metals). A single batch was used by the participating laboratories. Wire was used instead of powder because it was considered less prone to oxidation in the event of residual oxygen remaining in the apparatus. The potassium chromate was the ICTA standard material. The single point temperature calibration was carried out using the procedure specified by ASTM [2]. The melting temperature of aluminium was taken to be 660.37°C [3]. Duplicate measurements were made on two samples of aluminium and potassium chromate. The sample mass was in the range 5–25 mg, depending on the sensitivity of the equipment. The samples were heated in alumina crucibles with loose fitting lids at 3°C min^{-1}, starting the experiments at least 50°C below the transition temperatures. An atmosphere of high purity nitrogen

TABLE 2

Transition temperature of ICTA potassium chromate

Laboratory	Instrument	Transition temperature (°C) [a]
Thermal Analysis Consultancy	Du Pont 9900 DSC	669.2 ± 0.1
	STA 1500	669.0 ± 0.1
	DTA 673	668.9 ± 0.2
University of Leeds	STA 1500H	668.9 ± 0.1
	DTA 673	669.3 ± 0.2
NPL	Perkin-Elmer DSC 2	669.2 ± 0.2

[a] Mean 669.1 ± 0.2.

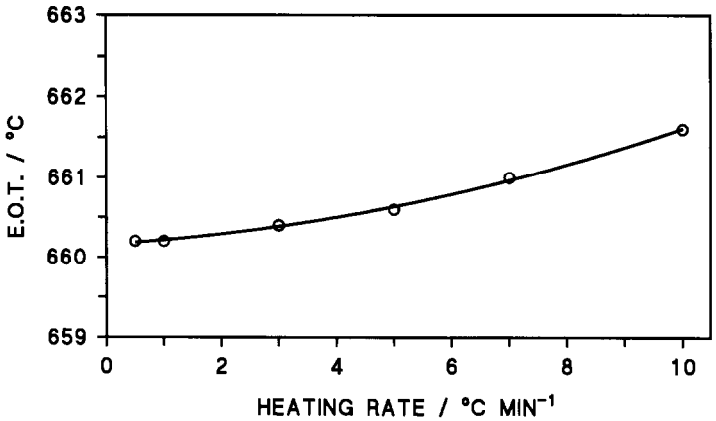

Fig. 1. Variation of the extrapolated onset temperature (EOT) with heating rate for the fusion peak of aluminium.

was maintained in the apparatus. The extrapolated onset temperatures were measured with a resolution of 0.1°C.

The experimental results for potassium chromate are listed in Table 2. The precision of the results and the agreement between different laboratories (and from different equipment) is the most encouraging. A similar precision was shown in the calibration experiments. The melting peak of aluminium was generally sharp but in a small number of experiments the first melting led to a slightly distorted peak shape and the calibration result was rejected. The dependence of the measured transition temperatures of both materials on the heating rate has been investigated. The results obtained with the STA 1500 equipment are shown in Figs. 1 and 2. The dependence of the extrapolated onset temperature on heating rate ($\leqslant$3°C min^{-1}) was similar for both materials and the effect of extrapolation

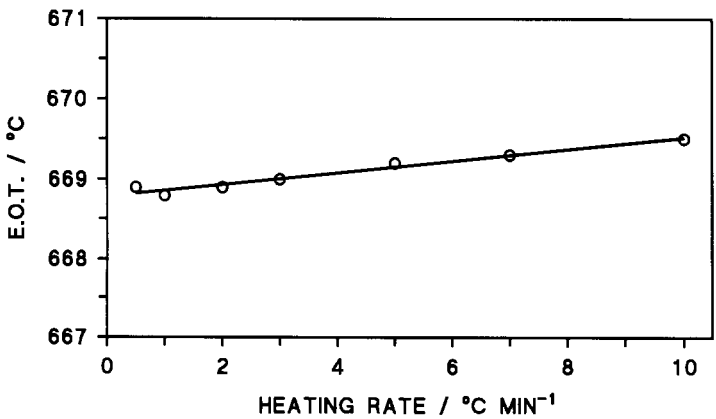

Fig. 2. Variation of the extrapolated onset temperature (EOT) with heating rate for the solid–solid transition peak of ICTA potassium chromate.

to zero heating rate was to decrease the temperature by less than 0.2°C. The present results point to the suitability of potassium chromate for development as an accurate temperature standard.

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