ELSEVIER

Thermochimica Acta 243 (1994) 223–230

thermochimica acta

Further consideration of temperature measurement and control in thermogravimetry ☆

R.P. Tye, A. Maesono, T. Masuda

ULVAC Sinku-Riko, Yokohama, Japan

Received 20 December 1993; accepted 5 May 1994

Abstract

A previous paper to NATAS in 1992 discussed the importance of more precise temperature measurement and control in quantitative thermoanalytical techniques. In particular, the locations of the temperature measurement and temperature control sensors are critical. These can have a significant effect on the determination of the beginning and ending of reactions and subsequent evaluation of relevant quantitative parameters.

Experiments have been carried out on the dehydration of calcium oxalate using a thermobalance utilizing an infrared gold image furnace with the measurement and control temperature sensors. These are disposed in the three different configurations that are used in thermoanalytical techniques. Significant differences have been found between the three methods. These illustrate that using one temperature sensor for both temperature measurement and for temperature control purposes provides the most relevant data for use in further analysis of reaction kinetics, etc.

Keywords: Isothermal; Precision; Temperature

1. Introduction

The many factors affecting the measurement and control of temperature in thermoanalytical techniques have been discussed by one of the authors previously [1,2]. In particular, the importance of the positioning of the temperature sensor(s) in thermobalances and in other quantitative measurement instrumentation was stressed [2].

☆ Presented at the 22nd Annual NATAS Conference, Denver, CO, 19–22 September 1993.

SSDI 0040-6031(94)01881-2

Table 1
Three methods for temperature measurement and control

Type	Temperature measurement with thermocouple		Temperature control with thermocouple	
	Specimen contact or non-contact	Location of thermocouple	Specimen contact or non-contact	Location of thermocouple
A	Non-contact	Near specimen	Non-contact	Near furnace
B	Contact	Specimen or cell [a]	Non-contact	Near furnace
C	Contact	Specimen or cell [a]	Contact	Specimen or cell [a]

[a] Cell indicates a specimen container.

The three types of system that are in general use in thermoanalytical techniques and classified according to the means of temperature measurement and control were discussed. These are summarized in Table 1. It was pointed out that for Types A and B, where the control sensor is located "close to" the furnace, significant differences can exist between the actual specimen and the control temperatures. This difference can become most significant during endothermic and exothermic reactions. Taking the former as an example, under isochronal heating conditions, the heating rate is slowed and thus the apparent onset and completion temperatures of a thermal decomposition process are shifted to higher than actual temperatures.

As a result, it was suggested that the Type C system, where a single sensor is used for both measurements of specimen temperature and control of temperature, was the most suitable for developing quantitative data suitable for most detailed analysis. Such a system is manifested in a thermobalance developed by the authors. This utilizes a low heat capacity infrared gold image radiant furnace which allows precise thermogravimetry to be undertaken in both constant heating rate and stepwise isothermal heating or cooling modes.

Results of experiments on calcium oxalate decomposition are described which illustrate the magnitude of the differences in temperature that can result from using the three systems under identical heating conditions.

2. Experimental details and results

A Sinku Riko TGD-7000-RH combination TG/DTA system was used.

Fig. 1 illustrates how this was modified by changing the temperature sensor locations in order to simulate representative Type A, B, and C systems.

In the first experiments, 10.13 ± 0.01 mg of calcium oxalate was used as the test specimen and a similar amount of alumina as the reference material. In each case, the specimens were heated at a programmed rate of 20°C min^{-1} in a static air environment. Detailed curves for Types B and C systems are shown in Figs. 2 and

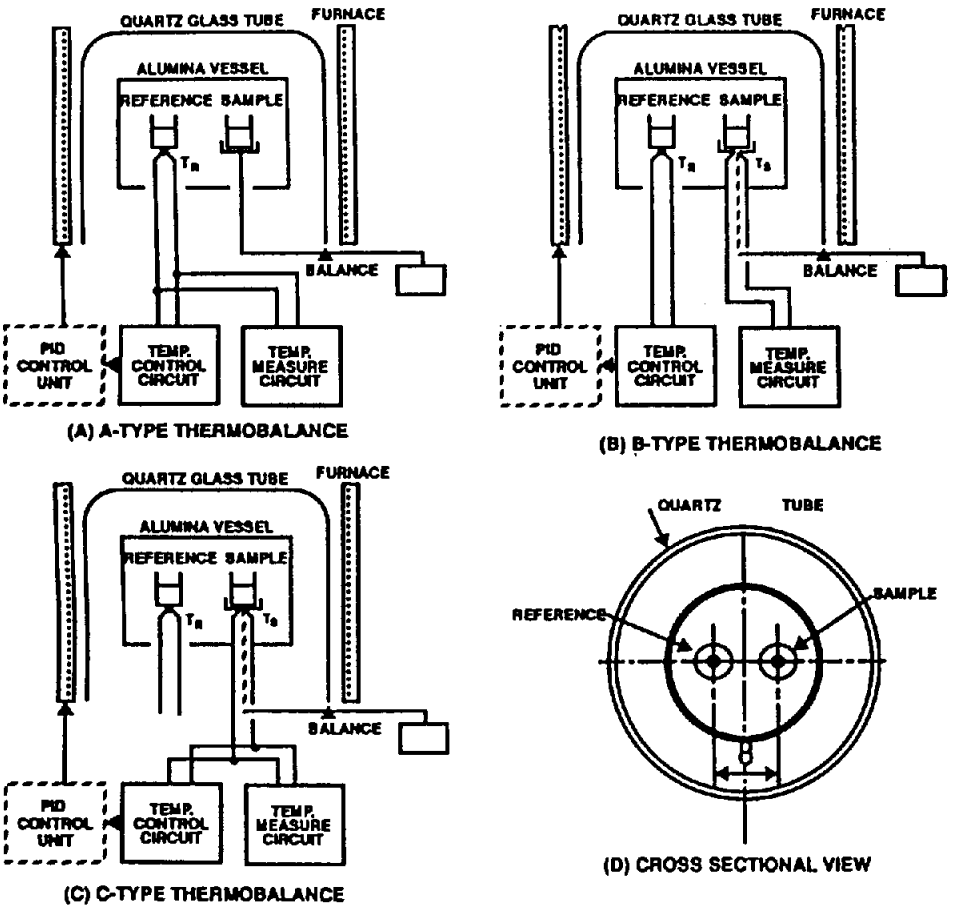

Fig. 1. Block diagrams illustrating the different locations of temperature sensors in the TGD-700-RH system to simulate Types A, B, and C measurement and control systems.

3 and the results using the three systems are compared in Fig. 4 and summarized in Table 2.

In the second experiment, Type B and C systems, using the same mass as in the first experiment, were heated rapidly (100°C min^{-1}) to attain an isothermal temperature of 156°C. This heating rate was chosen as being the maximum controlled rate that can be attained reproducibly and precisely in current resistively heated furnaces. The results are shown in Figs. 5 and 6 respectively.

3. Discussion

The results of the first experiment illustrate clearly that the Type C system not only provides more precise measurements of the beginning and end of the dehydra-

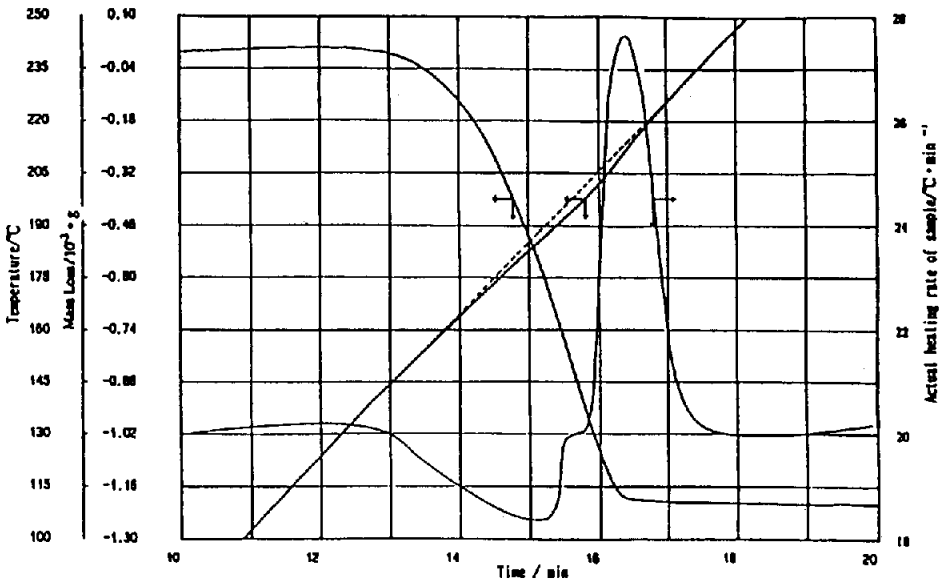

Fig. 2. Type B: specimen temperature and actual heating rate vs. time.

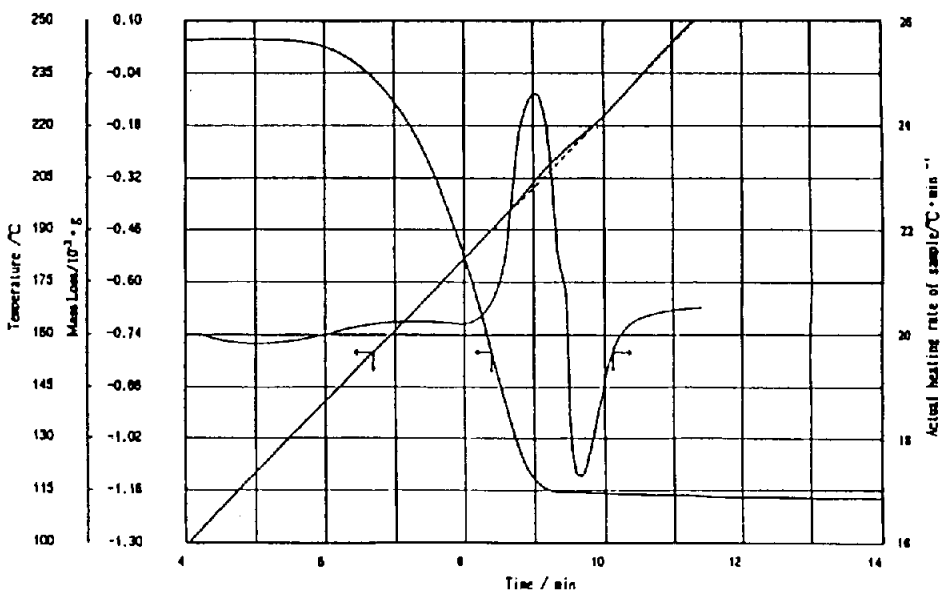

Fig. 3. Type C: specimen temperature and actual heating rate vs. time.

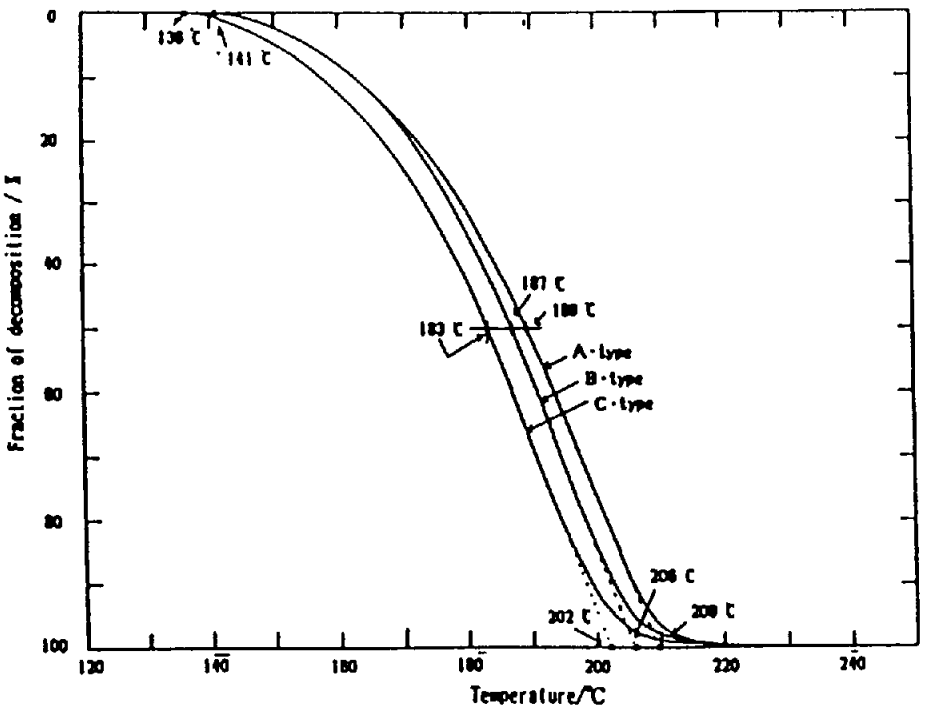

Fig. 4. Comparison of the results using Type A, B, and C systems.

Table 2
Beginning, middle, and end temperatures of dehydration of $CaC_2O_4 \cdot H_2O$ obtained from isochronal thermogravimetry [a]

Type	Start	Middle	End
A	141°C	189°C	209°C
B	141°C	187°C	206°C
C	136°C	183°C	202°C

[a] Programmed heating rate 20°C min^{-1}; environment, static air; specimen mass, 10 mg.

tion process, but also improved temperature control to overcome the effects of the endothermic reaction which takes place. This is illustrated further in Fig. 7. It can be seen from Figs. 2 and 3 that the dehydration process is completed in less than 10 min using the Type C system, whereas for Type B the total time exceeds 16 min. Furthermore, the actual heating rates of the specimens during the reaction do change significantly from the programmed rate but occur over a much shorter time period for the Type C system. Results for Type A show much longer times and

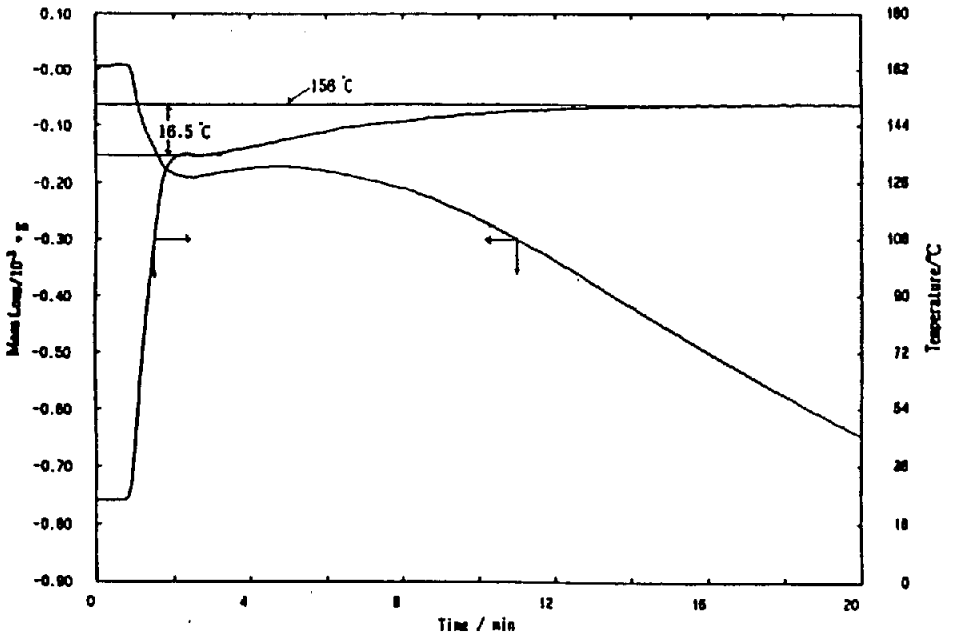

Fig. 5. Type B: isothermal TG curve at 156°C (note appreciable deviation from desired level for over 10 min).

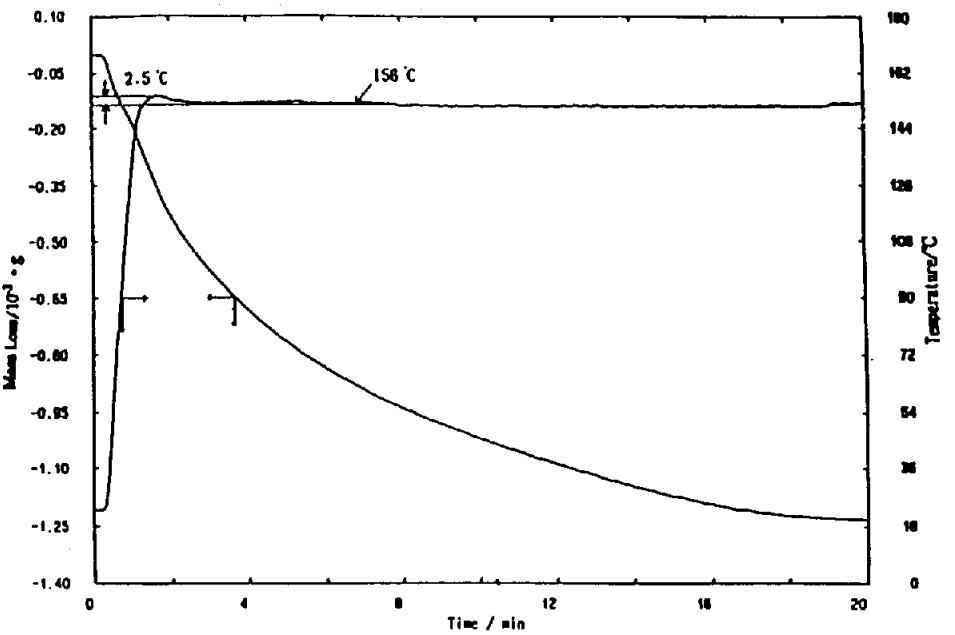

Fig. 6. Type C: isothermal TG curve at 156°C.

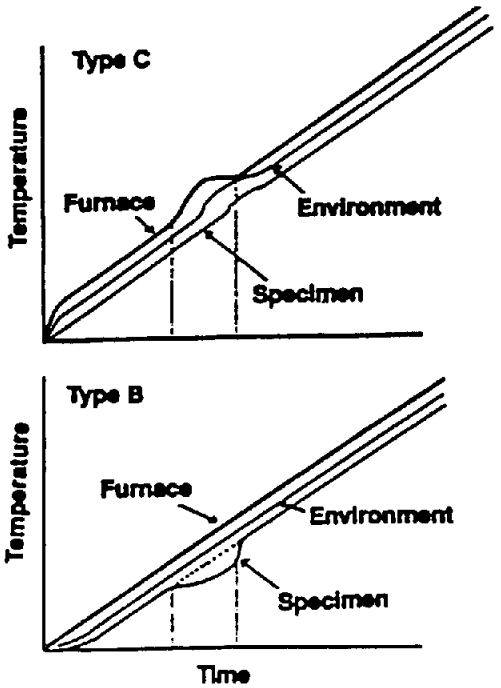

Fig. 7. Schematic curves of temperature vs. time of specimen, furnace and specimen environment for types B and C during the endothermic dehydration process of $CaC_2O_4 \cdot H_2O$.

larger variations in specimen heating rate. It should be mentioned that some Type A systems are still in use but the majority of commercial systems now conform generally to Type B.

The results of the second experiment illustrate the particular advantages of the Type C system for isothermal studies. In the current study, the specimen in the Type C system attains 156°C (to better than 1°C) within 3 min and attains constant mass loss (1.24 mg) within less than 20 min. However, for Type B the time to attain 156°C (to 1°C) is over 11 min and the specimen is still losing mass after 20 min. In fact, it has lost 0.65 mg, only half of the total mass loss expected to occur at this isothermal temperature.

Overall, the temperature and mass loss differences obtained in these experiments indicate that further quantitative analysis to produce reaction rates, heats of reaction, etc., will differ significantly. It should be pointed out further that the current Type A and B systems were simulated with a low mass radiation furnace. A majority of Type A and B systems use furnaces that are resistively heated and of higher mass. Thus, the current differences will be magnified due to the effects of the higher mass. Furthermore, with Type C systems, heating rates up to 100°C s^{-1} are possible. In consequence, isothermal (including stepwise)

heating (and cooling) can be attained much more rapidly [3] than in the current example, thereby improving the precision of results for experiments carried out in this mode.

References

[1] R.P. Tye and R.L. Gardner, The contribution of precise temperature measurement and control to thermoanalysis, presented at the 21st NATAS Conference, Atlanta, GA, 13–16 September 1992. Thermochim. Acta, 226 (1993) 343.

[2] R.P. Tye, Temperature measurement and control: critical parameters in thermoanalysis techniques, presented at the 10th ICTA Congress, Hatfield, UK, 24 28 August 1992. J. Therm. Anal., 40 (1993) 1009.

[3] M. Kikuchi, J. Jpn. Appl. Phys., 26(6) (1987) 1066.