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ADAPTING A THERMOBALANCE TO CONSTRAINED RATE THERMOGRAVIMETRY

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Abstract

A thermobalance has been converted to allow interactive control of the heating rate from the rate of mass loss of the sample (Constrained Rate Thermogravimetry). The interfacing of the balance and temperature controller both to an ACORN RISC microcomputer and to a PC microcomputer is described along with an outline of the software required. This provides an economic route for the conversion of existing thermobalances. Problems of achieving effective control and acceptable data recording are outlined. The nature of the TG curves obtained from interactive temperature control and the influence of control parameters is discussed.

Keywords: constrained rate thermogravimetry, new software

Introduction

Conventional thermogravimetry subjects samples to a uniform heating rate and it is widely realised that heating rate can have a major influence on the information content of the TG curves obtained [1]. With solid samples, high heating rates can lead to poor resolution of intermediate stages; with organic compounds, particularly polymers, ill-defined TG curves are frequently obtained which require presentation in derivative mode for characterisation. Reduction of heating rate will increase resolution but has an obvious penalty in the form of increased run times which may be unacceptable in industrial applications.

Attempts to achieve better resolution without incurring an excessive time penalty are summarised by Reading [2]. He discusses the development from the Constant Rate Thermal Analysis (CRTA) initiated by Paulik and Paulik [3] and Rouquerol [4] to more flexible temperature control regimes. The approach to be discussed here involves using a computer program to relate the heating rate to the rate of mass loss of the sample. This has been called Dynamic Rate TGA [5] but Reading proposes the descriptor of Constrained Rate Thermal Analysis (CaRTA) for control systems in which the power supplied to the furnace is a

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function both of the measured response of the sample and the rate of change of sample temperature.

The key to such an approach is the use of the computer to monitor data signals from the property transducer (e.g. an electronic microbalance) and the sample temperature and to use these to set parameters for the power flow to the furnace or other heating element. As Reading points out, nothing in these systems is constant.

CaRTA attempts to optimise resolution of thermal processes without having extensive run times. It can be seen as a logical progression from the use of computers to control thermal instruments by software which mimics the pre-microprocessor hardware to a greater utilisation of the flexibility inherent in computer interfaced instrumentation. The computer program can allow a great deal of flexibility in setting heating rates (including constant ramp rates and "ramp and hold" temperature profiles) but the thermal curves obtained are influenced not only by the usual thermogravimetric variables but also by the control parameter algorithms in the software.

At this point in time, commercial software for CaRTA is limited but this paper will attempt to show that suitable software and interfaces can be readily developed by any organisation with a modicum of electronic and programming expertise. Commercial instruments are now being sold which are specifically designed for CaRTA but many older thermobalances can be readily converted provided sufficient expertise is available to write software and construct the simple interface units. In this University we have adapted a Stanton Redcroft TG-770 thermobalance to interface either an ACORN A3000 microcomputer running in-house written software in BBC BASIC or a PC microcomputer running software in turbo Pascal.

Design and construction of interfaces

The typically 0 to 10 mV level signals from the balance mechanism and the sample thermocouple require to be amplified. The ACORN has an on-board ADC chip which operates over a 0 to 1.7 V range and the PC was fitted with a 12 bit A/D board (Brain Box) operating over a −5.0 V to +5.0 V range. These required separate amplifier units which were each constructed from readily available non-inverting operational amplifiers with appropriately selected resistors. Low-pass passive filters were also fitted to reduce signal noise.

In the Stanton Redcroft TG-750 temperature controller the power output to the furnace is controlled by a stepper motor. In conventional use the rotational rate of the stepper motor and hence the heating rate is switch selected. This switch selects one of a number of resistors. In essence, a switch was inserted which selected the maximum heating rate and the power supply to drive the

stepper motor was diverted through a relay, activation of which was controlled by an output signal from the computer – via the User Port on the ACORN and the TTL port on the A/D card in the PC. This allows the stepper motor to be driven in both heating and cooling directions and to be switched on and off under software control. The ACORN system was developed first but either computer system can be selected from a simple plug and socket as they both use the same temperature controller interface.

This approach can be adapted to other forms of temperature programmer if they can be set at a pre-determined ramp rate and switched on and off by a relay. With microprocessor controlled temperature programmers it may be possible to vary the power input by outputting a binary number from the computer.

The computer systems and software

The ACORN Archimedes series of RISC processor computers are widely used throughout the UK and provide a relatively cheap computer with good memory capacity, very fast data processing, good screen displays and a widely known programming language. The disadvantages are that an expansion board to provide the analogue to digital conversion and the User Port has to be purchased and that the data is not readily transferable into the more widely used MS-DOS environment. Also, the analogue to digital convertor readily available is not reliable above 10 bits and has a relatively slow conversion rate compared to the PC based system. One further caveat is that printing out TG curves requires transfer of data files into a (supplied) utility program. Where transfer of data files is not required and hard copy does not have to be frequently generated the ACORN system is very cost effective.

PC based systems are more expensive but have the undoubted advantages of the greater availability of expansion boards, transferability of files, greater ease of generating hard copy and a much larger installed user base.

Although separate software was written for both systems, in BBC BASIC for the ACORN and PASCAL for the PC, both use similar approaches to the control algorithms. The strategy is to define a time segment and to switch the stepper motor on for a proportion of the time segment which is calculated from the change in the mass signal over the previous time segment. If the sample is not appreciably losing mass the temperature will be ramped at the maximum rate. If the sample is losing mass rapidly the stepper motor will be switched off throughout the time segment and the sample temperature will be constant. At intermediate rates of weight loss the stepper motor is switched on for a proportion of the time segment to give a range of heating rates controlled from the software.

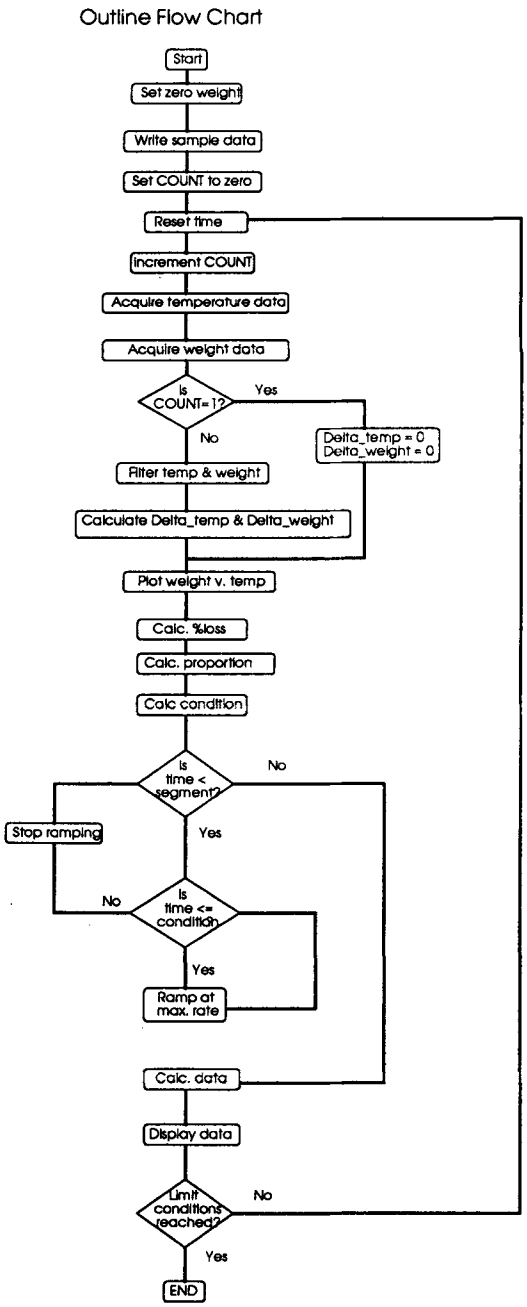

Fig. 1 Outline flow chart for software program

Problems arise due to conflicts between sensitivity of control and the length of the time segment. For high precision it is desirable that the system respond rapidly to genuine changes in the rate of mass loss. This would imply using a short time segment but then the measured changes in mass are small and more subject to noise in the signal and quantisation errors in the analogue to digital conversion.

It will probably be found necessary to use some form of software filtering as well as the hardware low-pass filters in the interface. A compromise has to be arrived at unless the instrument quality is such that the balance signal is virtually noise free. In addition to the signal and software constraints it is also essential that the furnace has a low thermal inertia and the heat flux to the sample changes rapidly with power input to the furnace.

The algorithm which converts the calculated change in mass (Δw) to a proportion of the time segment can take a variety of forms. A linear relationship is the most obvious choice but can lead to an over-sensitivity to spurious changes in the calculated value of the mass change and consequently extended run times. Minor fluctuations in Δw can be smoothed by using a DIV function and thus generating a quantised series of control parameters. The value of the DIV number then becomes a sensitivity parameter. Other more elaborate functions can be used and/or a series of IF...THEN statements. This part of the software is crucial in optimising the conflicting demands of resolution and run time and should be easily edited or controlled by keyboard inputs. An outline Flow Chart is given in Fig. 1.

The analogue signal acquired from the sample thermocouple is non-linear with temperature and its digital convert will have to be converted to a true temperature using an appropriate thermocouple equation. An approximate equation for a Pt *vs.* Pt/13%Rh thermocouple is:

$$T(°C) = CJT + 153.4(mv) - 18.2(mv)^2 + 2.49(mv)^3 - 0.16(mv)^4 + 0.0035(mv)^5$$

where CJT is the cold junction temperature in °C.

The use of too short a time segment causes problems in that the calculated values of Δw will normally be small and more subject to noise, even with data averaging within the time segment loop. The length of segment should be chosen from consideration of the temperature precision required and the maximum ramp rate. It is also recommended that Δw be calculated as a percentage of the initial weight.

With short time segments and unconditional data storage large numbers of data point weight and temperature pairs are accumulated, giving large data files with small differences between successive members. Where mass loss processes are intrinsically slow at their minimum occurrence temperatures, notably

with polymers, this can be unnecessarily cumbersome. Most TG curves can be satisfactorily defined with 200 to 300 pairs of data points (provided that they are in the right places!) and derivative plotting is simpler with relatively low numbers of data points. Conditional data storage using IF.....AND.....THEN statements may be preferred. However one of the potential advantages of CaRTA is that collecting data on a time basis during a period of rapid and hence quasi-isothermal mass loss can allow kinetic analysis to be carried out. While such experimental conditions may not satisfy the rigourous requirements of the kinetic specialists, the ability to extract kinetic information may be an additional tool in Quality Control by thermogravimetric analysis.

Unless very stable and noise-free data analogue signals are generated and analogue to digital conversion is carried out at a high number of bits, data smoothing will be required for TG curve presentation and derivative plotting. Some data averaging can be done within the time segment and bit filtering be applied within the software but, in most cases, further smoothing will have to be carried out on the stored data. Smoothing algorithms such as the Savitsky–Golay [6] may be used although the more brutal box-car averaging has the advantage of simultaneously smoothing and reducing the size of the data set.

Derivative plotting can be carried out on either a dw/dt *vs.* T or dw/dT *vs.* T basis. The latter form emphasises steep regions on the w *vs.* T TG curve but, under quasi-isothermal conditions, an artificial constraint has to be applied to the minimum ΔT value used to calculate dw/dT to avoid values going to infinity. This mode of derivative plotting is artificial but can give impressive looking derivative curves. Extensive data smoothing will be required to produce smooth derivative curves.

Advantages of constrained rate thermogravimetric analysis

Reading [2] has discussed these with particular emphasis on solid state decompositions. The main advantage of CaRTA is that it gives improved resolution of intermediate stages in thermal decomposition as shown in the dehydration of hydrated copper sulphate (Fig. 2) and in the loss of pyridine ligands from tetrapyridinonickel(II) bromide (Fig. 3). With samples which remain in the solid state throughout, this gives better separation of intermediate stages compared with constant ramp rates of around 20 deg·min^{-1} as illustrated in the decomposition of hydrated potassium trisoxalato-iron(III) (Fig. 4). However, in most such cases it is unlikely that any significant new information will emerge.

Where significant differences do emerge and where CaRTA may have an important future is in the decomposition of polymers. The TG curves obtained for an epoxy resin (Fig. 5) and polycarbonate (Fig. 6) when heated at around

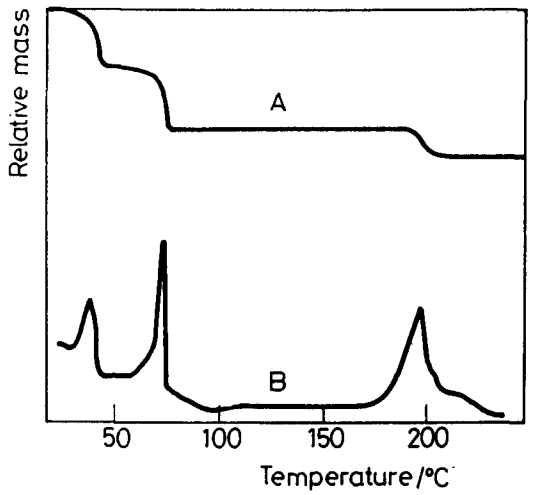

Fig. 2 TG (A) and DTG (B) plot for $CuSO_4 \cdot 5H_2O$ under CaRTA conditions (run time 17.25 min)

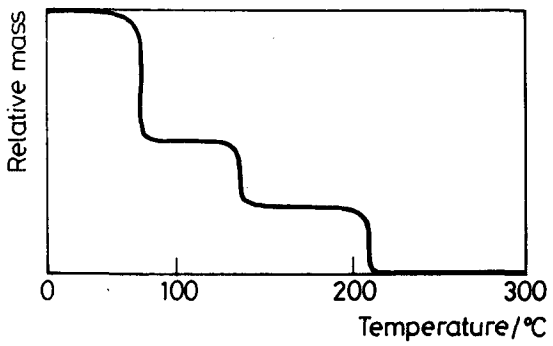

Fig. 3 TG plot for the removal of pyridine ligands from $[Ni(C_5H_5N)_4]Br_2$ under CaRTA conditions (run time 13.5 min)

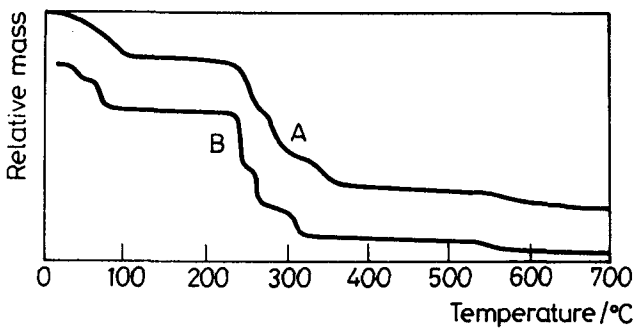

Fig. 4 Comparison of the TG plots for the decomposition of $K_3[Fe(C_2O_4)_3] \cdot nH_2O$ at constant ramp rate (run time 39.5 min) (A) and under CaRTA conditions (run time 33.75 min)

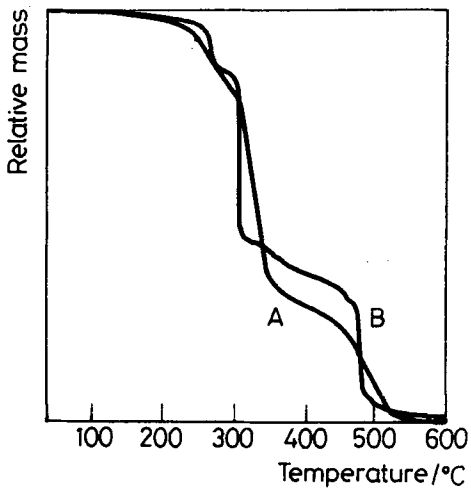

Fig. 5 Comparison of the TG plots for the decomposition of an epoxy resin at constant ramp rate (run time 63 min) (A) and under CaRTA conditions (run time 52 min) (B)

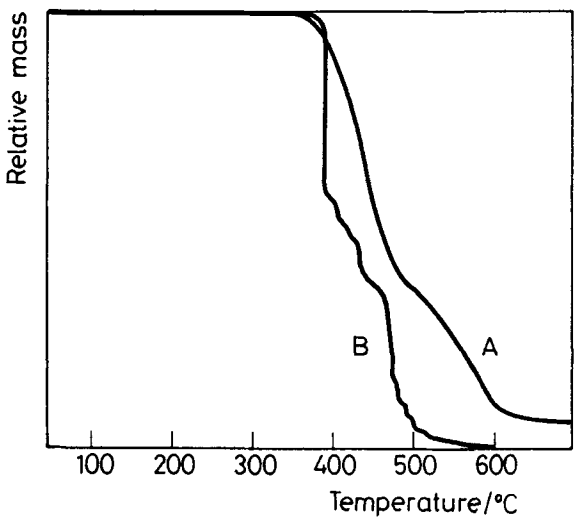

Fig. 6 Comparison of the TG plots for the decomposition of polycarbonate at constant ramp rate (run time 32 min) (A) and under CaRTA conditions (run time 45.5 min) (B)

20 deg·min^{-1} and under CaRTA conditions, using the ACORN system, exemplify the dramatic changes that can be observed. This should make it possible to characterise polymers and plastics in a more distinct manner without using extensive run times, although some polymers (e.g. ABS copolymers) lose volatiles slowly and give run times of about 60 min. To date, only runs in a flowing

dry air atmosphere have been carried out and the TG curves will probably involve both depolymerisation and oxidation processes. Much further study is required here.

Implications of CaRTA for thermogravimetric analysis

Interfacing with computers is now the standard in thermal analysis but a full appreciation of the flexibility of control over the experimental conditions that can be obtained has only recently started to emerge. The CaRTA technique is expected to become more widespread, probably through the introduction of commercial software packages, and should make thermogravimetric analysis a more precise analytical tool. TG is also likely to become more important in the study of polymer degradation and polymer Quality Control.

There are also implications for instrument design. If the power input to the furnace is controlled by feedback from the data signals, the furnace is merely acting as a responsive source of thermal energy. There seems to be no intrinsic need for a carefully constructed and hence expensive furnace. Given efficient control of the energy input to the sample, small heat sources of various types may be preferred for cheapness and lower thermal inertia. One can envisage radiant heat sources (possibly even pulsed lasers) of other small devices replacing the conventional furnace. There are indications that instrument manufacturers are already thinking along these lines.

If the furnace is replaced with a small heating element, thermobalances will become smaller and more easy to interface with e. g. mass spectrometers. Looking (perhaps optimistically) further ahead, the current electronic microbalances with their delicate mechanisms may be replaced by piezoelectric force sensors as only changes in relative mass rather than absolute mass need to be measured. There are considerable problems in such an approach but the very sensitive force transducers developed for Scanning Tunneling Microscopy and Atomic Force Microscopy indicate the potential.

* * *

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References

1 C. J. Keattch and D. Dollimore, An Introduction to Thermogravimetry, 2nd. Ed. Heyden Publisher, London 1975, pp. 29–30.

2 M. Reading, Thermal Analysis - Techniques and Applications, E. L. Charsley and S. B. Warrington (Eds.), Royal Society of Chemistry, Cambride 1992, pp. 126–155.

3 J. Paulik and F. Paulik, Anal. Chim. Acta, 56 (1971).
4 J. Rouquerol, Bull. Soc. Chim. Fr., 31 (1964).
5 S. R. Sauerbrunn, P. S. Gill and B. S. Crowe, 5th ESTAC, (1991) 0–6 Heyden, London 1992.
6 A. Savitsky and M. J. E. Golay, Anal. Chem., 36 (1964) 1627.

Zusammenfassung — Zur Erlangung einer interaktiven Kontrolle über die Aufheizgeschwindigkeit anhand der Geschwindigkeit des Massenverlustes der Probe wurde eine Thermowaage entsprechend umgewandelt. Unter Hinweis auf die benötigte Software wurde der Anschluß der Waage und der Temperaturkontrolleinheit sowohl an einen ACORN RISC Mikrocomputer als auch an einen PC beschrieben. Dies stellt einen ökonomisch gehbaren Weg für die Umwandlung von bereits vorhandenen Thermowaagen dar. Es erfolgen Hinweise auf die Probleme beim Erlangen einer wirksamen Kontrolle und einer annehmbaren Datenaufzeichnung. Weiterhin wird die Natur der mittels interaktiver Temperaturkontrolle erhaltenen TG-Kurven sowie der Einfluß der Kontrollparameter diskutiert.