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TEMPERATURE CONTROL IN THE PERKIN-ELMER TGS-2/SYSTEM 4*

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ABSTRACT

A detailed investigation has been made of the relative merits of various possible means of temperature control available with the Perkin-Elmer System 4 microprocessor controller for the TGS-2 thermogravimetric system. The dynamic compensating factor or rate parameter of the controller may be put to far more extensive use than indicated in the instrument operating manual. Temperature calibration by use of magnetic standards has enabled the development of mathematical relationships for the prediction of the appropriate value for the rate factor. Over the entire working range of the instrument and over a wide range of temperature programming rates, it is now possible to select the value of this parameter such that the sample and programmed temperatures agree within ±2°C. Two procedures have been developed for use at low and high programmed heating rates: the fixed and variable rate factor methods. The merits of these procedures are discussed and compared with the internal calibration method.

INTRODUCTION

Thermogravimetry has been employed extensively to study the thermal decomposition of complex materials, inorganic, organic and polymeric. Numerous mathematical treatments have been developed for evaluating kinetic parameters from thermogravimetric data [1]. Many of the several techniques necessitate the use of varying heating rates in acquiring data. As Flynn and Wall [1] point out, although it is best to use the lowest feasible values, there may be circumstances where it is expeditious to heat at high rates. Van Krevelen et al. [2] studying the pyrolysis of coal, used heating rates of the order 1–2°C min^{-1}. Friedman [3] evaluated thermogravimetric data obtained at 1–6°C min^{-1} to determine the kinetics of the degradation of char-forming plastics. In studying the energetic changes characterizing such thermal decompositions using differential scanning calorimetry, data evaluation must take into account the concomitant weight losses, as pointed out by Mahajan et al. [4]. In the absence of instrumentation enabling the simultaneous measurement of the TG and DSC data, the accuracy and precision of temperature control and

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measurement in separate TG and DSC instruments must be comparable. DSC heat capacity and enthalpy measurements are usually made at higher rates than kinetic TG measurements, specifically in the 10–20°C min^{-1} range. Certain aspects of coal thermal research neccessitate heating at much higher rates, in the range 50–150°C min^{-1}.

In order to accomplish this end, it has been found necessary to study the operational behavior of the Perkin-Elmer TGS-2 thermogravimetric instrument under the control of the System 4 microprocessor. It is essential that a furnace heating control procedure be developed enabling an accurate sample temperature, based on known internal standards, to be maintained over the widest possible programmed temperature and heating rate range. The zero and range analog controls of the heater control module of this instrument are in themselves not capable of providing the necessary control for these extreme conditions. The microprocessor provides a further means of minimizing thermal lags in the furnace through the dynamic compensating or rate factor. This parameter may be put to far more extensive use than indicated in the instrument operating manual (No. 993–9446).

It is my purpose to indicate how this keyboard operated parameter may be used in either a fixed or variable mode in conjunction with the existing analog controls to obtain highly accurate and precise temperature control in the system. A second means of temperature control is provided by an internal calibration procedure, incorporated into the microprocessor hardware. The efficacy of this method of control will be compared with that obtained under normal operating conditions, using suitable selected zero control and rate factor values.

SYSTEM 4 RATE FACTOR

The rate or dynamic compensating factor controls the power applied to the furnace heater windings. If, for any particular setting of the analog heater controls, a well-defined thermal event occurs at a programmed temperature, T, when rate $= 0$, then for $0 <$ rate < 300, the event will occur at $T - \Delta T$, where $\Delta T =$ rate $\times \beta/100$ and β is the programmed heating rate.

EXPERIMENTAL PROCEDURE

The experimental set-up employed simulates the conditions under which the apparatus is to be operated on samples of interest. To simulate coal or oil shale, ca. 10 mg of pure graphite powder (Union Carbide Corporation, Carbon Products division, type SP-3) was placed in the platinum crucible. Magnetic transition standards, when used, were placed on a bed of, and totally covered by, this material. Contrary to the suggestion in the operating manual (No.993–9446), the thermocouple was not bent and positioned laterally with the tip in the plane of the crucible, but

symmetrically located immediately below the crucible base. This is achieved in the following manner. The thermocouple is inserted into the furnace in the normal fashion, according to the operating manual (No.993–9195). With the balance recorder range set at high sensitivity, the furnace is heated to, and held isothermally at the highest programmed temperature to be used, in this case 950°C. With the furnace mount vertical screw adjustment, the furnace is raised until the thermocouple tip just touches the crucible base, thereby disturbing the balance. The furnace is then lowered until the balance is just free. With this procedure, even if any of the components, crucible, supporting stirrup, balance hang-down wire, furnace tube or thermocouple are replaced, the crucible and hence, the sample, may be located in the same position relative to the furnace, as for the calibration experiments. A nitrogen flow rate of 100 ml min^{-1} through the balance and convection shield assembly, and 30 ml min^{-1} via the upper side-arm of the furnace tube was maintained. Magnetic transition standard calibrations were performed in the usual manner, using the program mode of the microprocessor, with the loss in "magnetic effective weight" recorded as a function of the programmed temperature, T. Studies of the relationship between T and both the dynamic and isothermal thermocouple indicated temperatures, (TC_{DYN} and TC_{ISO}), were carried out in the manual mode of the System 4. The furnace was heated at the chosen heating rate until a pre-defined value of TC_{DYN} was obtained. The system was instantaneously put on hold, enabling the instantaneous value of T, and the fully equilibrated value of TC_{ISO} to be recorded.

MAGNETIC TRANSITION STANDARDS

Th four magnetic materials, alumel, nickel, Perkalloy and iron, with transition temperatures, T_s = 163, 354, 596, and 780°C, respectively, (Perkin-Elmer), were used in preference to the ICTA certified reference materials, (distributed in the United States by the National Bureau of Standards as GM761). Norem et al. [5] indicate that T_s values for the Perkin-Elmer materials are accurate to ±2°C, from measurements in a highly uniform heat zone furnace. The span and standard deviations from the means reported for the ICTA materials used with bottom loaded balances are large, especially at the higher temperatures. If the difference, $\Delta T = T - T_s$, is plotted as a function of T for all materials, monitored consecutively in one scan, one finds that the Perkin-Elmer standards obey a reasonably well-defined linear relationship, whereas the ICTA materials deviate markedly and randomly from this linearity, even at the ICTA specified heating rate of 1°C min^{-1}. The successful calibration of the TGS-2 depends upon establishing the slope and intercept of the linear relationship.

RESULTS

The difference between the observed program temperature and the known magnetic transition temperature at the transition midpoint, $\Delta T = T - T_s$, increases with

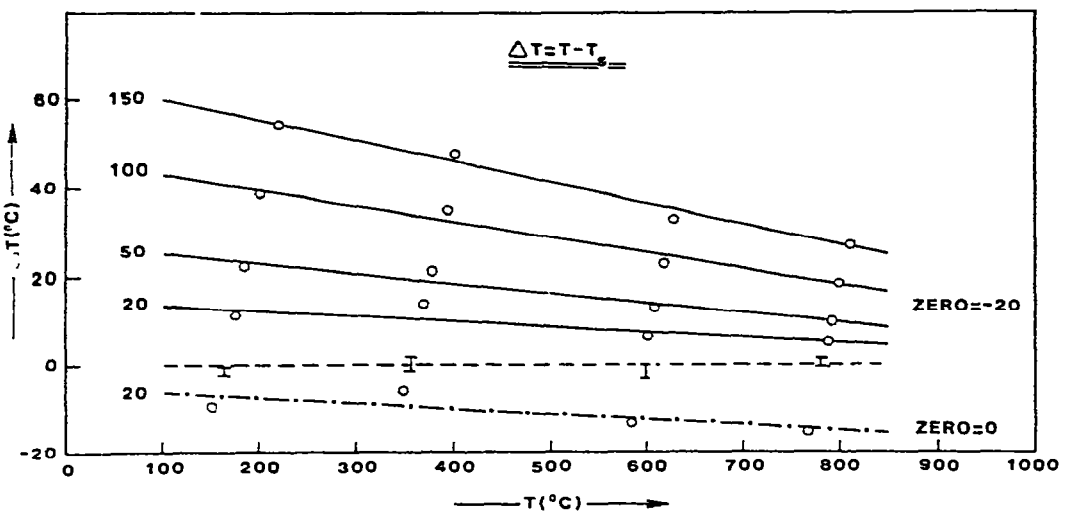

Fig 1 Summary of magnetic transition temperature difference calibration data

decrease in the value of the zero control setting with a range setting of zero at a fixed rate factor value, decreases with decrease in heating rate, and decreases with increase in program temperature. Figure 1 shows a set of ΔT values for zero $= -20$, rate $= 0$, range $= 0$, at different heating rates, covering the range 20–150°C min^{-1}. The lines are least squares fits to the data. For comparison, the 20°C min^{-1} data for zero $= 0$ is also shown. It is not necessary to repeat such measurements at different values of the rate factor, since the effects are calculable. ΔT decreases by $\beta \times$ rate/100. The positive rate factor opposes the effect of the negative zero setting. It is easily shown that for the condition $\Delta T = 0$, the rate factor takes the value given by eqn. (1a)

$$\text{Rate} = \frac{K_1(1 + K_{21}) - K_3\beta + K_4(1 + K_5\beta)T}{1 - K_6\beta} \tag{1a}$$

The coefficients are listed in Table 1. For any given heating rate, one sets range $= 0$,

TABLE 1

Calibration rate equation coefficients

Eqn (1)	Eqn (3)	Eqn (4)
Condition $T = T_S$	Condition $TC_{DYN} = TC_{ISO}$	Condition $TC_{DYN} = T$
$K_1 = 993$	$K_1 = 32\,2$	Normal system
$K_{21} = 0\,0829 \times Z$	$K_2 = 0\,94$	$K_1 = 31 - 86\,(7\,64 + Z)/\beta$
$K_{22} = 0\,165 \times Z$	$K_3 = 0\,075$	$K_2 = 75 \times 10^{-6}\,(Z - 189) - 4\,45/\beta$
$K_3 = 30\,7\,(1 - 0\,71 \times 10^{-3} \times Z)$	$K_4 = 0\,18$	$K_3 = 0\,035 \times 10^{-2}/\beta$
$K_4 = 0\,668$	$K_5 = 0\,19 \times 10^{-3}$	System internally calibrated
$K_5 = 0\,032$	$K_6 = 0\,79$	$K_1 = 28\,(1 - 0\,002 \times Z) - 107\,(13\,7 + Z)/\beta$
$K_6 = 0\,859$	$K_7 = 0\,53$	$K_2 = 225 \times 10^{-6}\,(Z - 44) + 0\,03\,(Z + 127)/\beta$
$K_7 = -0\,82$	$K_8 = 2\,01$	$K_3 = -0\,45 \times 10^{-4}\,(Z - 88)/\beta$

Z = Zero; β = heating rate.

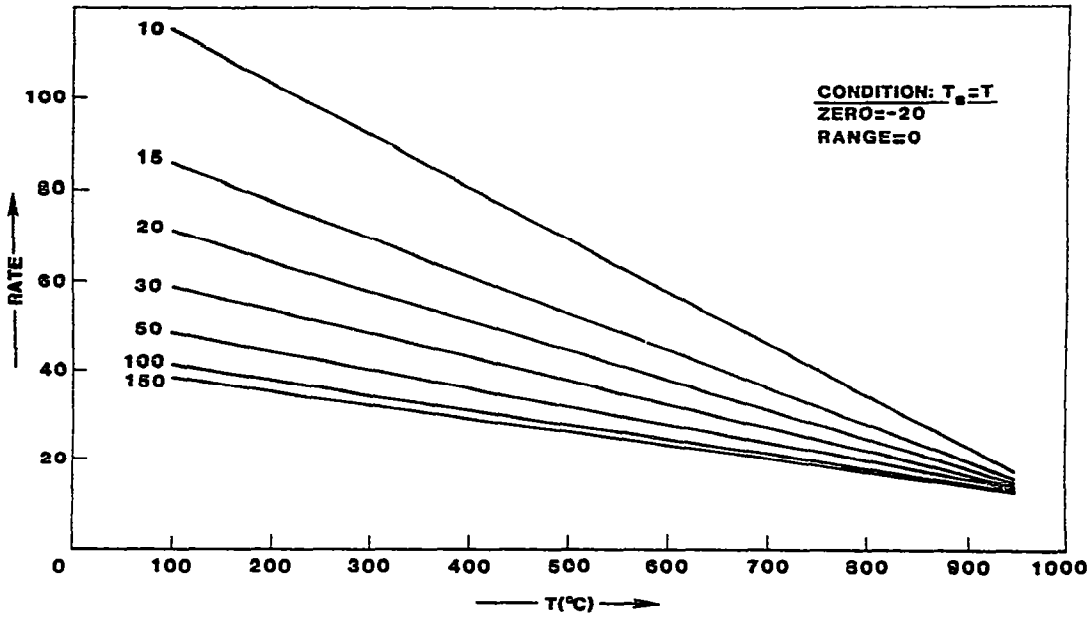

Fig 2 Rate factor variation as a function of program temperature for the condition, sample temperature equals program temperature

and selects a suitable value of zero, such that the calculated values of rate at different program temperatures are within the limits $0 < \text{rate} < 300$. An easily repeatable zero setting should be chosen; -20 has been found to be suitable, as shown in Fig. 2. Use of eqn. (1a) is referred to as the "variable rate" procedure. Figure 3 shows the effective weight loss curves for the four magnetic materials, alumel, nickel, Perkalloy and iron, heated at 75°C min^{-1}. The data were recorded using the $X-Y_1-Y_2$ recorder time base, 20 s cm^{-1}, in order to be able to monitor the thermocouple output simultaneously. This is equivalent to 25°C cm^{-1}, which is the normal recorder temperature mode for a total span of 1000°C. As can be seen the control is excellent, the actual magnetic transition midpoint temperatures are 161, 355, 595, and 780°C. The increasing lag of the thermocouple indicated temperature behind the program, and hence, sample temperature is easily discernable. At 900°C,

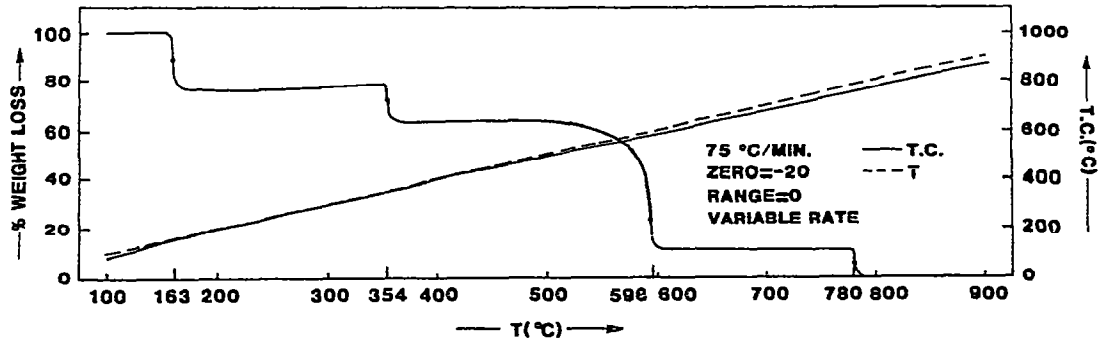

Fig 3. Magnetic transition effective weight loss curves measured using the variable rate procedure.

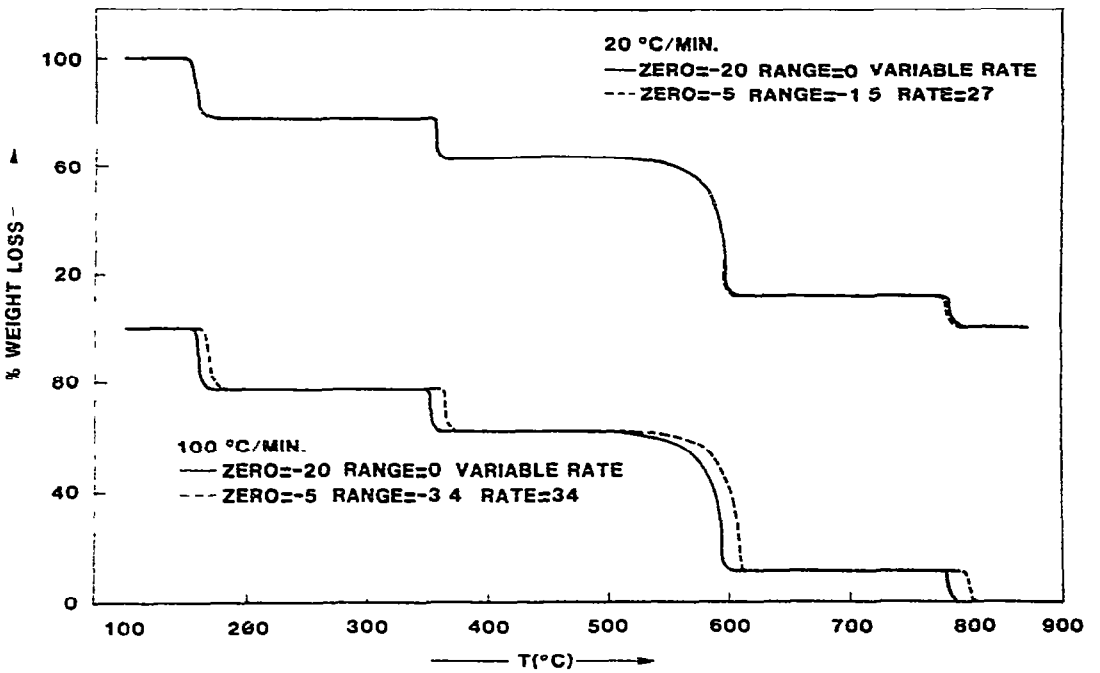

Fig 4 Magnetic transition effective weight loss curves Comparison of variable and fixed rate procedures

it is in the order 30–35°C. A second means of control is available, referred to as the "fixed rate" procedure. For a set value of zero, the linear data of Fig. 1 can be expressed in terms of a fixed rate and range value, given by eqns. (1b) and (1c)

$$\text{Rate} = \frac{K_1(1 + K_{22}) - K_3\beta}{1 - K_6\beta} \tag{1b}$$

$$\text{Range} = K_7(1 + K_5\beta) \tag{1c}$$

Except for K_{22}, the coefficients are as in eqn. (1a) (see Table 1). Figure 4 shows the magnetic transition curves at two heating rates, using both means of control. With the variable rate method at both the medium (20°C min^{-1}) and fast (100°C min^{-1}) scan rates, the transitions occur within ±2°C of the literature values [5]. Although the fixed rate procedure gives essentially the same results as the variable rate method at 20°C min^{-1}, this is not the case at 100°C min^{-1}. Here, ΔT varies from +8°C for alumel (163°C) to +17°C for iron (780°C). In Fig. 1, the short vertical bars on the dashed line through $\Delta T = 0$ show the maximum deviations obtained over a wide range of heating rates using the variable rate procedure with zero = −20.

Figure 5 shows the variation of the temperature difference, $TC_{ISO} - T$ as a function of the programmed temperature, T, over essentially the entire instrumental range. By displacing the zero control from 0 to −20, the entire set of values are displaced by this amount, as shown. From 200°C to 950°C, the values fit the parabolic relationship

$$TC_{ISO} - T = \text{zero} + 9 + 0.036 \times T - 0.51 \times 10^{-4} \times T^2 \tag{2}$$

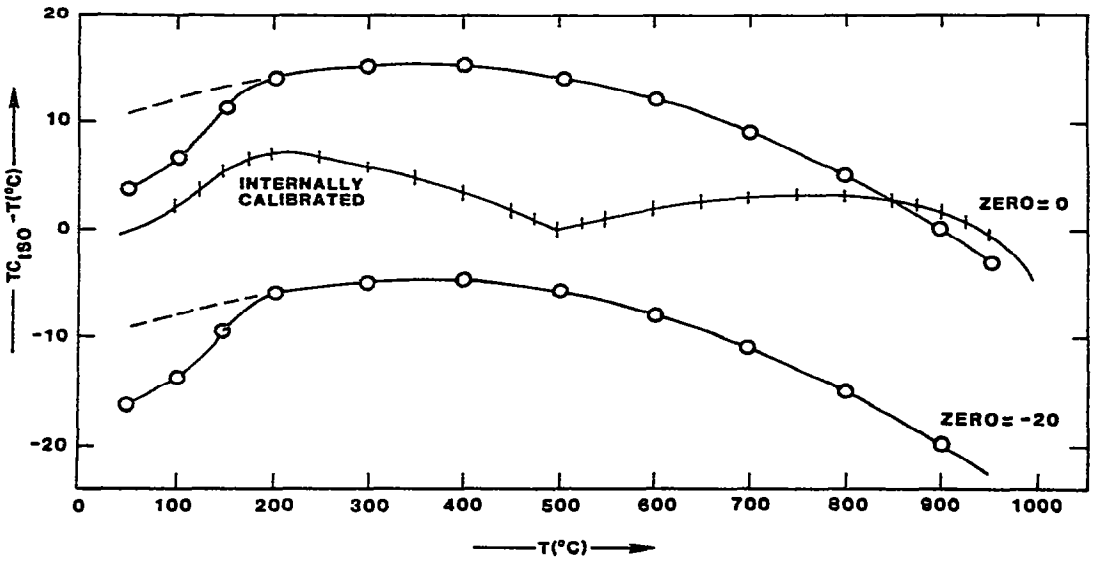

Fig 5 Variation of the isothermal thermocouple indicated temperature—program temperature difference as a function of program temperature

The System 4 internal calibration forces $TC_{ISO} = T$ at three points, the minimum, midpoint and maximum program temperatures, selectable by the operator. It also reduces the overall $TC_{ISO} - T$ values in the intermediate regions, as shown in Fig. 5. The internal calibration and resulting temperature difference curve are independent of the rate factor, the gas flow rates, and the presence or absence of the platinum crucible and supporting stirrup above the thermocouple. The short vertical bars on the internally calibrated curve show the variation in values when the internal calibration was performed with the zero control set at 0 and −20.

Figure 6 shows the variation of the differences between the thermocouple output under isothermal and dynamic scan conditions, $TC_{ISO} - TC_{DYN}$, as a function of the program temperature, T, at 100, 50, 25, and 10°C min^{-1}, with the heater control unit zero and range analog controls, and the System 4 rate factor set to zero. Measurements at 100°C intervals over the entire temperature range have verified the linearity and confirmed the adequacy of the three point calibration. The linear relationships are independent of the zero control setting, the gas flow rates and irrespective of whether the system is operated normally or following internal calibration. The position and slope of the linear plot is significantly affected by the values of the rate factor. Compare the $TC_{ISO} - TC_{DYN}$ values for $\beta = 100$°C min^{-1}, rate = 0 and rate = 30. For the condition, $TC_{DYN} = TC_{ISO}$, the rate factor is given by eqn. (3) with the coefficients in Table 1.

$$\text{Rate} = \frac{K_1(1 + K_2\beta) - K_3(1 + K_4\beta)T}{K_5(1 - K_6\beta)T - K_7(1 - K_8\beta)} \tag{3}$$

This equation is shown plotted in Fig. 6, for different heating rates. Essentially, eqn. (3) defines the conditions whereby temperature overshoot is precluded.

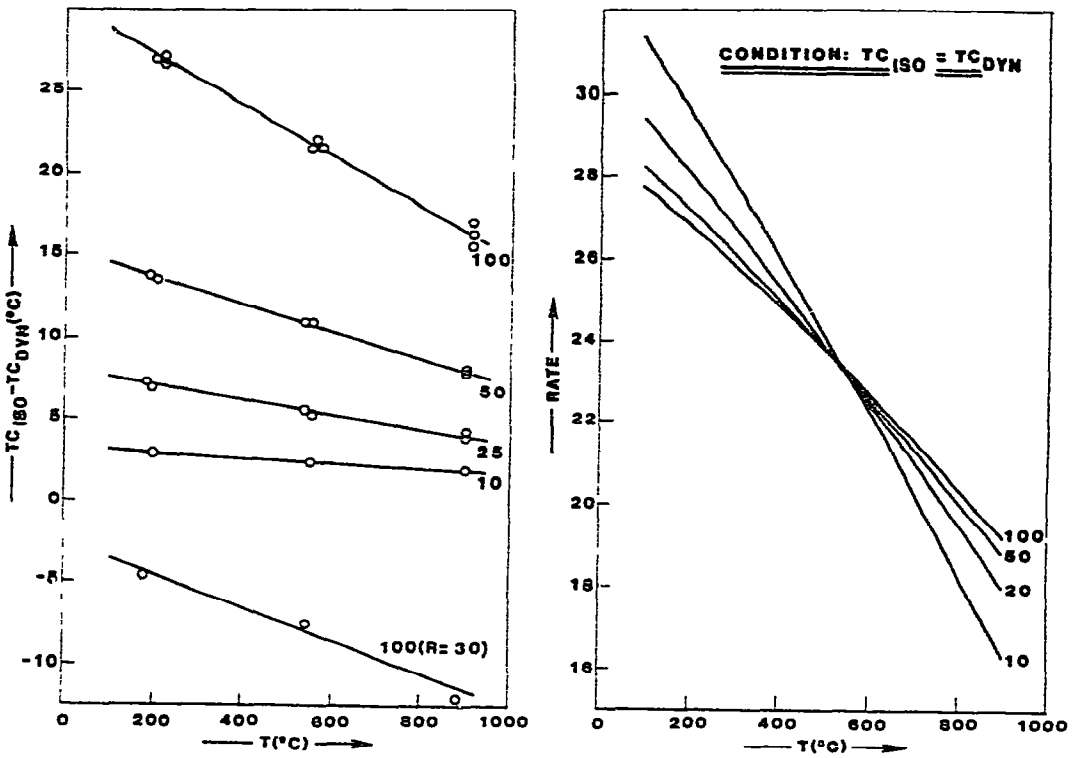

Fig 6 Thermocouple indicated temperatures under isothermal and dynamic scan conditions as a function of program temperature Rate factor variation for the equality condition $TC_{ISO} = TC_{DYN}$

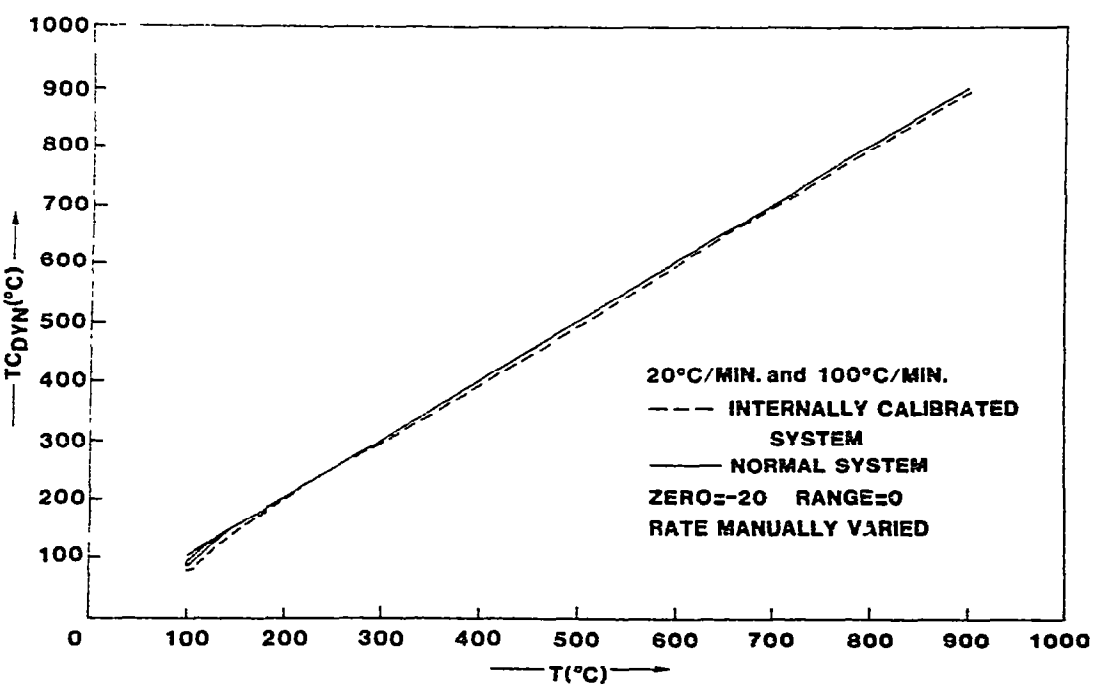

Fig. 7. Comparison of the dynamic scan thermocouple indicated temperature as a function of program temperature for a normally operated and internally calibrated system

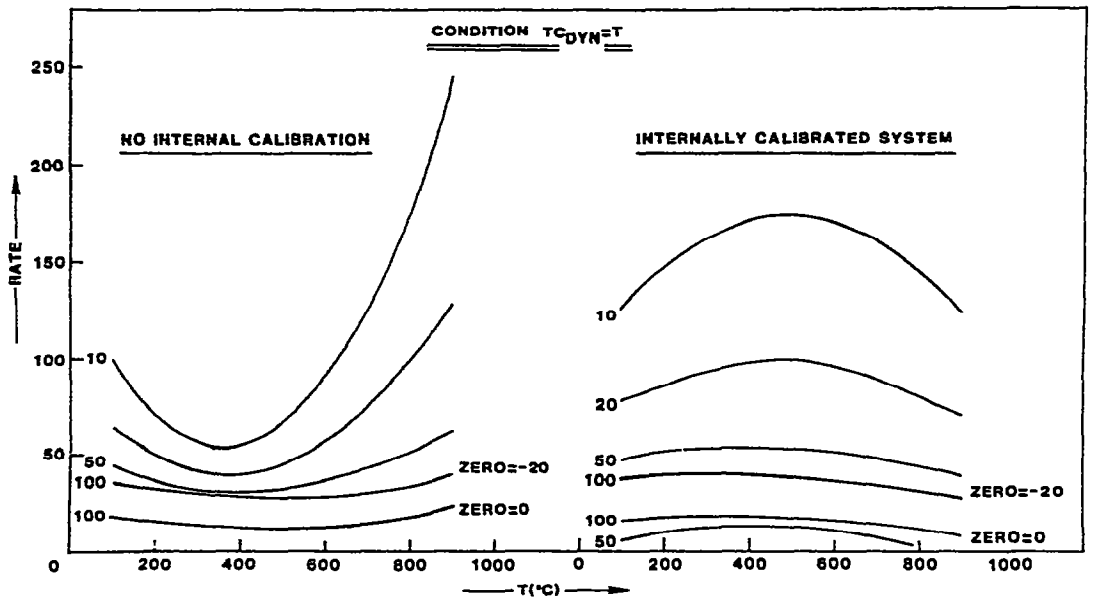

Fig 8 Rate factor–program temperature relationships for the condition $TC_{DYN} = T$

Consideration of the same data from which these results were obtained enables the temperature difference, $TC_{DYN} - T$, to be evaluated as a function of the program temperature, T. One finds that for $TC_{DYN} = T$, the rate factor is given by the parabolic equation

$$\text{Rate} = K_1 + K_2 \times T - K_3 \times T^2 \quad (4)$$

The values of the coefficients differ according to whether the system has been internally calibrated or not, as indicated in Table 1. In Fig. 7 the thermocouple indicated temperature at 20°C min^{-1} and 100°C min^{-1} is shown recorded as a function of the program temperature. The rate factor was continuously varied as shown in Fig. 8. As is seen in Fig. 7, the condition $TC_{DYN} = T$ is followed much more closely for the system operated normally rather than following internal calibration. This is due to the fact that the internally calibrated data did not fit the parabolic relationship (4) as successfully as that obtained under normal operating conditions.

CONCLUSIONS

The use of the System 4 rate factor as a viable means of furnace temperature control has been confirmed. Setting the appropriate values of the zero and range analog controls and the rate factor from magnetic transition temperature calibration data provides excellent temperature control (±2°C) over a wide range of programmed temperatures and heating rates. The variable rate procedure must be used for high heating rates (>20°C min^{-1}), but for $\beta \leqslant 20$°C min^{-1}, the fixed rate

method is eminently suitable. Since the acquisition of these data and the development of the procedures, it has become necessary to replace both the furnace and the indicating thermocouple. It has been found that the coefficients listed in Table 1 for eqns. (1) apply to the new furnace. This is not considered a fortuitous circumstance. It would be of considerable interest to see if the claim that the calibration data presented here applies to all furnaces could be substantiated by other users of this microprocessor controlled thermogravimetric system.

The internal calibration procedure appears to be of little use. If the accurate magnetic transition standards calibration is not utilized, then the system may be operated normally. Using the variable rate technique, the system may be programmed such that the dynamic thermocouple indicated temperature follows the program temperature within $\pm 2°C$. This is achievable for a broad range of heating rates over the entire temperature range of the instrument. However, contrary to the magnetic transition standards calibration, it is not possible to achieve this precision using a fixed rate factor procedure. At medium and low heating rates this necessitates fully attended operation, which defeats the purpose of the microprocessor controller. Furthermore, it must be emphasized that, irrespective of the method of control employed, the thermocouple indicated temperature always lags the actual sample temperature within the platinum crucible. As is to be expected, the magnitude of the lag increases with increase in program temperature, but it is slightly less when the variable rate factor values are calculated for the condition $TC_{DYN} = T$ [eqn. (4)] than for the condition $T = T_s$ [eqns. (1)]

In this laboratory, the magnetic transition standards calibration fixed and variable rate procedures are used solely for studies on coal and oil shale. For certain procedures in which it is only important to maintain a known isothermal temperature, for example, proximate analysis [6], eqn. (2) is used to calculate the desired program temperature for a required isothermal temperature. It has to be assumed that under isothermal conditions, the signal from the thermocouple is close to the actual sample temperature. In this regard it should be mentioned that the magnitude of the coefficients of eqn. (2) appear to be characteristic of each individual furnace, but the general parabolic features of Fig. 5 are maintained.

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