Journal of Thermal Analysis, Vol. 40 (1993) 1009-1016

TEMPERATURE MEASUREMENT AND CONTROL
Critical parameters in thermal analysis techniques

R. P. Tye, R. L. Gardner and A. Maesono

ULVAC/SINKU-RIKO, INC., ANDOVER MA, USA

Several factors in temperature measurement that can affect the precision of melting points and phase-change phenomena are discussed. In many cases, critical errors may arise in the measurement and control of temperatures due to incorrect placement and/or interpretation of the output of temperature sensors in the various system types that are in current use. Advantages can be obtained by using one temperature sensor only for temperature measurement and temperature control in a low mass infrared gold image furnace for the analytical studies in both the constant rate and stepwise isothermal thermoanalytical heating and cooling modes. Illustrations of the use of this instrumentation for measurements in both modes are given.

Keywords: critical parameters in thermal analysis, heating and cooling modes, temperature control, temperature measurements

Introduction

During the past two decades significant advances and improvements have been made in thermoanalytical techniques and their broad use for both characterizing and understanding the basic behaviour of material. Many of these techniques have been or are in the process of being standardized at both national and international levels. However, in the development of precision and bias statements for these methods, suprisingly poor agreement has often been found between results of different organizations involved in interlaboratory studies. Recent discussion of this issue [1] has indicated that the current degree of uncertainty in parameter measurements especially thermogravimetry and dilatometry is not acceptable if thermoanalytical techniques are to be basis for interpretation of material behaviour.

This discussion drew particular attention to the important roles that temperature measurement and temperature control play in techniques involving absolute change of mass, length or other parameters. The impact of various factors that contribute to errors were discussed, and it was concluded that some of the uncer-

John Wiley & Sons, Limited, Chichester
Akadémiai Kiadó, Budapest

tainties could be reduced providing more attention was paid to often-neglected temperature measurement factors.

The essential point involving temperature measurement is that *a temperature sensor measures only its own temperature*. In any thermal measurement it is incumbent on the designer of the apparatus and test procedure to ensure that a measured temperature represents that of the appropriate artifact involved. This is often easier to say than to carry out, particularly in transient techniques involving small specimens mounted in conventional high-mass heating and cooling units.

The major interrelated factors contributing to temperature errors can be summarized as follows:

1) Specimen type, form, and amount – this effects the thermal diffusivity of specimen and container.

2) Experimental conditions – differences in conductive, convective, and radiative heat transfer, especially in conjunction with heating rate differences, affect both temperature response, actual temperature and temperature control.

3) Type and size of temperature sensor and type of control system – affects response times, conduction losses, contamination problems, and output sensitivity.

4) Conversion of sensor output to temperature – individual or standard calibration tables, amplification, ice-point, and electronic circuitry effects, affect the absolute temperature.

5) Number and placement of temperature sensors – yield uncertain and often unmatched temperatures such that it is preferable to use one sensor only for both measurement and control of temperature.

While all five factors have to be considered and addressed, the effects of the first four are reduced in 'comparative' methods, e.g. DTA or DSC, where the specimen behaviour is compared to that of a reference material contained in an identical container. However in 'absolute' techniques, e.g. TGA or TMA, where direct measurement of a physical parameter is undertaken, the last factor is particularly critical. The present paper discusses the issues related to temperature placement in detail, with particular reference to thermogravimetry.

Types of system

Essentially there are three types of systems that are used in thermoanalysis. These are illustrated in Fig. 1 which uses thermogravimetry as the example.

Types I and II are the more generally used in 'conventional' types of thermoanalysis systems which utilize relatively high-mass, slow response, resistively heated, separately controlled furnaces. In these, the temperature of the specimen, T_s, is assumed to be that of the environment surrounding the specimen, T_e,

measured with the thermocouple at or close to the specimen. It is also assumed to be the same as that of the controlled temperature of the furnace, T_c, which is measured by a separate sensor attached at some point within or on the furnace.

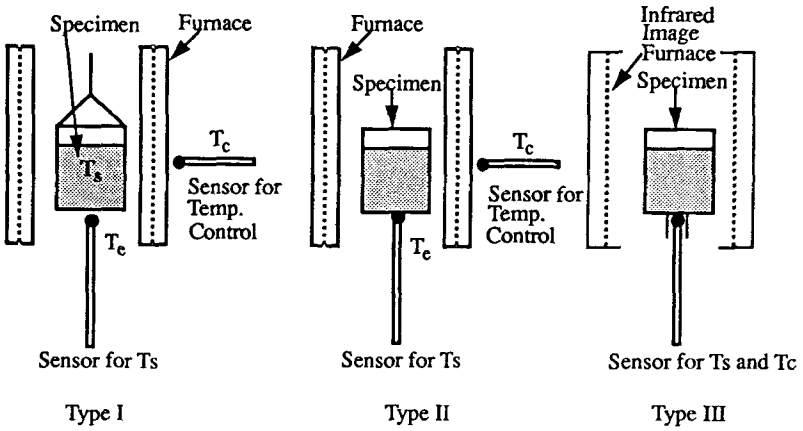


Fig. 1 Three types of temperature measurement and control for thermo-analysis studies

It can be seen that Type I can be subject to the effects of all of the factors described earlier. In particular, the temperature of the sensor never truly represents that of the specimen. It may even vary under so-called identical conditions of heating rate, gas flow, etc. In this case

$$T_s \neq T_e \neq T_c$$

In type II some of the effects are the same, but when the sensor is attached directly to the specimen or container it more represents the specimen temperature. However the combination of placement of the sensor in the high-mass furnace assembly and the heat transfer diffusion are such that:

$$T_s = T_e \neq T_c$$

In type III, one sensor only attached directly to the specimen or container measures both the temperature and controls heating and cooling rates of a very low mass system. Under these circumstances:

$$T_s = T_e = T_c \text{ at all times}$$

The major contributing factor to errors is now only that of conversion of sensor output.

A typical Type III system developed by Sinku-Riko is illustrated schematically in Fig. 2. A low-mass, very fast response, controlled environment, infrared

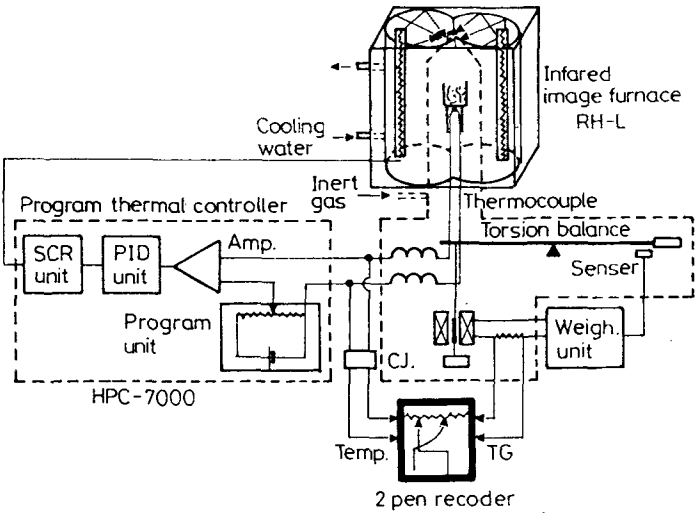


Fig. 2 Thermobalance with infrared gold image furnace

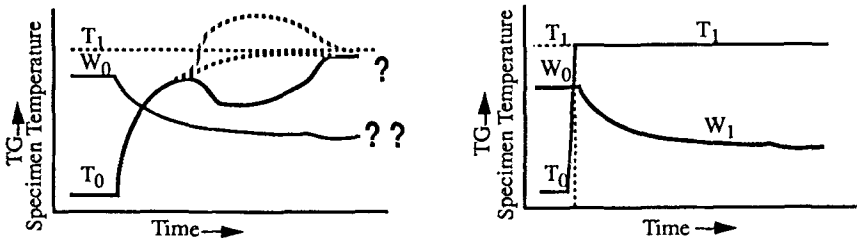
gold image furnace/cooling unit replaces the more conventional type of high-mass heated furnace. Provided that a suitable specially designed temperature controller is used, the gold image furnace can be heated (and cooled) at precise heating rates from the conventional 1–20 deg·min^{-1} to much higher levels up to 100 deg·sec^{-1}.

This combined ability of directly measuring specimen temperature precisely and using the same sensor for precise control of furnace heating or cooling rates allows thermoanalytical studies to be undertaken in the stepwise (constant temperature) mode as well as the normal isochronal (constant rate) mode. This flexibility of use is particularly valuable when undertaking absolute measurements of change of a parameter, e.g. mass and length.

Illustration of systems performance

Figure 3 illustrates the differences in the degree of uncertainty of temperature history and in overall performance of the different types of systems. Where a constant heating rate is used (Fig. 3A) with control of temperature of the furnace as in Type I and II the specimen temperature will rise asymptotically and attain a temperature close to that of the set furnace temperature. Furthermore, as decomposition or other reactions occur during the temperature excursion, the specimen temperature will be affected, e.g., upper dashed curve for exothermic reaction and lower solid curve for endothermic. Since each change is temperature-dependent,

these excursions provide uncertainties in the mass change-temperature relationship.



(A) Furnace temperature controlled (B) Specimen temperature is controlled

Fig. 3 Schematic isothermal TG and specimen temperature curves

However, in the Type III system (Fig. 3B) where the specimen can be step–heated rapidly the end set-point is attained precisely and almost immediately. Thus the mass change can all be attributed to that for the appropriate set-temperature. This type of system provides a more appropriate tool for undertaking kinetic studies of thermal decomposition by the isothermal method. Using Type I and II systems several minutes can elapse between onset of decomposition and attainment of the set temperature and thus the point $t = 0$ is hard to determine.

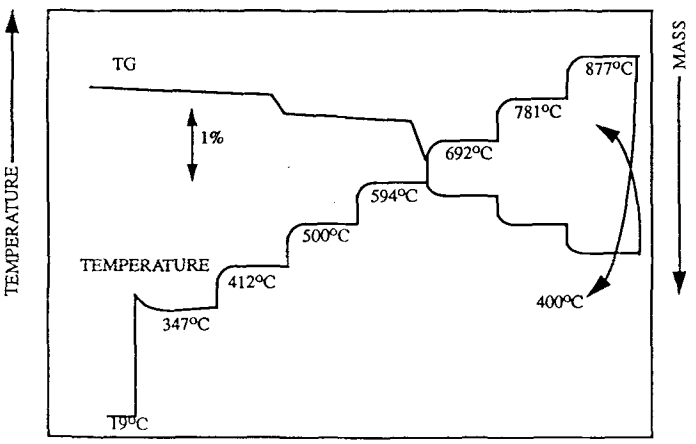


Fig. 4 Thermogravimetry curves of $YBa_2Cu_3O_{1-x}$

The Type III system has been particularly useful in the development and understanding the behaviour of superconducting oxides [2]. These undergo a number of reactions on heating involving small mass changes. Figure 4 illustrates the

changes in O_2 content of $YBa_2Cu_3O_7$ as it is heated in the stepwise mode between 340° and 880°C and then cooled. Precise control for times at specific temperatures is necessary to obtain accurate quantitative measurements. Use of Type I and II systems would provide a much lower precision of measurement curves and actual heating rates.

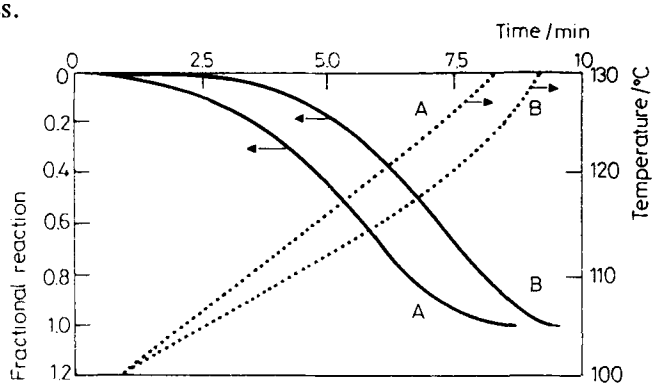


Fig. 5 TG-temperature curves for dehydration of $Li_2SO_4H_2O$ (A) specimen temperature controlled isochronally, (B) furnace temperature controlled isochronally

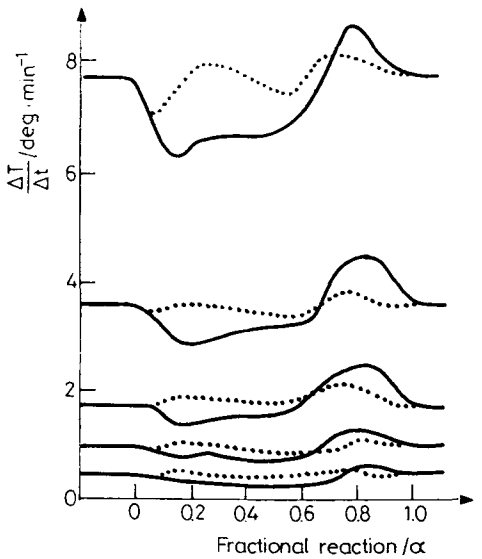


Fig. 6 Actual heating rate of TG during dehydration of $Li_2SO_4H_2O$; case A ····, case B ——

Figures 5 and 6 are reaction temperature and actual heating rate curves to illustrate a direct comparison of the effects of the different type of temperature control for the decomposition of $Li_2SO_4H_2O$ [3]. In each case the specimen was

heated in a controlled isochronal mode at 3.8 deg·min^{-1}. Curve 5A represents the decomposition behaviour using the specimen temperature for control, while curve 5B illustrates the case where control is by the furnace temperature sensor. For latter case the specimen takes longer to attain the final temperature due to the self-cooling effect of the endothermic reaction in the specimen. As a result, the activation energy of this dehydration determined from analysis of the curves was found to be 10% lower the experiment recorded in curve B.

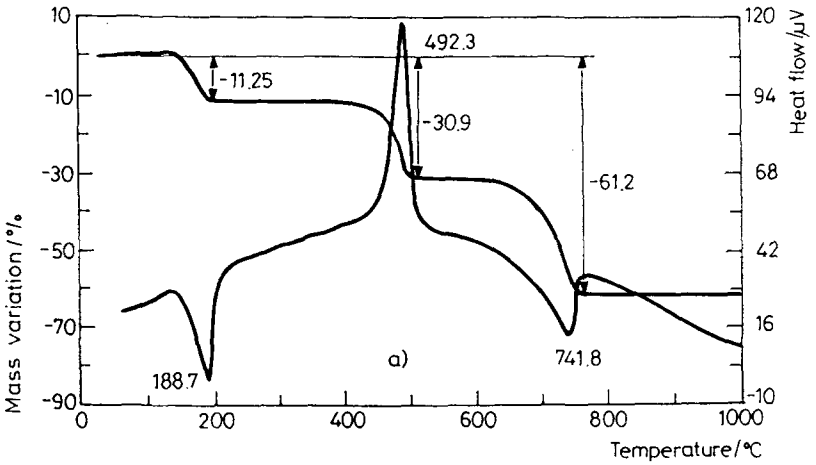


Fig. 7A TGD data processing

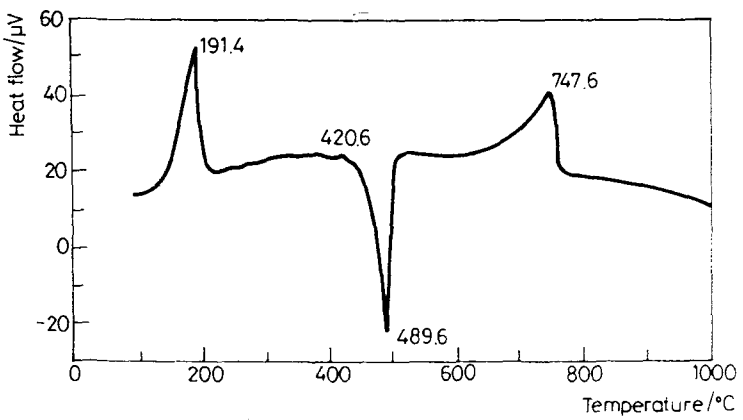


Fig. 7B TGD data processing

The last-example shown in Fig. 7-A, B, is a comparison of two techniques used for the decomposition of calcium oxalate, showing the two endothermic and

one exothermic reactions at approximately 190°, 740° and 490°C respectively. Figure 7A shows the TG and DTA curves for the decomposition when the control is based on the actual temperature as measured in the specimen, and Fig. 7B the DTA curve where control is based on a reference temperature 'close' to the specimen. The influence of the reactions on the actual peak temperatures attained can be seen, as can the better agreement between those obtained with the TG and DTA case.

Conclusions

The important parameters of temperature measurement and temperature control in quantitative thermoanalytical methods have been examined and means to minimize their impact evaluated. Illustrations of the use of a system utilizing a low-mass infrared gold image furnace with the ability to heat and cool at both conventional and very high heating rates and using a single temperature sensor for measurement and control of temperature have shown that it is the most advantageous type for precise quantitative measurements.

References

1 R. P. Tye, and R. L. Gardner, "The Contribution of Precise Temperature Measurement and Control to Thermal Analysis", to be presented at the 21st NATAS Conference, Atlanta, GA, 14–16 September 1992.
2 M. Kikuchi, J. Jpn. Appl. Phys., 26, (1987) 1066.
3 H. Tanaka, Proceedings of 26 Japan Calorimetry and Thermal Analysis Conference, Hakata, Japan, Thermal Analysis Society, Tokyo, November 1990, pp. 88–99.

Zusammenfassung — Es werden einige Faktoren diskutiert, die bei Temperaturmessungen die Genauigkeit von Schmelzpunkten und Phasenumwandlungen beeinflussen können. In vielen Fällen können sich bei der Messung und Steuerung der Temperatur in den verschiedenen angewendeten Systemen kritische Fehler durch inkorrektes Plazieren und/oder durch inkorrekte Auslegung des Outputs von Temperaturfühlern ergeben. Für thermoanalytische Untersuchungen von sowohl gleichmäßig als auch stufenweise veränderlicher isothermer thermoanalytischer Erhitzungs- und Kühltechniken ist der Einsatz eines einzigen Temperaturfühlers sowohl für Temperaturmessung als auch -regelung durch Anwendung eines "low mass infrared gold image furnace" von Vorteil. Es werden Anwendungsbeispiele dieses Gerätes für beide Einsatzgebiete angeführt.