

## THERMOGRAVIMETRIC APPARATUS TEMPERATURE CALIBRATION USING MELTING POINT STANDARDS

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### ABSTRACT

Temperature calibration of thermogravimetric apparatus is demonstrated using a dropping weight and fusible links made from melting point temperature standards of the International Practical Temperature Scale of 1968. Precision of the individual measurements is  $\pm 1.1^\circ\text{C}$ . When used with a DuPont 951 Thermogravimetric Analyzer, temperature calibration to within  $\pm 2^\circ\text{C}$  is obtained with a single linear calibration curve over the full  $1200^\circ\text{C}$  temperature range of the instrument.

### INTRODUCTION

Temperature calibration of thermogravimetric apparatus (TGA) is a problem which has faced the thermal analysis community since its earliest days. In thermogravimetric experiments, the specimen temperature is usually indirectly measured. The independent experimental parameter, "temperature", may actually be derived from a measurement made of the environment temperature near (within a few mm) the test specimen, the environment far from (within a few cm) the test specimen, the furnace temperature or even time multiplied by the heating rate, depending upon the design of the particular TGA. Instruments of different design also show differing dependencies of the indicated "temperature" to changes in heating and purge gas rates.

Early attempts at TGA temperature calibration were based upon reproducibly defined portions of the weight loss thermal curves for proposed standard materials. These procedures were abandoned because large impreci-

sions (i.e.  $> 25^{\circ}\text{C}$ ) were obtained among workers [1,2].

A second approach was that of measuring the point at which specimen heating became discontinuous as it underwent a large enthalpic transition [3]. This technique showed good precision but did not find wide use because of the required equipment design.

A third approach used magnetic transitions as a means of temperature calibration [4,5]. In this procedure, a magnetic material was heated in the TGA under the influence of an imposed magnetic field. The material lost its magnetic properties (i.e. became paramagnetic) over a narrow temperature range. This was observed as an apparent weight gain (or loss, depending upon the location of the magnetic field). The temperature of this transition, called the Curie temperature, was then used for calibration. This technique has gained widespread use because it is applicable to many instrument designs and requires no instrument modification. It is not totally acceptable, however, because of the modest precision of the measurement,  $\pm 3.6^{\circ}$  [6], and the lack of availability of certified calibration materials of known or specified transition temperatures.

Under the auspices of the International Confederation for Thermal Analysis (ICTA), a set of magnetic reference materials was 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 published results reflect only mean values, however, and are suitable, therefore, only for interlaboratory correlations and not for calibration [6]. Moreover, the mean values for several of these materials are dramatically at variance with values obtained by other calibration methods [7,8].

Fortunately, most intralaboratory thermogravimetric work does not require high accuracy temperature calibration. A large majority of the weight loss curves observed in thermogravimetry cover several tens of degrees and thus highly accurate temperature calibration is not required. In addition, much work records only differences between materials run on the same instrument rather than measuring absolute values. Provided the same experimental conditions are used from one experiment to the next, differences among specimens are easily observed without high accuracy temperature calibration. The exception to this fortuitous situation is the determination of decomposition kinetic parameters. The value for activation energy may be obtained without temperature calibration, but the estimation of the reaction rate constants or the pre-exponential factor requires accurate temperature information.

In this work, the use of the melting temperature of highly pure materials as a means of calibration is investigated. The use of the melting transition for temperature calibration has powerful precedence. The melting temperatures of several highly pure metals are the basis for the International

Practical Temperature Scale of 1968 [9]. The transition temperatures are, therefore, well defined to within a few hundredths of a degree. Moreover, these same materials are commonly used in the temperature calibration of differential scanning calorimeters and differential thermal analyzers [10].

In this approach, a small inert platinum weight is suspended within a TGA sample boat using a fusible link composed of the temperature calibration material. When the apparatus is temperature programmed through the melting region of the calibrant, the platinum weight is released. The weight is either caught in the sample boat, producing an "action/reaction" blip on the thermal curve, or is dropped through a hole in the bottom of the sample boat producing a dramatic, discontinuous weight loss. These events may then be used to calibrate the TGA for the experimental conditions used.

Carrying out temperature calibration within a typical specimen boat (rather than suspending the calibrant in lieu of the boat) is desirable since the high conductivity of the metal boat produces a very uniform temperature environment where the effects of radiation (either into or out of the boat) are minimized. This experimental arrangement also more closely approximates the test specimen environment.

## EXPERIMENTAL

All work was performed with a DuPont 1090 Thermal Analyzer and 951 Thermogravimetric Analyzer. The sample thermocouple was placed inside the sample boat and as close as was practical to the test specimen. The apparatus was initially calibrated at room temperature using the procedure described in the instrument operator's manual. Data analysis was carried out using the General Analysis Utility program. A nitrogen purge gas at 50 ml min<sup>-1</sup> was used, unless otherwise noted.

The indium, tin, lead, zinc, aluminum, and silver standards were obtained as 99.99 + % purity wires of 0.25 mm or smaller diameter from A.D. Mackay Company (Darien, CT 06820). The gold standard was of similar diameter and purity but was obtained from Alfa Ventron (Danvers, MA 01923).

Two experimental procedures were used. In the first case, the so-called "action/reaction" technique, a fine platinum wire, nominally 0.34 mm diameter and 2 cm in length, is flattened at one end and spot-welded to the outside of a standard DuPont platinum sample boat (part No. 950166-901). The wire is then carefully bent into a "U" shape so that the cantilevered end is located at the center of the sample boat (see Fig. 1). Suspended from this wire support, by a fusible metal link, is a platinum weight of about 50 mg. The weight was prepared by tightly winding a quantity of 0.25 mm platinum wire. One loop of the wire is distended to provide a convenient connecting "loop". The fusible metal link is made from a nominal 5 mm length of the wire temperature standards bent to a sigmoid shape. When this suspension

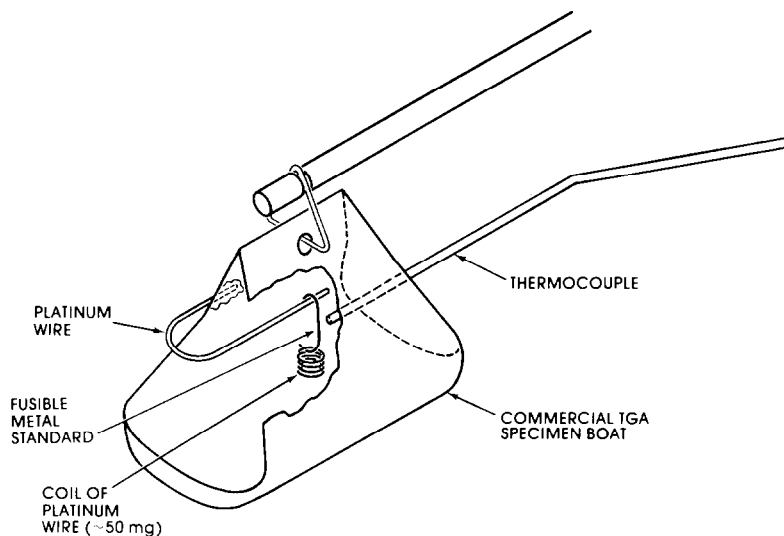


Fig. 1. Fusible link calibration. Welded wire schematic.

system is heated, the fusible link melts and the weight falls into the sample boat. This produces an “action/reaction” blip on the recorded thermal curve without any weight loss. A typical thermal curve is shown in Fig. 2. The recorder action is small and fast and must ordinarily be observed at high sensitivity and data acquisition rates. The measurement of the transition

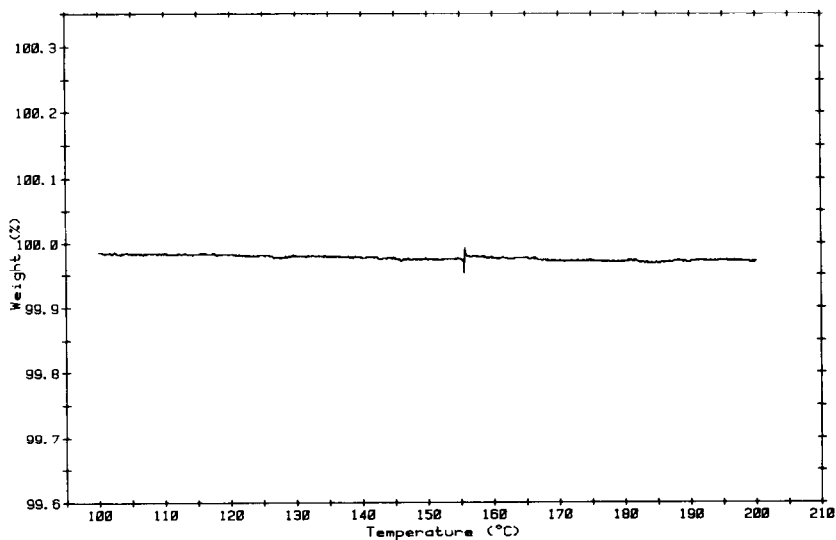


Fig. 2. Action/reaction thermal curve.

temperature for the “action/reaction” blip is determined by manual means, since data analysis programs typically treat events of this nature as “noise”.

While this technique works well, several real and potential difficulties were encountered, the most troublesome of which was “alloying” of some of the temperature standard materials (notably silver and gold) with the platinum wire support and the sample boat itself. Ultimately, “alloying” leads to holes being eaten in the boat bottom, making the boat unusable. To overcome this difficulty and to give a sharper transition indication, a second procedure, that of the “drop technique” was carried out. This approach is similar in principle but instead of a platinum wire support, a quartz rod was used and instead of catching the falling weight within the sample boat, it is allowed to fall through a hole cut in the bottom of the sample boat. The surplus fusible metal and platinum weight are retained by the quartz furnace tube and are easily recovered upon cooling.

The sample boat was created, again, by modification of a commercial DuPont platinum sample boat. Holes are pierced in either side of the boat far up on the sides using a needle. Through these holes is threaded a short length of small diameter quartz rod. (In this case, a surplus quartz balance arm rod, part No. 950162-901, was used.) This rod is a nominal 1 mm diameter and is used to support the suspended fusible link and weight.

The hole in the boat bottom is cut, from the inside out, using an Exacto<sup>®</sup> knife with a triangular shaped blade, cutting through the boat onto a soft surface. Figure 3 illustrates this experimental arrangement, and a typical thermal curve thus obtained is shown in Fig. 4. The transition temperature is objectively determined using the “onset temperature” feature of the General Analysis Utility program on the 1090 Thermal Analyzer.

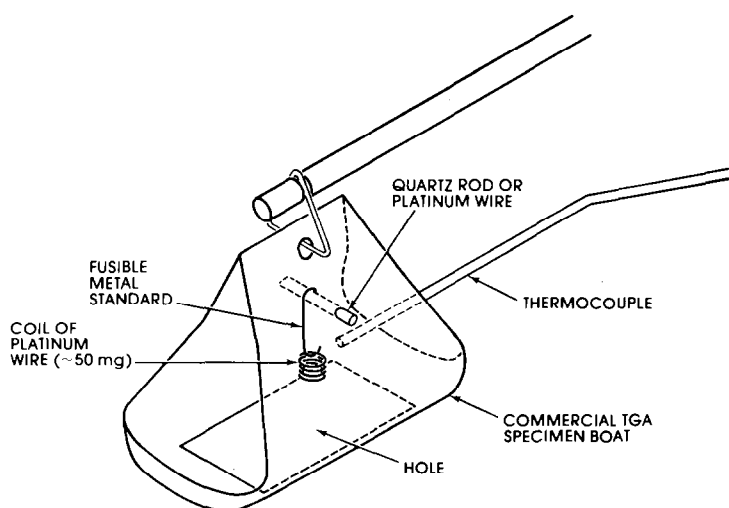


Fig. 3. Fusible link calibration. Dropping weight schematic.

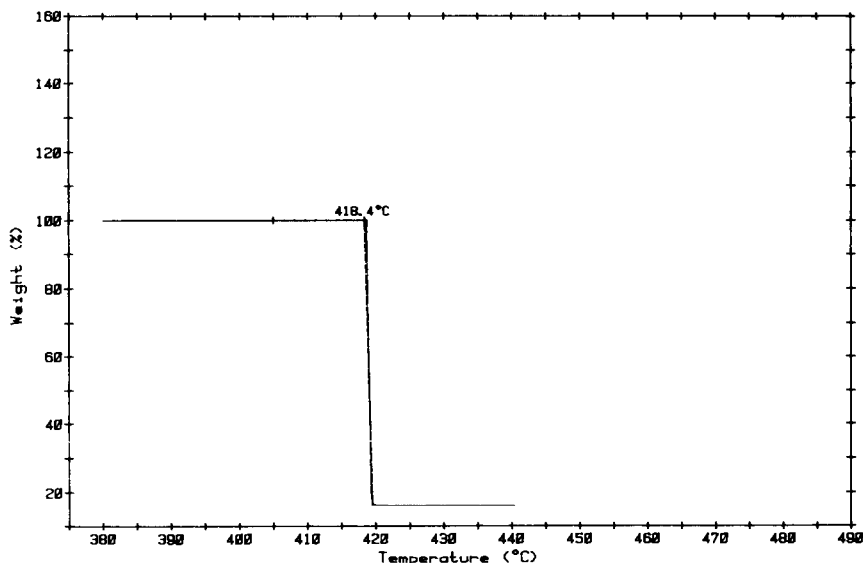


Fig. 4. Weight drop thermal curve.

## DISCUSSION

Using the “action/reaction” technique, the transition temperatures for six metal temperature standards, ranging from 157°C (indium) to 962°C (silver) were observed in triplicate. The mean values and standard deviations for these individual metal determinations are presented in Table 1.

These mean values may be compared to the “true” transition temperatures for these standards [9] and deviation values calculated. The deviations are plotted vs. temperature in Fig. 5, where the error bars reflect the pooled standard deviation of  $\pm 1.7^\circ\text{C}$  observed for all 18 observations. Qualitatively, the shape of the curve generated by these data points is concave

TABLE 1

Action/reaction calibration data

Material	Obsd. temp. ( $^\circ\text{C}$ )	Corrected temp. ( $^\circ\text{C}$ )	Lit. temp. ( $^\circ\text{C}$ )	Deviation from lit. value ( $^\circ\text{C}$ )
Indium	$157.00 \pm 0.90$	155.72	156.63	-0.91
Tin	$233.25 \pm 0.66$	232.45	231.97	0.48
Lead	$329.75 \pm 0.75$	329.56	327.50	2.06
Zinc	$420.92 \pm 3.4$	421.31	419.58	1.73
Aluminum	$659.50 \pm 0.87$	661.40	660.37	1.03
Silver	$956.75 \pm 1.80$	960.52	961.93	-1.41

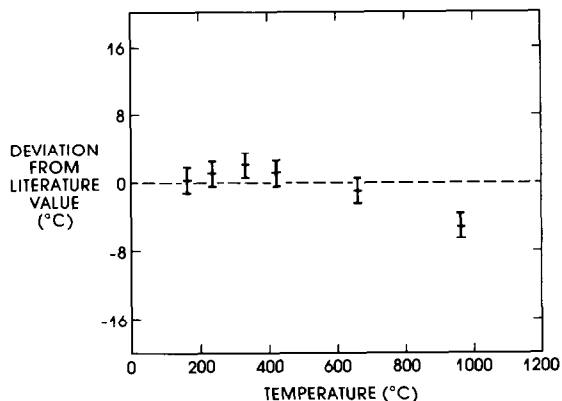


Fig. 5. Observed melting temperature. Action/reaction technique.

downward, with deviations from the expected linear calibration being more pronounced at higher temperatures. In a quantitative sense, however, this deviation is not more than a few degrees until temperatures in excess of 700°C are attained.

To enhance the instrument calibration, the individual observed transition temperatures were compared to the “true” values [9] using a least-squares best-fit straight line creating a linear calibration curve. The corrected melted temperatures (obtained from this linear calibration curve) are tabulated in Table 1 and are plotted in Fig. 6. Under these conditions, the corrected transition temperatures all lie within  $\pm 1.7^\circ\text{C}$  of the calibration curve over the temperature range of ambient temperature to 1000°C.

In a second set of experiments, the “drop technique” was used with another set of six metal temperature standards. In this case, the low

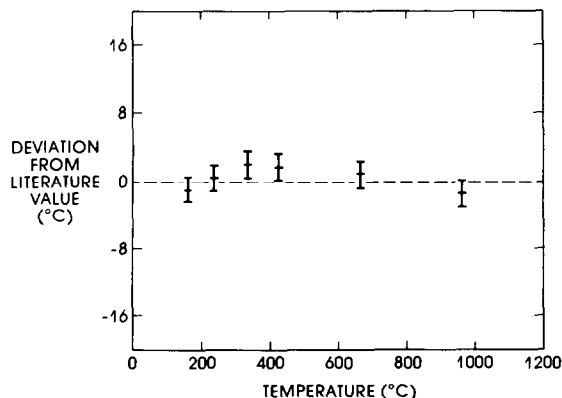


Fig. 6. Corrected melting temperature. Action/reaction technique.

temperature tin standard was replaced with a high temperature gold standard. These results (minimum of triplicated determinations) are tabulated in Table 2.

When the observed melting points are compared to the "true" values, again the deviation generally increases with increasing temperature, as illustrated in Table 2. When a least-squares best-fit straight line calibration curve is calculated and the experimental values thus corrected, the maximum deviations are reduced to  $\pm 2.4^\circ\text{C}$ . This information is shown in Fig. 7.

Comparing the two approaches to temperature calibration, it appears that the two methods are equally precise at about  $\pm 1.1\%$ . The  $\pm 1.7$  pooled standard deviation observed for the "action/reaction" approach is reduced to  $\pm 1.1$  if the value for zinc is discarded, as one might do based upon the "95% confidence" test. This is equivalent to the  $\pm 1.0$  value observed for 23 determinations of the dropped weight approach.

Both approaches indicate that the uncorrected temperature response of the instrument is accurate to within  $\pm 2^\circ\text{C}$  below about  $500^\circ\text{C}$ , the region where most polymer characterization is carried out. Above  $500^\circ\text{C}$ , both techniques show increasing deviation from the "true" value with increasing temperature.

Both techniques indicate, however, that temperature calibration to within  $\pm 2^\circ\text{C}$  may be obtained over the complete  $1200^\circ\text{C}$  temperature range of the instrument using a linear calibration curve. This curve may be directly entered into the 1090 Thermal Analyzer and used for future work.

Practical experimental considerations appear to dictate which of the two techniques one might use. The "action/reaction" approach offers the benefit of calibration in an environment most closely aligned to actual experimental conditions (i.e. the sample surrounded by the temperature equalizing platinum boat). In addition, the potential is offered of more than one temperature calibration during a given experimental run or running a calibration simultaneously with an actual test specimen.

The "action/reaction" technique is not without its problems. In addition

TABLE 2  
Dropping weight calibration data

Material	Obsd. temp. ( $^\circ\text{C}$ )	Corrected temp. ( $^\circ\text{C}$ )	Lit. temp. ( $^\circ\text{C}$ )	Deviation from lit. value ( $^\circ\text{C}$ )
Indium	$159.90 \pm 0.97$	154.20	156.63	-2.43
Lead	$333.02 \pm 0.91$	331.05	327.50	3.55
Zinc	$418.78 \pm 1.08$	419.68	419.58	0.10
Aluminum	$652.23 \pm 1.32$	659.09	660.37	-1.28
Silver	$945.90 \pm 0.52$	960.25	961.93	-1.68
Gold	$1048.70 \pm 0.87$	1065.67	1064.43	1.24



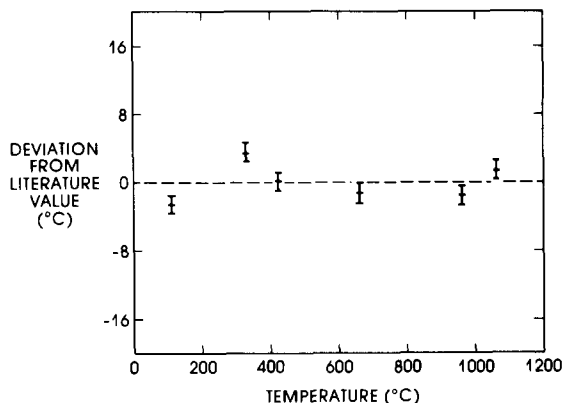


Fig. 7. Corrected melting temperature. Dropping weight technique.

to the problem with “alloying”, there is the difficulty in loading the fusible link and weight. This is due to the operator’s view being axial to the supporting wire. In addition, some of the softer metal standards tend to “stretch” prior to melting. This “stretching” of the link may actually lower the weight until it rests on the bottom of the sample boat. Thus, when the fusible link melts, no blip is seen on the thermal curve.

Another limitation with this technique is that the data acquisition rate must be fairly high, 0.5 s per point or better, when used with digital data recording. If longer data acquisition times are used, the “action/reaction” blip may actually be smoothed by the analog-to-digital converter used to collect data.

The dropping ball technique overcomes some of these handicaps. Loading of the sample is easier because the suspending rod is located perpendicular to the operator’s view. In addition, if the fusible link “stretches”, the weight is just partially lowered through the hole in the bottom of the boat. Of course, alloying problems are minimized by the inert quartz support and the non-retention (in the platinum boat) of the melted fusible link.

Determination of the transition temperature is much easier with the dropping ball technique since a very large, discontinuous signal is obtained which can be easily and objectively analyzed using data analysis programs. Similarly, the determination of the transition is not data acquisition rate sensitive provided data are collected fast enough to obtain the desired temperature precision or resolution. However, this technique is not without its own set of difficulties. The hole in the boat bottom and use of an insulating support (quartz) material provide an environment which may not be the same as that of a test specimen. This was suggested by different linear calibration curves being obtained by the two techniques. In addition, the short length of the quartz support makes it difficult for more than one

standard material to be tested in a given experiment. Moreover, an unknown specimen may not be run at the same time as the calibration run. Finally, the dropping weight technique is only useful on the horizontal balance and some vertical hang-down instrument designs, where a hole may be cut in the bottom of the sample boat. The "action/reaction" technique, however, appears to be adaptable to most instrument designs.

A comparison of either of these fusible link methods with earlier calibration techniques shows clear advantages. The measurement precision of these fusible link methods is at least twice as good as that of the calibration based upon magnetic standards [5,7]. This high precision, coupled with the ready availability of high purity calibration standards, makes the melting point temperature calibration procedure the calibration method of choice for thermogravimetric apparatus.

#### ACKNOWLEDGEMENT

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