Thermochimica Acta, 226 (1993) 343–351
Elsevier Science Publishers B.V., Amsterdam

The contribution of precise temperature measurement and control to thermal analysis[1]

R.P. Tye * and R.L. Gardner
ULVAC Sinku-Riko, Inc., Andover, MA 01810 (USA)

(Received 31 March 1993; accepted 14 May 1993)

Abstract

Several factors in temperature measurement that affect the precision of phase changes and related phenomena are discussed. Critical errors can arise in the measurement and control of temperature due to incorrect placement and/or interpretation of the sensor output. The use of different furnace types and sensor placements illustrates the advantages of using a single sensor for measurement and control of temperature. The discussion concentrates on the case of themogravimetry and similar thermal analysis techniques where absolute measurements of change in property with change in temperature are made.

INTRODUCTION

Thermoanalytical techniques have become very widely used in materials characterization studies, particularly during the last two decades. Thermoanalysis has changed from being considered essentially qualitative or comparative to a more precise quantitative tool that can provide information required for understanding basic materials behavior, reaction phenomena, etc. Significant advances, often accompanied by claims of superior precision, have been made in the development of different measurement methods and especially of commercial instrumentation based on new, improved or combined techniques. Some of the most significant advances have been made in the automation of the instrumentation and, particularly, in the subsequent analysis of the particular curves that are generated. Results based on computer-generated and analyzed curves are now the accepted norm.

A number of the basic techniques have been standardized while others are in the process of being standardized. In general these cover both manual and computer-operated systems, assuming their technical equivalency. Temperature measurement is usually made with thermocouples

---

* Corresponding author.

[1] Presented at the 21st Annual NATAS Conference, Atlanta, GA, 13–16 September 1992.

and the total temperature measuring and recording system is calibrated with standards, e.g. pure metals having definite known melting points or other known parameter behavior at definite temperatures within the range of use of the particular instrument and method.

Standard test methods, especially those developed by ISO and ASTM, require precision and bias statements. These are generally developed by means of inter-laboratory studies (often mistakenly called Round-Robins) to determine an appropriate parameter (s), e.g. melting, or transition temperature, heat of transformation, etc., of a selected material or range of materials. Glass transition temperatures have been reported to five significant figures, even though the glass transition is actually a temperature range often of varying degree [1].

The results of such studies are often most surprising and very discouraging in that the agreement between organizations, and sometimes within the same organization (reproducibility) is much worse than could be expected based on the precision claims for individual method instrumentation. In particular cases, where two different methods, e.g. DSC and TMA, have been used to determine a particular parameter, this degree of disagreement has been of even greater magnitude.

Many examples exist in the thermal analysis literature where temperatures have been reported to tenths of degrees (and some cases even to an additional significant figure) at elevated temperatures where even the known accuracy of the particular thermocouple type is 0.5°C at best [1]. Differences of ±5°C (or ±10% in other parameters) at moderate temperatures (say less than 300°C) and ±10°C (or ±20% or greater) at higher temperatures are not unknown in such studies. This degree of uncertainty is not acceptable if thermoanalytical techniques are to be used for more accurate interpretation of quantitative results. Certainly the differences do not support high precision claims for the measurement of absolute temperatures.

The present paper discusses the various factors involved in temperature measurement and its control and the potential impact of these factors on thermoanalytical techniques. The discussion will concentrate on the temperature sensor and sensor placement, particularly for thermogravimetry and similar techniques such as dilatometry where absolute (rather than relative) changes of property with change of temperature are undertaken and analyzed.

BASIC PROBLEM

Thermoanalytical techniques involve essentially two parameters, namely the change in some physical or other property on heating or cooling and temperature, including the rate of change of temperature. There are various factors in each which can affect the precision of a technique or individual apparatus. Much attention has been paid to making improvements and advances in the determination of the change in a particular thermal electrical or mechanical property under standardized operating conditions. However, it is believed that significantly less attention has been directed to the effects of the second parameter and their significance on the overall precision. In many cases the experimental design and the analysis do not ensure that the recorded final temperature(s) support assumptions that are made [2].

The essential factor to consider is that

A SENSOR MEASURES ONLY ITS OWN TEMPERATURE

It will measure a desired temperature only when sufficient efforts are made to ensure that it does represent the temperature of the particular artifact involved. This can only be accomplished ideally by direct attachment of a very small sensor shielded from extraneous and varying heat transfer effects to a body of high thermal conductivity and heat capacity. This is a somewhat difficult requirement in thermoanalytical techniques.

Thermoanalysis involves measurement of absolute or relative change in a property as a test specimen is heated or cooled at a constant rate of change of temperature. Where relative measurements are made, the behavior of the test material is compared to that of a "standard" or inert reference material having known characteristics. The specimen and reference are contained in "identical" containers placed very close together and are assumed to have identical thermal responses under the conditions of the test.

In general, the test and reference specimens and their containers, holders or supports are very small and direct attachment of the temperature sensor, usually a thermocouple, is often not practical. Special holders of various types and configurations are designed for use with appropriate thermocouple sizes and forms. Depending on the technique and the particular type or model instrument, a sensor is placed in contact on or within the holder but in many cases "close to" the specimen and its holder. The basic assumptions made in all cases are that a uniform temperature exists around the specimen, and that the specimen is small enough and of sufficiently low capacity that its absolute temperature is measured by the thermocouple, wherever and however it is placed.

For a test, the specimen, including the reference where appropriate, is placed in a controlled temperature environment, usually a resistive-heated furnace, and heated (or cooled) at a controlled rate. Depending upon the specific requirement, this is usually between 2 and 10°C $\min^{-1}$ through the temperature regime of particular interest. Under these conditions, it is assumed that a constant temperature is maintained in and around the specimen at any moment in time and that this temperature represents that of the specimen and is the one recorded by the measurement system. This assumption is very difficult to maintain for all conditions at all heating and cooling rates.

INDIVIDUAL CONTRIBUTIONS TO ERROR

Based on the particular absolute or relative technique and instrumentation used, the experimental conditions and the assumptions made, errors in measurement can occur due to a number of interrelated factors as follows.

Specimen type, form and amount

The thermal diffusivity (thermal conductivity divided by the product of density and specific heat) will differ for different forms of a specimen. For example, the thermal conductivity of a solid material can be at least an order of magnitude greater than for its powdered form. However the density difference for the same mass may only be a factor of two or three while the specific heat remains the same whatever the material form.

Experimental conditions

The heat transfer to the specimen and thus to the temperature sensor from the surrounding environment can differ significantly depending upon the conductive heat transfer from the surrounding gas. For example, the thermal conductivity of helium (if used as protective gas) is some five times greater than that of nitrogen. Convective heat transfer can also take place and this will differ depending upon the orientation of the test stack. For example, in thermogravimetry the specimen can be installed either vertically or horizontally depending upon the type of balance that is utilized. Convection is much more significant for the former orientation. If flowing gas is used, the conductive and convective heat transfer components will also be different. If tests are undertaken in vacuum, heat transfer is by radiation alone and the emittance of the specimen and containers have to be the same or very similar. All of these parameters will be affected, often significantly, by the heating rate.

Type and size of thermocouple

Various thermocouples types are used depending upon the temperature range of the apparatus. Chromel/alumel is most often used for temperatures up to 1000°C while platinum–rhodium/platinum is preferred for temperatures up to 1500–1600°C and for oxidizing environments. The former has a relative high voltage output, approximately $40\,\mu V\,°C^{-1}$

between 0 and 1000°C, whereas the latter is much lower, rising from about 6 $\mu V\ °C^{-1}$ at 20°C to 10 $\mu V\ °C^{-1}$ above 1000°C. Such sensitivity differences will affect the measurement significantly, especially at the lower temperature end of the range of operation.

However, chromel/alumel is much less stable, even at moderate temperatures, due to phase transitions and to migration of alloy components especially in the alumel. This changes the composition and hence the output of the junction. This combination is also subject to oxidation and contamination, and replacement is often required especially if small-gauge wires are used. Continuous checks of stability of the calibration or regular replacement of the thermocouple are required. In general, the thermocouple needs to be fabricated from small-diameter wires (preferably less than 0.15 mm). Faster responses can be obtained with smaller thermocouples but these are more fragile and are subject more rapidly to contamination.

Evaluation of measured temperature

The output voltage from the thermocouple is converted to temperature using an appropriate calibration. This can be either a separate calibration for the actual sensor or, more usually and less accurately, the "standard" calibration tables for the specific thermocouple type. These calibrations are all based on the cold (or reference) junction of the thermocouple being maintained constant in an ice/water mixture at 0°C. In many cases electronic "ice points" are now used for the reference junction. Temperature variations of up to 0.5°C can be obtained with these devices if they are not well insulated from other instrument components which may be installed close to the unit and that generate heat.

More recently, with the continuing improvement in electronic components and computer hardware and software, conversion of the thermocouple voltage is now of carried out by using an equation relating the output voltage (often amplified) to temperature. In some of the simplest cases, a linear relationship between voltage and temperature has been used for a "relatively small" temperature range. However, this has been interpreted differently by different people and the assumption can lead to sensor errors depending upon the range for which linearity is considered. Gross errors are possible if the linear relationship is assumed to exist over more than 100–200°C and should not be assumed at all at temperatures below 0°C.

Table 1 contains details of the "worst case" type of errors that can exist if a simple linear relationship is assumed for different temperature intervals. Linearity over smaller intervals or a best-fit line will improve matters somewhat, but may only reduce the uncertainties by a factor of 2 or 3. To attain the same precision as can be derived from the direct conversion by

TABLE 1

Maximum temperature measurement errors based on output linearity

Assume linear relationship over the range/°C	Error at			
	500°C	400°C	300°C	−100°C
0–300	−8	−2		+10
0–500	–	4	6	12
−100–500	−3.5	0	3.5	6

use of the thermocouple tables, a second- or third-order polynomial equation is necessary. This also assumes that additional errors have not been introduced by any electronic amplification which may have been included prior to conversion.

Placement of temperature sensors

This factor is one that can be most critical to thermoanalytical techniques, particularly when using quantitative data for analysis of materials behavior, e.g. length or dimension changes or mass changes for reaction kinetics.

Using thermogravimetry as the example, Fig. 1 illustrates three types of specimen, furnace, and control system that can be used.

Types I and II are the more generally used "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

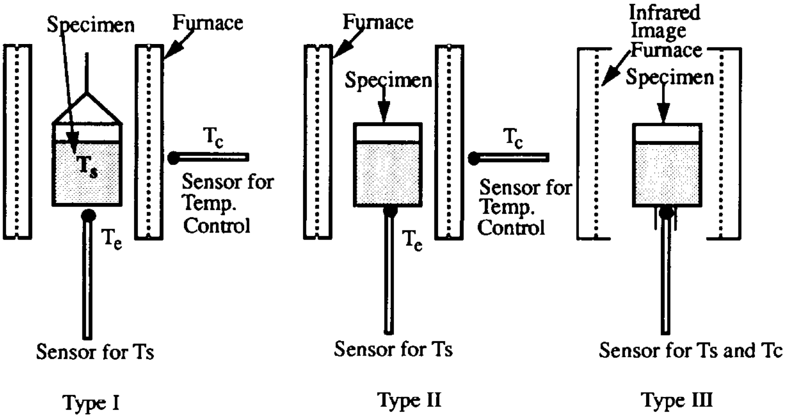


Fig. 1. Three types of temperature measurement and control for thermal analysis studies.

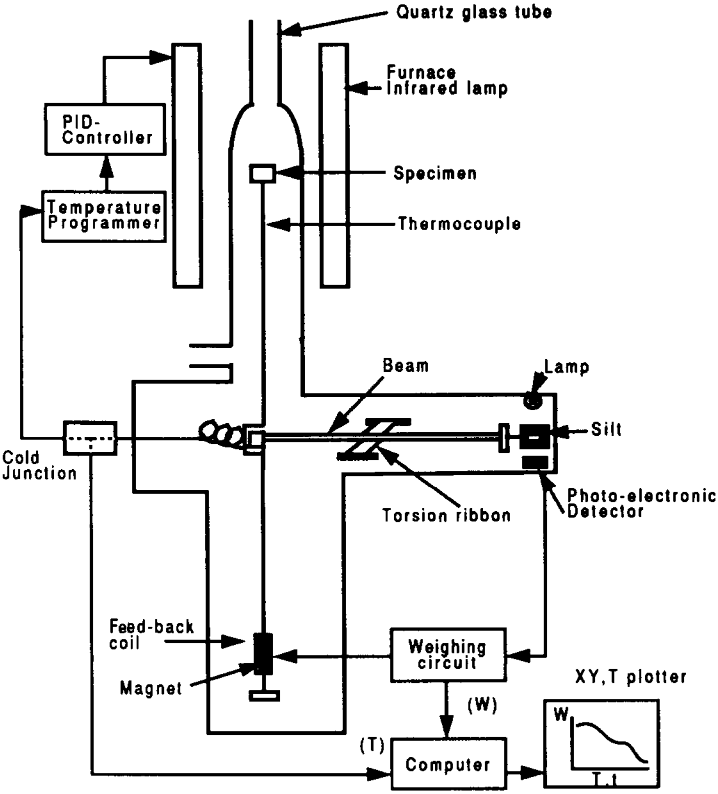


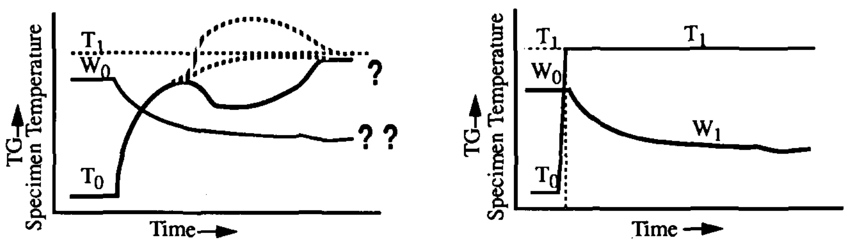
Fig. 2. The Sinku-Riko TGD-7000-RH, TG/DTA system (schematic).

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. However, due to a combination of the various factors discussed above: for type I, $T_s \neq T_e \neq T_c$; for type II, $T_s = T_e \neq T_c$.

However, where one contacting thermocouple only is used, not only to measure the specimen temperature but also to control the furnace temperature, it can be seen that for type III, $T_s = T_e = T_c$ at all times.

The type III system, illustrated schematically in Fig. 2, is achieved by Sinku Riko by the replacement of the conventional type of resistive-heated furnace with a low mass, very fast response, controlled environment, infrared gold image furnace [3]. Such furnaces can be heated (and cooled) at very precise rates including those used for conventional measurements, 1–50°C min^{-1}, up to levels as high as 100°C s^{-1}.

The combined ability to control heating and cooling rates from conventional levels up to 100°C s^{-1} and to measure the specimen temperature precisely, even at such rapid rates, allows thermal analysis



(A) Furnace temperature is controlled

(B) Specimen temperature is controlled

Fig. 3. Schematic isothermal T_g and specimen temperature curves.

studies to be made not only in the normal isochronal (constant heating rate) mode but also in a stepwise isothermal (constant temperature) mode.

As shown in Fig. 3, when the furnace is controlled separately there is uncertainty in the difference between the specimen and furnace temperatures during heating to the final required temperature level. Thus the total mass loss cannot be attributed to that for a known specific temperature or condition and this uncertainty will affect subsequent calculations. However, the use of rapid heating rates and direct specimen temperature as the control parameter eliminates these uncertainties. In this way, very precise quantitative measurements of mass or other parameter changes and of reaction kinetics during endothermic and exothermic transtions at very precisely controlled temperatures can be undertaken simply and rapidly.

These factors indicate that many uncertainties exist regarding the precision of the temperature measurement parameter in thermoanalytical studies. Certainly claims of derived temperatures to tenths and hundredths of kelvins cannot be substantiated from experimental curves. In the analysis of their results, thermal analysts claim that the temperature scale of their instruments is “calibrated” with the use of reference materials of well-known melting points. Thus, they claim a similar high precision of measurement of derived temperatures from analysis of curves based on these calibration values entered into the software.

However, such claims are erroneous. It is true that melting points of reference materials are known to such high precision levels. Melting points are determined under “steady-state” conditions using sophisticated experimental apparatus and temperature measurement systems having very much higher orders of precision than that which can be obtained using only one thermocouple placed in an uncertain position and being heated and cooled under varying transient conditions.

To overcome this problem it is recommended that thermal analysts accept the limitations in temperature measurement claims. In future, reports of transitions temperatures should be referred to more realistic precision levels. In the analysis of results this will entail entering into the analytical program, melting point calibration values that are based on more realistic levels (0.5–1 K at best) that can be attained with the particular measurement system. In this way, reported temperatures will be more practical and less misleading.

CONCLUSIONS

The various factors affecting temperature measurement and temperature control in quantitative thermoanalytical methods have been examined, and means to minimize their impact have been evaluated. A particular type of system utilizing a low mass, infrared gold image furnace with the ability to heat and cool at both conventional and very high heating rates, using a single temperature sensor for measurement and control of temperature, is found to be most advantageous for precise quantitative measurements. Recommendations are made concerning the reporting of more realistic values of temperatures in thermoanalytical techniques.

REFERENCES

1 For various examples see, Proc. 20th Annual NATAS Conf., Minneapolis, MN, September, 1991.
2 R.P. Tye, R.L. Gardner and A. Maesono, Temperature Measurement and Control: Critical Parameters in Thermal Analysis Techniques, presented at 10th ICTA Congress, Hatfield, UK, August 1992. In the course of publication in J. Therm. Anal.
3 M. Kikuchi, J. Jpn. Appl. Phys., 26(6) (1987) 1066.