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THE USE OF MAGNETIC TRANSITIONS IN TEMPERATURE CALIBRATION AND PERFORMANCE EVALUATION OF THERMOGRAVIMETRIC SYSTEMS

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Acceptable standard materials for the temperature calibration of a TGA apparatus are not common. Transitions or decompositions which involve loss of a volatile product are usually irreversible, non-isothermal, and controlled by kinetic factors. As an example, Fig. 1 shows a thermogram in both TG and DTG modes of calcium oxalate monohydrate in flowing nitrogen. Under these conditions the observed temperature range over which any of the reactions occur will be determined by factors such as the temperature scanning rate, the efficiency of removal of the volatile products, and the shape of the sample container; none of the observed thermal changes occur at temperatures which have any thermodynamic significance. However, a reaction, such as the final stage of the oxalate decomposition, $CaCO_3 \rightarrow CaO + CO_2$, can provide satisfactory points for temperature calibration in a controlled atmosphere of the volatile product, in this case CO_2. According to the *Phase Rule*[1], the reaction will not proceed from left to right until a temperature is reached where the equilibrium vapor pressure over $CaCO_3$ and CaO exceeds the pressure of the CO_2 atmosphere. At this temperature, if the initial reaction rate is rapid enough, a sharp break will be observed in the TG curve. Fig. 1 also shows a superimposed run of calcium oxalate monohydrate made in CO_2 at 1 atm pressure. The dehydration and decarboxylation reactions are relatively little affected by the change in atmosphere, but the $CaCO_3$ decomposition is markedly different as predicted. The point of intersection of the extrapolated lines before and after the break may be taken as the temperature of initial decomposition of $CaCO_3$ in 1 atm of CO_2 which is known to be 898.6°C.

Dehydration reactions and of course boiling points are also potentially useful for temperature calibration, but again the transitions are not generally sharp unless the surrounding atmosphere is that of the vapor phase and is carefully controlled. Although this is seldom practical in most TGA systems, because of the problem of vapor condensation in the colder parts of the apparatus, it is possible to simulate a controlled atmosphere of the vapor phase by encapsulating the sample in a sealed pan with a tiny pin-hole in the cover. In this case no significant amount of weight loss will occur until the vapor pressure inside the pan exceeds 1 atm at which point vapor will stream from the pin-hole under a positive pressure. Fig. 2 shows DTG runs made in this fashion with samples of water and of dioxane. The intersection of the extrapolated leading edge of the DTG peak and the baseline should occur at the normal boiling point of the sample when the external pressure is 1 atm.

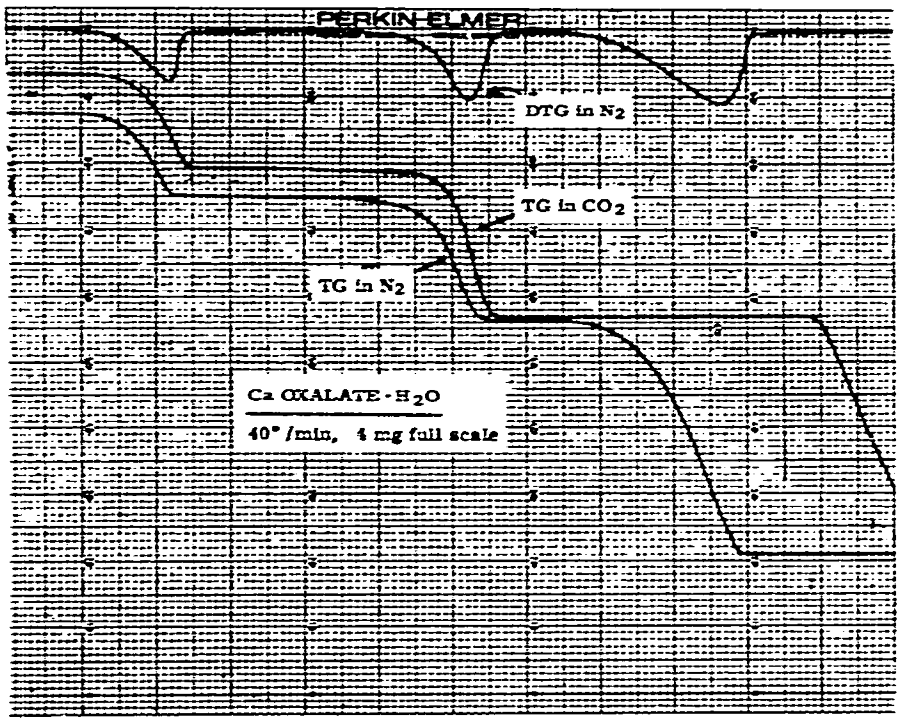

Fig. 1. A simultaneous TG and DTG of calcium oxalate monohydrate from room temperature to 1000 °C in nitrogen with a TG run in CO_2 superimposed.

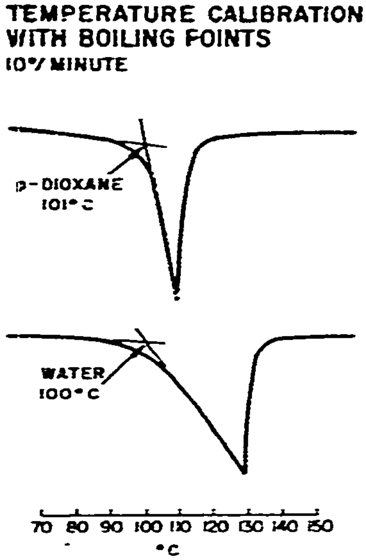

Fig. 2. DTG runs of *p*-dioxane and water in a sealed sample pan with pin-hole. Note greater sharpness of dioxane peak due to its lower heat of vaporization.

These methods typify conventional means of calibrating a TGA system with standard samples. Obviously they are not as convenient as those methods which can be used for DSC or DTA calibration. They are useful only under rather special conditions of atmosphere; a new sample must be prepared for every calibration; and only one calibration point can be determined per run.

In the course of the development of a new instrument for thermogravimetric analysis, the usual problems associated with sample temperature measurement in TGA coupled with the lack of convenient temperature standards were recognized as limiting the progress of TGA as an analytical technique. Accordingly, a promising alternate approach to TGA temperature calibration was investigated in some detail. This involved the use of ferromagnetic materials having Curie points over the range from room temperature to 1000°C.

The magnetic domains in ferromagnetic materials are known to become disoriented over characteristic temperature ranges where the materials more or less sharply transform to the paramagnetic state. One method of determining these characteristic temperatures. or Curie points, is to suspend a sample from a balance beam in a magnetic field which is oriented so that a vertical component of magnetic force acts on the sample. The magnetic force on the sample acts as an equivalent "magnetic mass" on the balance beam to increase the apparent sample weight. However, when the sample is heated through its Curie point, the equivalent magnetic mass will diminish to effectively zero; and the balance will indicate an apparent weight loss. A TGA apparatus is ideally suited to this type of measurement provided it is designed so that the sample can be placed in a magnetic field and a changing thermal environment simultaneously. Since the apparatus under development employed a cylindrical micro furnace mounted inside the hangdown tube, a simple and small permanent magnet could be placed around the sample area. Fig. 3 shows such a magnet in position around the hangdown tube of the Perkin-Elmer Model TGS-1 Thermobalance.

Although TGA had been previously employed for the measurement of Curie points, the converse, namely, the use of accurately known magnetic transition temperatures for internal standardization of TGA systems, had evidently never been investigated or at least not reported. Our investigation of this attractive possibility was to determine whether or not ferromagnetic materials could be found which met a number of criteria which were considered characteristic of an ideal standard.

(*1*) The transition must be sharp; that is, its natural or true width should extend over a small temperature range.

(*2*) The energy required to effect the transition should be small [under the dynamic scanning conditions of TGA, the "sharpness" of a transition is inversely proportional to transition energy (see Fig. 2 and ref. 2)].

(*3*) The transition temperature should be unaffected by the chemical nature of the atmosphere and independent of pressure.

(*4*) The transition should be reversible so that the same sample can be run repetitively to optimize or check the calibration.

(*5*) The transition should be unaffected by the presence of other standards so that several can be run simultaneously to obtain a multipoint calibration in a single experiment.

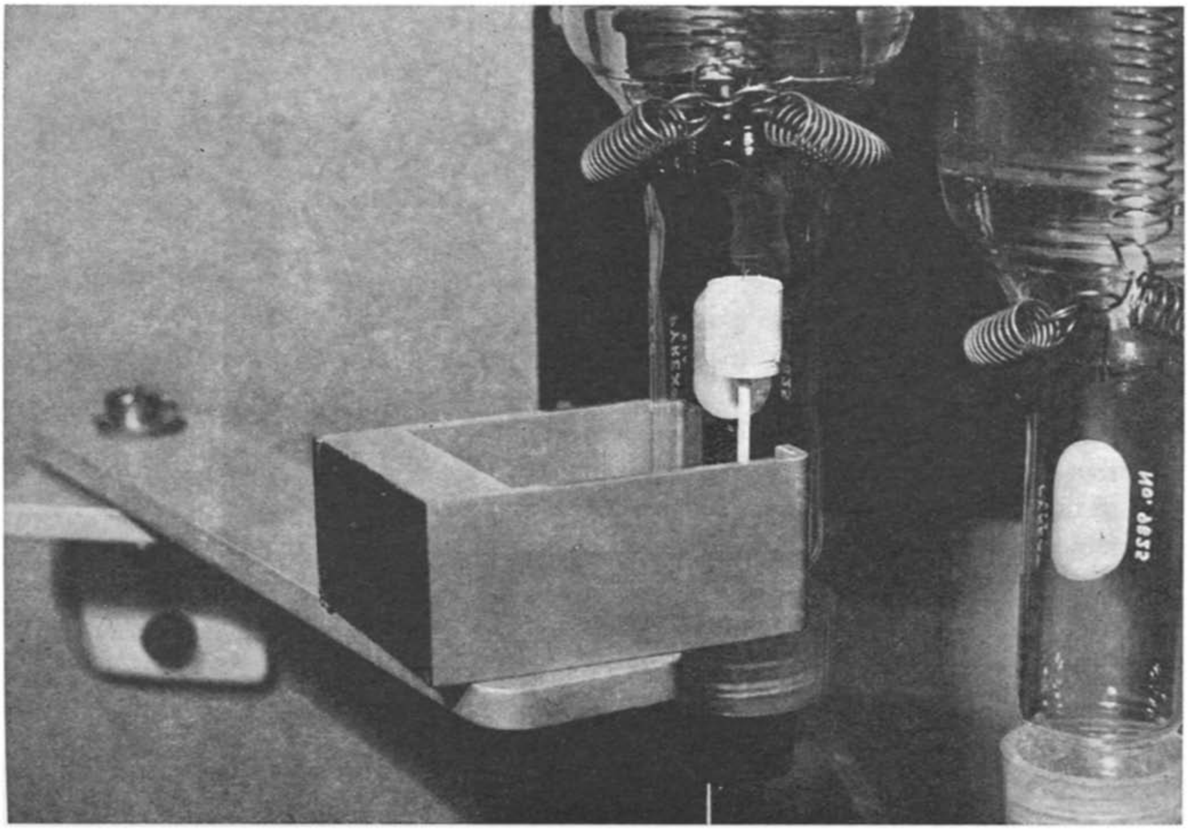

Fig. 3. The hang-down tube and internal furnace of the Model TGS-1 thermobalance with permanent magnet.

(6) The transition should be readily observable using standard samples in the mg range — comparable to normal sample sizes investigated with the apparatus.

Fig. 4 shows a very slow scan (0.625 °C/min) of a ferromagnetic alloy, Perkalloy, through the region of its magnetic transition temperature. This thermogram illustrates the typical shape of a ferromagnetic standard selected to meet the above criteria. Note that the transition is 80% complete over a range of only 3 °C.

The width of the transition in degrees is very little affected by scanning rate as shown in Fig. 5. This is a consequence of the very low energy required to effect a magnetic transition. Because of this low energy, the transition occurs with negligible incremental thermal lag other than the normal constant lag due to the finite instrumental time constant (*vide infra*). Fig. 5 was obtained by repetitive scanning of the same sample at different rates, 5, 10, 20, 40, 80, and 160 °C/min on the same piece of chart paper. The chart speed was increased in the same ratio for each run, and the temperature pip marks on the scale were superimposed.

The effect of scanning rate on the observed initial temperature of a transition is given by the equation $T_{\text{indicated}} = T_{\text{isothermal}} + RC_s\dot{T}_p$ where R is the effective thermal resistance between heat source and sample container of the apparatus and C_s is the effective heat capacity of the sample and its container. The product, RC_s, is the

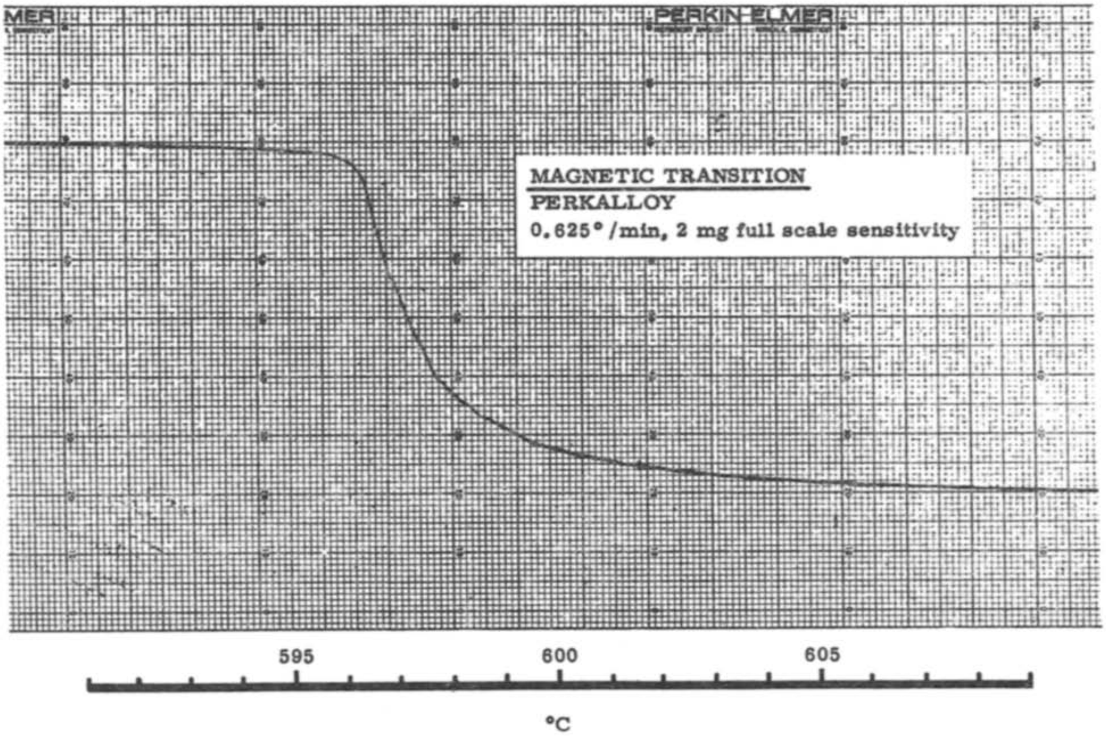

Fig. 4. A high resolution scan of the ferromagnetic alloy, "Perkalloy".

instrumental time constant, the single most important parameter characterizing the performance of a thermal analysis instrument of any kind. The instrumental thermal time constant is easily evaluated from the data of Fig. 5; $T_{\text{indicated}}$ is plotted *vs.* the scanning rate, $\dot{T}_p$. The slope of the straight line so obtained is RC_s, and the intercept at zero scanning rate is the true isothermal temperature. Knowledge of RC_s conversely permits a calibration made at one scanning rate to be converted simply for use at any other through the above equation.

The reversibility of magnetic transitions is shown in Fig. 6 where both TG and DTG modes were recorded simultaneously on a two-pen strip chart recorder*. The Perkalloy transition occurs at 596°C. The heating run was taken to about 650°C and then reversed to programmed cooling at the same rate. The recovery of the effective magnetic mass on cooling back through the transition is complete. However, it is found that magnetic transitions in common with phase transitions supercool and hence are not useful for calibration in the cooling mode except at very low scanning rates. The same sample of Perkalloy may be cycled back and forth through the transition indefinitely with no change in the shape, magnitude, or position of the record. This is true to a lesser extent with other suitable ferromagnetic materials, but those which we have selected as standards for use with the instrument may all be

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*All simultaneous TG and DTG runs shown in this paper were made with Cahn Instrument's "Time Derivative Computer" connected to the Perkin-Elmer Model TGS-1 Thermobalance.

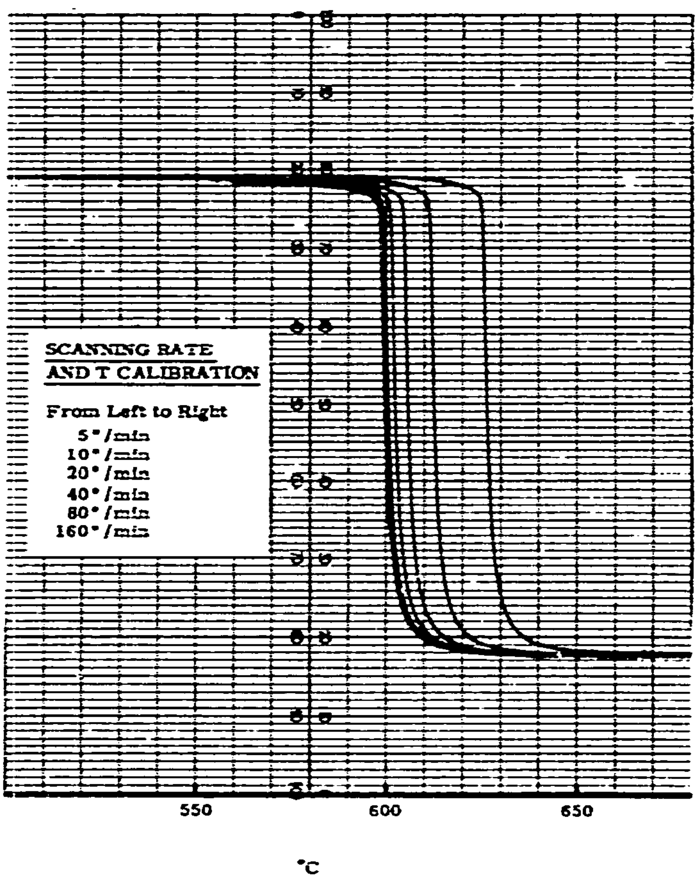

Fig. 5. Superimposed runs of Perkalloy at various scanning rates.

cycled many times before reaction with the atmosphere or structural changes within the material destroy the usefulness of the sample.

Fig. 7 is a typical calibration run again recorded simultaneously in the TG and DTG modes. Five standards, each of mass less than 1 mg, were placed in the sample pan. This was actually the third repetitive run of these standards, and it was identical to the second except for an increase in the two small peaks just below the Perkalloy transition and a corresponding decrease in the iron peak. Evidently iron forms ferromagnetic oxides and/or nitrides rather rapidly on the surface of the sample. However, the presence of these ferromagnetic products of reaction with iron does not alter the sharpness of either the Perkalloy transition or the remaining iron transition. The first run of a series of standards, however, can show peculiar effects due to the release of stresses which may be present in the "virgin" materials. Preheated samples are therefore recommended for calibration purposes.

There is a further important influence on true sample temperature which we have not yet considered and which is, in fact, rarely considered in TGA experiments. This is the effect of the radiation properties of the sample itself on its temperature. At temperatures in excess of 500°C, radiation progressively becomes the dominant

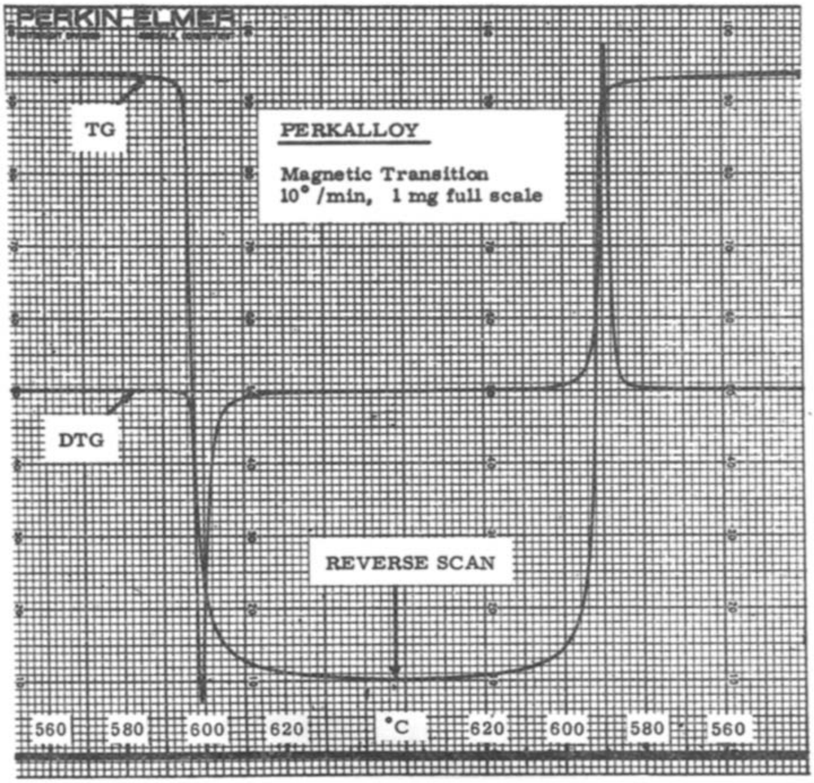

Fig. 6. Simultaneous TG and DTG scan of Perkalloy, heating and cooling.

mechanism for heat transfer in a TGA apparatus; and in an open-cup type of sample holder, radiation to and from the surface of the sample can become a significant factor. Consequently, a black sample such as graphite can be at a different temperature than a white sample such as alumina, all other conditions being the same. We have observed this difference to amount to as much as 20 °C in the region of 900–1000 °C. A further advantage of the magnetic standards is that they can often be "buried" in the sample to provide true internal calibration points during the actual sample runs, thus eliminating every source of calibration uncertainty. Of course there must be no chemical interaction between the standards and the sample for this approach to be applicable.

To establish the ferromagnetic materials as useful standards, a reproducible procedure for measuring the transition point was required. The Curie point is defined as that temperature where ferromagnetism completely disappears. However, it is evident from Fig. 4 that the termination of the transition as observed in a thermobalance is gradual rather than sharp. Accordingly, the intersections of a line drawn through the rapidly changing portion of the thermogram and a line extrapolated backwards from the horizontal baseline above the transition was taken as characterizing the transition point. It was found that this point was reproducible to within ±1 °C and was independant of sample size and magnetic field strength within the ranges of interest.

Using this procedure, it was expected and found that published Curie point

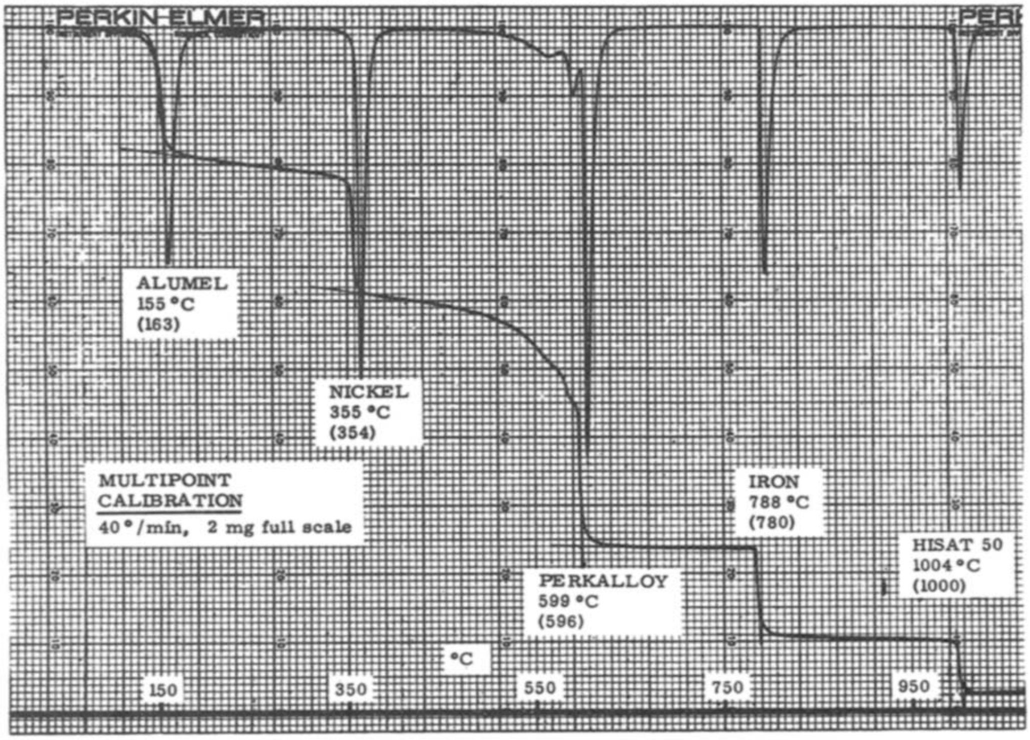

Fig. 7. Typical multi-point calibration run of 5 ferromagnetic standards. Temperatures in brackets are true transition temperatures.

temperatures did not correspond precisely with the measured temperature. To establish the true temperature of the points of intersection, a special hollow cylindrical furnace was constructed having a long gradient-free region in the interior. The temperature in this region was established at several reproducible settings of the furnace temperature by direct optical observation of the melting of several pure metals and inorganic salts contained in a platinum pan suspended in the furnace space. A calibration curve for the special furnace was obtained, and the transition points of the magnetic standards were then measured in the same furnace under the same conditions. Thus the recommended values for the magnetic transition temperatures were obtained relative to well-established melting point standards. The transition temperatures for five of the most useful metals and alloys are given in Table I. They are believed to be accurate to within ±2°C.

TABLE I

MAGNETIC TRANSITION CALIBRATION POINTS

Standard	*Transition temperature (°C)*
Alumel	163
Nickel	354
Perkalloy	596
Iron	780
Hi Sat 50	1000

The values can be expected to vary with purity of the metals and with changes in alloy composition. New sample batches should therefore be checked against the originals to insure that the variation is within allowable limits.

We have already briefly discussed an application of magnetic transitions in characterizing instrumental performance — the determination of RC_s. The smaller this value, the better the resolution of the instrument; or conversely, at comparable resolution, the faster the allowed scanning rate. Much of the lack of interlaboratory agreement which characterizes TGA data is due to very substantial differences in thermal time constant between the instruments employed. The specification of R and C_s for the TGA apparatus used in a published investigation is strongly recommended as it would communicate most of the instrumental information required for the analysis of the data and would place interlaboratory comparisons on a scientific basis.

A further important application of magnetic transitions is the determination of the isothermal temperature stability of a TGA system. In the study of decomposition kinetics of materials, it is often desirable to scan the sample very rapidly to a preselected temperature, come to a dead stop, and then observe the isothermal decomposition curve. In this type of temperature-sensitive experiment, it is most important that fluctuations and drift of the sample temperature be minimal throughout the course of the experiment. The magnetic standards provide a unique and very sensitive method of directly measuring the magnitude of isothermal fluctuations and drift in the sample location.

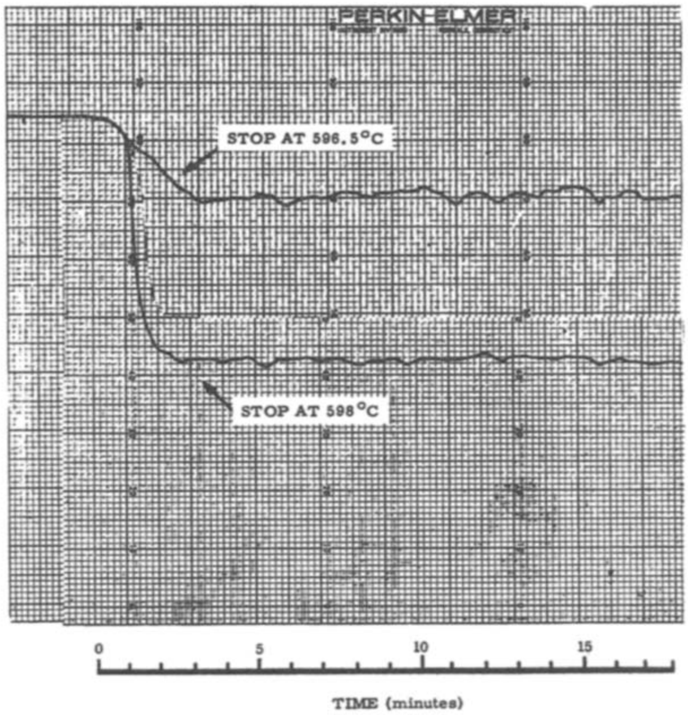

Fig. 8. Two superimposed isothermal runs in the magnetic transition region of Perkalloy. Scanning rate up to isothermal temperatures was 160°C/min.

One can scan the temperature of a ferromagnetic standard up to a point part way through the magnetic transition and stop. Referring again to Fig. 4 and particularly to the steeply descending part of the curve, we see that for this particular run a change in temperature of the sample of only 0.3 °C will cause a change in effective magnetic mass amounting to 10 small divisions displacement on the recorder chart. Thus any fluctuation or drift in the mass recording when the temperature is maintained nominally constant in the region of the magnetic transition can be converted to degrees. Fig. 8 shows two successive measurements of this kind superimposed. A Perkalloy sample was scanned up at 160 °C/min and stopped at two different temperatures about 1.5 °C apart in the middle of the magnetic transition. The observed maximum peak-to-peak fluctuation at the lowest temperature is found to be 3 divisions, which is equivalent to 0.1 °C. The fluctuation at the higher temperature is apparently smaller, but at this point the rate of change of magnetic mass with temperature is smaller also. When this is taken into account, the same result is obtained. Thus one can conclude that in the region of 600 °C the instrumental temperature stability is ±0.05 °C. Long-term drift can be measured in the same way.

In summary, ferromagnetic materials having sharp magnetic transitions are nearly ideally suited for temperature calibration standards in TGA systems where it is possible to place the sample area in a magnetic field. Further, they have many unique properties which allow the measurement of instrumental performance parameters which are required for the proper analysis of TGA data and for comparison of results obtained with different thermogravimetric systems.

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