Modern Instruments Section

A NEW HIGH SENSITIVITY THERMOBALANCE

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A new thermobalance is described which gives a direct plot of percentage weight loss versus sample temperature, without the need for replotting the results. The unit operates over the range ambient to 1000°C and features a miniature water-cooled furnace in conjunction with an electronic microbalance, giving sensitivities of 1—250 mg for full scale deflection on a potentiometric recorder. Heating rates of 1—100°C/minute are available and the furnace will cool from 1000°C to 50°C in less than four minutes. Typical applications of the unit are illustrated by reference to a number of inorganic and polymer systems.

Although recent years have seen considerable development in the field of differential thermal analysis instrumentation, thermobalance design has not proceeded to such a high level of sophistication. Thus samples of the order of 50—200 mg are still widely used, requiring slow heating rates to obtain good resolution. This, coupled with the slow cooling rate of conventional furnaces, makes thermogravimetry a fairly lengthy process.

In addition, the so-called "buoyancy effect" which causes an apparent increase in sample weight [1], requires the results to be replotted before a graph of percentage weight loss versus sample temperature can be obtained.

The aim of the present design was to construct a thermobalance which would enable samples of the order of a few mg to be studied with good resolution at high heating rates, with minimum cool-down time between experiments. It was also required that "buoyancy effects" should be reduced to a level where it was possible to obtain a direct reading of the weight changes.

Description of the Apparatus

A. *Furnace*

A cross-section of the furnace assembly is shown in Fig. 1. The furnace case, *C*, is made from chromium—plated brass and water-cooled by means of vertical channels. The sample is contained in a platinum dish, *S*, and heated using a microfurnace, *F*, constructed from mineral insulated nichrome wire sheathed in inconel; the sheath being in direct contact with the water-cooled body. The furnace, which

is approximately 12 mm in diameter and 20 mm long, is self-supporting and hence does not require a former, considerably reducing the thermal mass. The sample temperature is measured from a plate type platinum platinum-13% rhodium thermocouple, *T*, positioned immediately below the sample crucible.

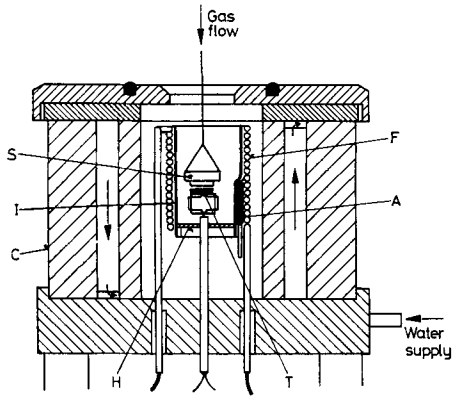

Fig. 1. Cross-section of furnace assembly

A range of switch selected heating rates from 1 – 100°/minute is obtained using a Stanton Redcroft 682 programmer, which controls from a chromel-alumel thermocouple, *A*, in contact with the furnace windings.

The gas is passed downwards over the sample and leaves the base of the inconel furnace liner, *I*, via the small hole at *H*. For gas analysis studies a capillary tube can be inserted at *H* and connected directly to the gas detector. Flow rates of 10 – 25 ml/min are normally used.

B. *Balance Assembly*

The complete balance and furnace assembly is shown in Fig. 2. The electronic microbalance, *B*, is housed in a glass bottle. It has a capacity of one gram and gives a range of switch selected sensitivities from 1 to 250 mg for full scale deflection on a 10 mV recorder. The sample crucible, *S*, is suspended in a platinum-rhodium stirrup attached to the beam via a single piece aluminium tube, *N*.

The suspension passes through a narrow bore glass hangdown tube, *H*, with a ground-glass flange, *F*, at one end. The furnace assembly, *C*, can be raised or lowered mechanically and seats against the bottom of this flange with an "O" ring ensuring a complete seal. Flow paths for the gas and water are shown in Fig. 2 and the system may also be evacuated via the glass bottle prior to flushing with an inert gas. Access to the reference pan is by means of the removable glass cap, *G*. The balance is provided with an electrical tare of 12 mg, enabling most samples to be balanced without the addition of weights.

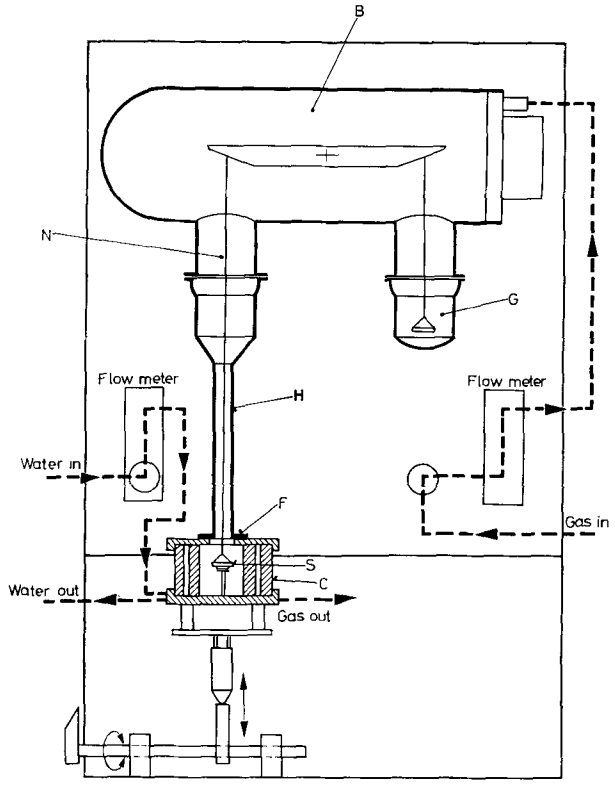

Fig. 2. Schematic diagram of balance and furnace assembly

A photograph of the balance and control unit is shown in Fig. 3 and a block diagram of the complete assembly is shown in Fig. 4. The balance output is fed to one channel of a two pen $X_1 - X_2$ potentiometric recorder while the thermocouple output is fed to the other channel. For the most effective operation of the TG-750 the recorder should have a continuously variable range facility.

Instrument Performance

Due to the low mass of the water-cooled furnace, it is possible to obtain fast heating and cooling rates together with good temperature response, so that isotherms may be established within a few seconds of switching the furnace to hold. This is illustrated by Fig. 5 which shows the temperature trace for a sample heated at 100°/min and taken through a series of isotherms. Isothermal stability is better than $\pm 1°$. The natural cooling curve at the conclusion of the run shows the rapid rate of cooling and it is possible to remove the sample crucible within

a minute of switching off at 1000°. Instrument down time between runs is therefore extremely low.

Since the furnace is very small and enclosed in a water-rooled case, problems due to heating up of the balance are eliminated and the furnace can be held at

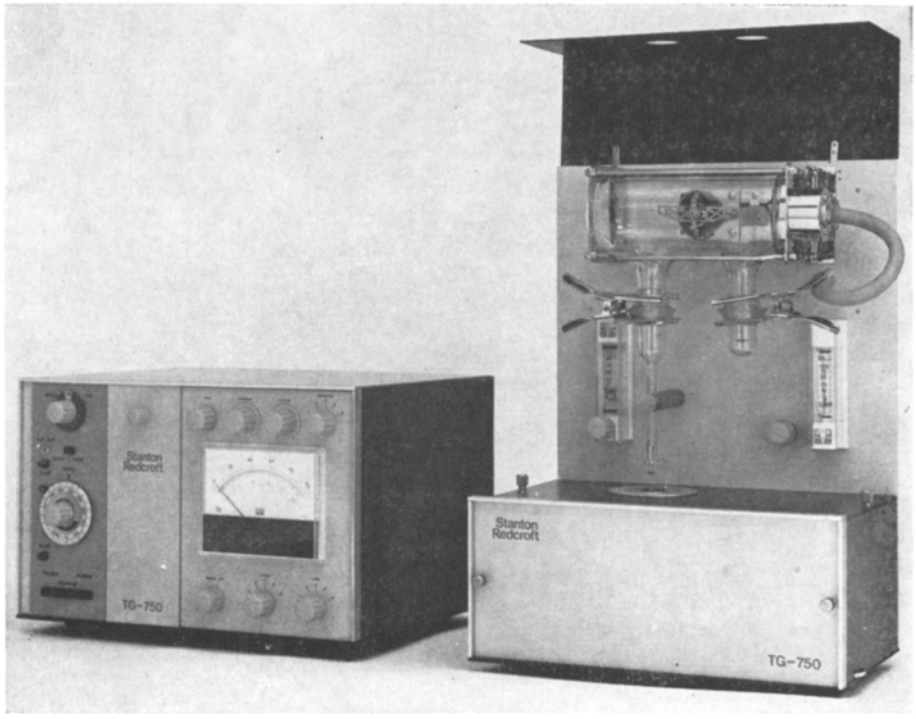

Fig. 3. Thermobalance and control unit

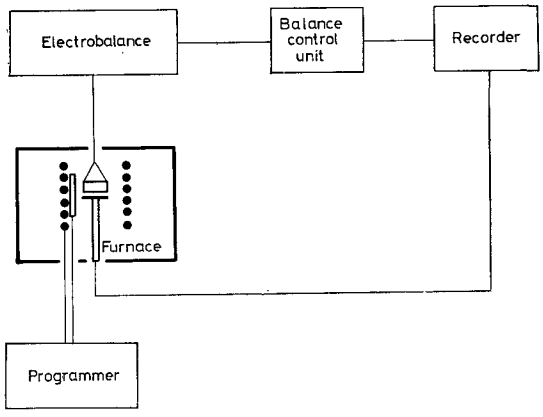

Fig. 4. Block diagram of complete assembly

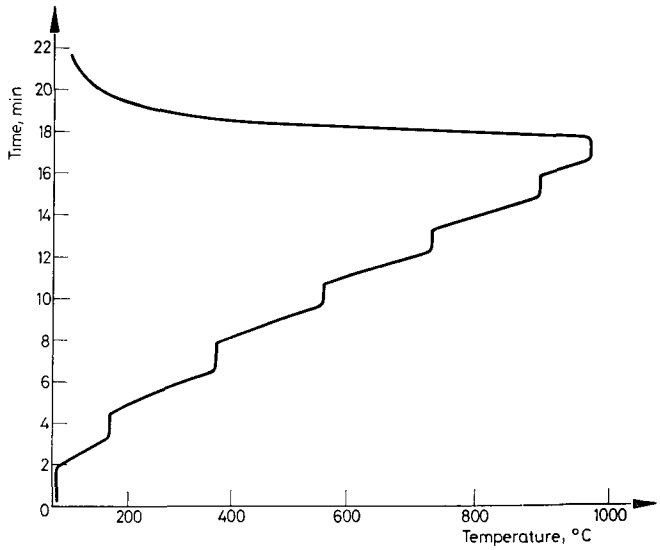

Fig. 5. Temperature trace at a heating rate of 100°/minute with programme arrests, followed by natural cooling

1000° without causing drift of the balance. The design also ensures that the volume of the sample container and hangdown system in the region of the furnace hot zone is very low and minimizes vertical temperature gradients, so that the "buoyancy effect" is reduced to a few μg and can normally be neglected.

Applications

In the following examples of the uses of the TG-750, the curves have been traced directly from the original charts without alteration.

Direct weight loss plots

The most useful feature of the TG-750 balance is the ability to directly plot TG curves in terms of percentage sample weight loss. The normal procedure is to zero the balance on the 10 mg range with the empty crucible in position and the required atmosphere flowing. The sample is then directly weighed into the crucible and the weight is recorded on the chart. The variable range facility of the recorder is then used to expand the sample weight to 100% of full scale.

The result for a 1.7 mg sample of calcium oxalate monohydrate is shown in Fig. 6. It can be seen that at this fast heating rate and high sensitivity there is no distortion of the weight loss curve due to "buoyancy effects".

It is also possible to expand the range so that small weight losses can be studied in detail. This is illustrated by the plot for $CuSO_4 \cdot 5H_2O$ shown in Fig. 7, the weight loss stages corresponding to the following reactions:

a) $CuSO_4 \cdot 5H_2O \rightarrow CuSO_4 \cdot 3H_2O + 2H_2O$
b) $CuSO_4 \cdot 3H_2O \rightarrow CuSO_4 \cdot H_2O + 2H_2O$
c) $CuSO_4 \cdot H_2O \rightarrow CuSO_4 + H_2O$
d) $CuSO_4 \rightarrow CuO + SO_3$

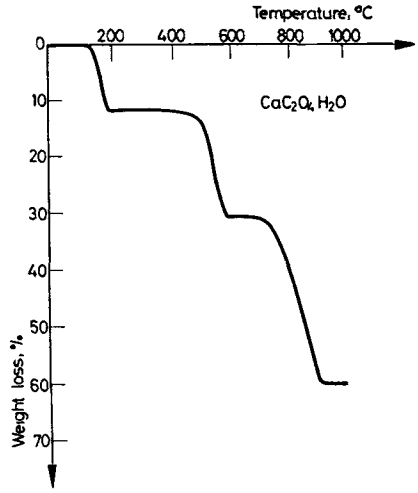

Fig. 6. TG curve for calcium oxalate monohydrate. Sample weight: 1.7 mg. Heating rate: 30°/min. Atmosphere: air, 10 ml/min

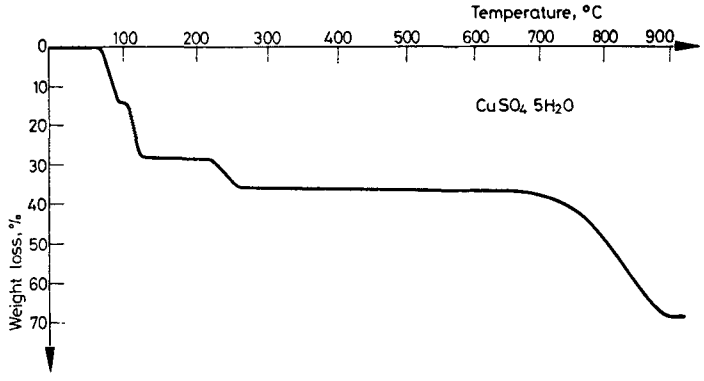

Fig. 7. TG curve for copper sulphate pentahydrate — 100% sample weight for full scale deflection. Sample weight: 5.9 mg. Heating rate: 10°/min. Atmosphere: air, 10 ml/min

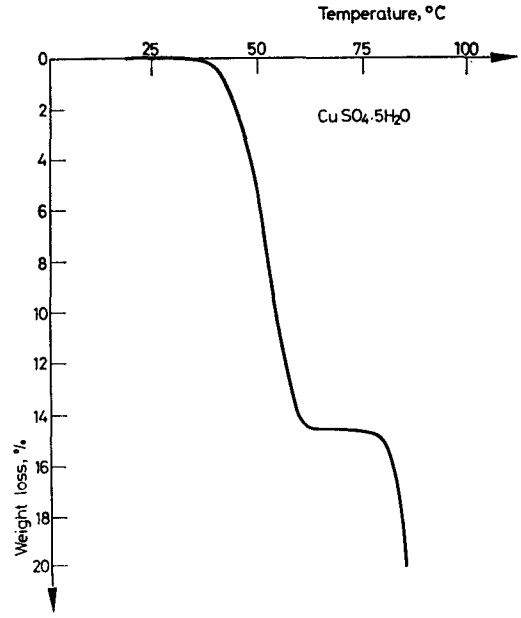

Fig. 8. TG curve for copper sulphate pentahydrate — 20% sample weight for full scale deflection. Sample weight: 6.6 mg. Heating rate: 2°/min. Atmosphere: air, 10 ml/min

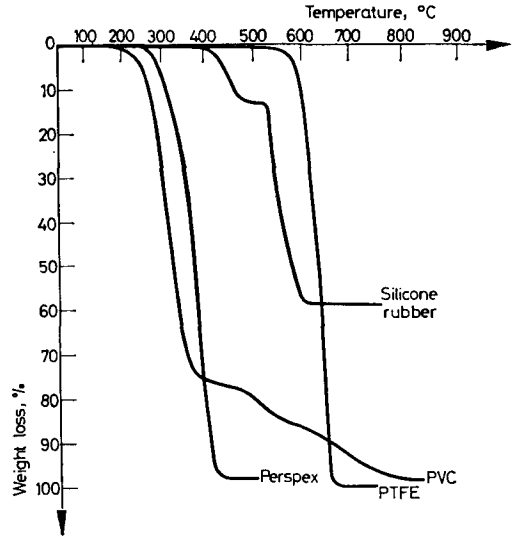

Fig. 9. TG curves for some plastics. Sample weights: 2—2.5 mg. Heating rate: 30°/min. Atmosphere: air, 10 ml/min

Due to the small sample size, reactions (a) and (b) are reasonably separated at a heating rate of 10°/min.

Fig. 8 shows the results of expanding the balance range to 20% of the sample weight for full scale deflection and using a slower heating rate to study the trihydrate formation in more detail. The sample was weighed out in the same way as before and the sample weight expanded to 100% full scale. The recorder sensitivity was then increased by a factor of five and the sample pen brought back on scale using the electrical tare.

For samples giving very small weight changes, sample weights of greater than 10 mg are taken and with the balance on the 1 mg range the weight changes are recorded directly in mg. In this way changes of below 0.005% can be recorded When a number of different samples are to be compared, plotting the results on an $X - Y$ recorder offers considerable advantages. Fig. 9 shows the traces for a number of plastic samples run on the same chart using an $X - Y$ recorder, enabling a direct comparison of thermal stability to be made.

Under the conditions used, approximately two samples per hour can be run and this throughput can be increased by using a faster heating rate. The apparatus can therefore readily be used for rapid quality control studies.

Derivative Thermogravimetry

In addition to TG traces the TG-750 will also plot DTG curves as an aid to the interpretation of complex reactions and in kinetic studies. A maximum sensitivity of 3 μg/min/mm is available, enabling small samples to be studied at slow

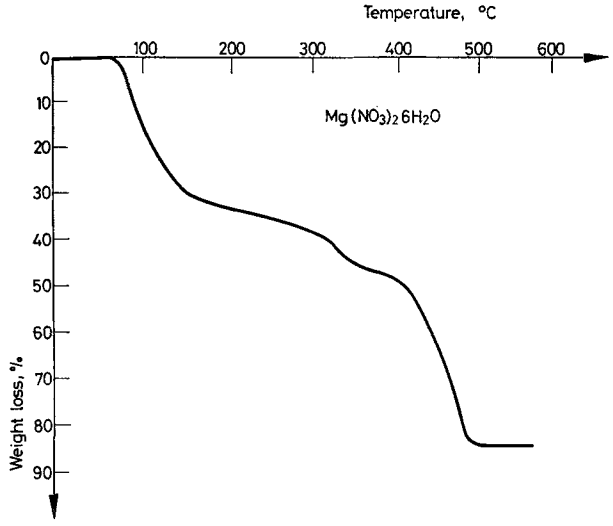

Fig. 10. TG curve for magnesium nitrate hexahydrate. Sample weight: 3.2 mg. Heating rate: 10°/min. Atmosphere: argon 10 ml/min

heating rates. A typical application of the DTG unit is illustrated by the thermal decomposition of magnesium nitrate hexahydrate, which has already been found, by simultaneous DTA-mass spectrometric analysis, to be a complex process [2]. Fig. 10 shows a TG run on the nitrate made in an atmosphere of argon and shows three overlapping weight losses. These can be seen more clearly in the corresponding DTG curve in Fig. 11, which also shows the complex nature of the individual stages.

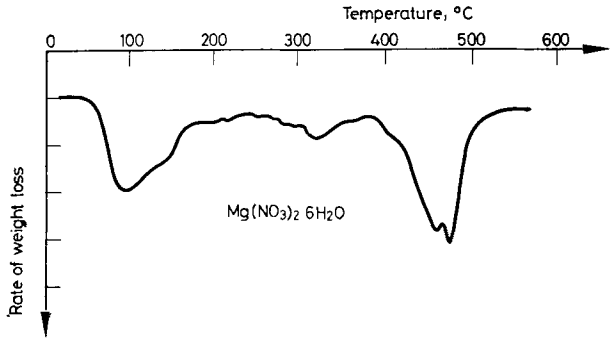

Fig. 11. DTG curve for magnesium nitrate hexahydrate. Sample weight: 3.1 mg. Heating rate: 10°/min. Atmosphere: argon 10 ml · min^{-1}

The amount of fine detail shown by a DTG trace, in addition to the convenient method of presentation, make this a useful technique for the qualitative comparison of similar groups of materials such as soils and clays.

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We would like to thank Dr. J. P. Redfern and Mr. R. A. Chapman for valuable discussions.

References

1. A. W. Coats and J. P. Redfern, Analyst, 88 (1963) 908.
2. M. L. Aspinal, H. J. Madoc Jones, E. L. Charsley and J. P. Redfern, Thermal Analysis, Ed. H. G. Wiedemann, Birkhäuser Verlag (1972) 303.

Résumé — On décrit une nouvelle balance thermique qui indique directement le pourcentage de la perte de poids en fonction de la température de l'échantillon, donc une transformation des résultats n'est pas nécessaire. L'appareil fonctionne dans un domaine de température de l'ambiente à 1000°C et contient un four miniature, réfrigéré par de l'eau et lié à une microbalance électronique. Cette dernière a une sensibilité de 1 à 250 mg à la déviation totale de l'enregistreur potentiométrique. Des vélocités de chauffage entre 1 et 100°C par minute sont possibles et le refroidissement du four de 1000°C à 50°C exige moins de 4 minutes. On donne quelques examples typiques de l'application de l'appareil, avec un nombre de systèmes inorganiques et polymères.

ZUSAMMENFASSUNG — Eine neue Thermowaage wird beschrieben, welche den prozentualen Gewichtsverlust in Abhängigkeit der Temperatur der Probe unmittelbar angibt und keine Umrechnung der Ergebnisse benötigt. Die Vorrichtung erfaßt einen Bereich von Zimmertemperatur bis zu 1000°C und besteht einem wassergekühlten Miniatürofen verbunden mit einer elektronischen Mikrowaage. Letztere hat eine Empfindlichkeit von 1 bis 250 mg bei vollem Ausschlag an einem potentiometrischen Registriergerät. Aufheizgeschwindigkeiten von 1 bis 100°C pro Minute sind möglich und der Ofen kann von 1000°C auf 50°C in weniger als 4 Minuten abgekühlt werden. Einige typische Anwendungsmöglichkeiten des Geräts werden an Hand einer Anzahl anorganischer und Polymersysteme beschrieben.

Резюме — Описаны новые термовесы, которые дают прямой график потери веса в процентах в зависимости от температуры образца. Прибор работает в области температур от окружающей до 1000° и содержит миниатюрную, охлаждаемую водой печь, в сочетании с электронными микровесами, чувствительность которых при полном отклонении на шкале самописца составляет 1—250 мг. Используемые скорости нагрева 1—100°/мин печь охлаждается от 1000° до 50° меньше чем за 4 минуты. Применение прибора проиллюстрировано на ряде неорганических и полимерных систем.