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TEMPERATURE CALIBRATION OF THERMOGRAVIMETRIC EQUIPMENT

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ABSTRACT

The dropping weight technique for temperature calibration has been investigated using equipment which allows both thermogravimetric and differential thermal analysis measurements. The results offer a partial validation of the technique but the general prediction of optimum experimental conditions can only be tentative.

INTRODUCTION

The temperature calibration of thermogravimetric equipment is seldom straightforward since its design generally rules out the direct measurement of sample temperature. A number of different approaches to the calibration have been adopted including the use of samples exhibiting magnetic transition [1]. Recently McGhie et al. [2] investigated the use of a dropping weight technique in which a small weight is released from a fusible metal wire link when the temperature inside the apparatus reaches the known melting temperature of the wire. The authors concluded that the precision of the calibration was significantly better than that acheived with magnetic samples. Furthermore, the technique has the obvious merit of using the same materials as those commonly employed in the calibration of differential thermal analysers and differential scanning calorimeters. Even so, some ambiguity necessarily arises in the interpretation of the results since there is no independent check on the validity of the technique. In the present work we have investigated the dropping weight technique with the Stanton Redcroft thermal analyser (model 781). This equipment has a considerable advantage over that used in the previous work (Du Pont) by allowing both thermogravimetric and differential thermal analysis measurements. Thus we have been able to compare the technique directly with conventional calibration measurements using powdered metals.

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EXPERIMENTAL

The Stanton Redcroft simultaneous thermal analyser consists of two platinum – 13% rhodium, platinum plate thermocouples suspended from a 5 g capacity electrical microbalance. The hangdown assembly incorporates ceramic baffles which enclose the thermocouples in a ceramic "micro-environmental" cup inside the furnace. The instrument provides a record of both the thermogravimetric and differential thermal analysis curves.

The calibration experiments were carried out using gallium, indium, tin, lead, aluminium and gold ($\geqslant$ 99.99% pure) obtained from Koch Light and Goodfellows. Gallium was used in the form of foil and the other metals as both fine powders and wires (0.25 mm in diameter). The experiments with the metal powders used samples weighing 30 mg. Indium, tin and lead were pressed between aluminium crucibles previously washed in dichloromethane and dried. Aluminium was used in inconel crucibles and gold in thin quartz crucibles. The arrangement for the dropping weight experiments is shown in Fig. 1. The wire link (4–5 mm in length) was attached to the quartz hook which passed through the lowest ceramic disc. The wire was immediately above a sample crucible and supported a weight made of platinum wire (0.2

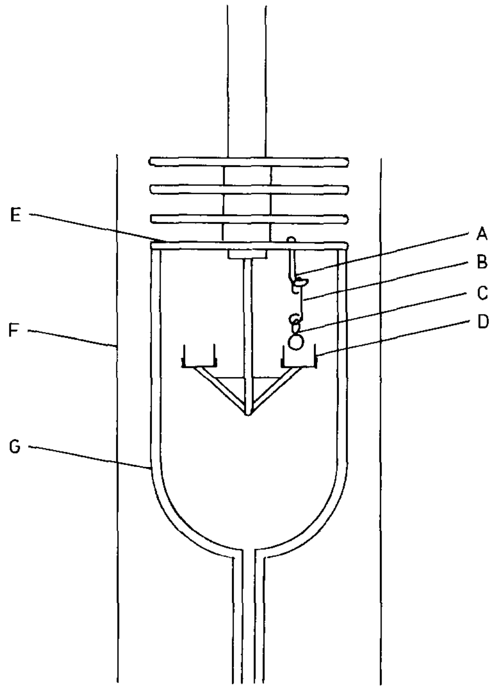

Fig. 1. Hangdown assembly modified for the dropping weight experiments. A, quartz hook; B, metal wire link; C, platinum weight; D, crucible; E, ceramic disc; F, furnace; G, ceramic cup.

mm diameter) just inside the crucible. This weight was 50 mg, except with indium and aluminium where it was changed to 20 and 100 mg respectively. For indium the change was necessary to ensure that the link retained its shape. The increase in weight with aluminium was needed to obtain a clean break at the melting temperature. The experiments with gallium used the foil either in alumina crucibles or made into a link between the quartz hook and the platinum weight.

The results were recorded on a chart recorder. The melting temperature of the powders was identified with the extrapolated onset temperature whereas that of the wires was taken as the temperature corresponding to the sudden increase in weight of the sample crucible. A precision voltage source was used to back-off the temperature signal to increase the precision of the measurements. The experiments were carried out in an argon atmosphere (20 cm^3 min^{-1}) at a heating rate of 10°C min^{-1}, except with gallium where it was reduced to 1°C min^{-1} to ensure that a linear rate was established before the melting temperature was reached.

RESULTS AND DISCUSSION

The results of the calibration experiments are given in Table 1. The mean experimental errors are ±0.1°C with the metal powders and ±0.6°C with the wires. The success of the dropping weight technique depends inter alia on the uniformity of the temperature distribution in the furnace and the nearness of the wire to the conventional position of the sample. The close agreement between the results obtained by the two methods offers some validation of the dropping weight technique. We have observed that a change in the value of the platinum weight or the heating rate may affect the results so that it is difficult to predict the optimum experimental conditions for other equipment. Reducing the heating rate from 10 to 1°C min^{-1}

TABLE 1

Results from the calibration experiments

Metal	Lit. value [a]	Melting temperature (°C)		ΔT [b] (°C)
		T_1, powder	T_2, wire	
Gallium	29.8	30.7	31.4	−0.7
Indium	156.6	156.1	156.8	−0.7
Tin	231.9	231.2	231.3	−0.1
Lead	327.5	326.8	326.6	0.2
Aluminium	660.4	656.2	657.0	−0.8
Gold	1064.4	1063.2	1063.9	−0.7

[a] Values taken from refs. 3 and 4.

[b] $\Delta T = T_1 - T_2$.

lowered the apparent melting temperature of the wires, significantly for aluminium and gold. For aluminium the result changed from being higher to lower than the melting temperature of the powder and in principle we may select a heating rate to eliminate the discrepancy. The results were unaffected by changing the atmosphere to static argon but became erratic when high flow rates (> 40 cm^3 min^{-1}) were introduced.

The Stanton Redcroft equipment also allows us to carry out the two techniques simultaneously. The experiments are of interest because of their novelty. Both measurements were carried out on the sample thermocouple side of the hangdown assembly since we observed a small temperature asymmetry across the thermocouples. However, the unusual configuration gave rise to a slightly increased discrepancy between the results with the apparent melting temperature of the wires consistently less than that of the powders.

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