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# A HIGH TEMPERATURE AND HIGH SENSITIVITY MICRO-THERMOBALANCE

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## ABSTRACT

A thermobalance which ensures a sensitivity of $1 \times 10^{-6}$ g and an excellent stability up to 1500 °C has been developed. A sample, which is suspended from one end of the beam of the balance, is heated in a compact furnace with a small heat capacity. Temperature is measured by a Pt–PtRh (10%) thermocouple placed close to the sample. Use of an alumina mantle ensures easy control of atmosphere: at room temperature, the evacuation can be done down to $1 \times 10^{-4}$ Torr, and stable operation can be done up to 1500 °C in air or inert gas at a flow-rate smaller than 50 ml min$^{-1}$. It is also possible to use a corrosive gas as atmosphere. In a blank test with platinum cell support (6.5 mm diam. and 0.1 mm thick) suspended in an air stream of 50 ml min$^{-1}$ and heated up to 1500 °C at 10 °C min$^{-1}$, the drift was smaller than $20 \times 10^{-6}$ g and the reproducibility was better than $10 \times 10^{-6}$ g. This paper refers to the construction of the thermobalance, and its performances. And some examples of high temperature thermogravimetry through the results of analyses of $CaCO_3$, quick lime and byproduct lime are also reported.

## 1. INTRODUCTION

Thermogravimetry is one of the most important techniques in thermal analysis, and it is almost essential to the studies of thermal stability and thermal decomposition of materials. Various types of instruments that permit analysis in a temperature range up to 1000 °C are commercially available[1] and there are reports[2,3] on instruments that permit analysis up to even higher temperatures. But no instruments are now available that ensure a satisfactory stability and high sensitivity in a temperature range from ambient to 1300 ~ 1500 °C.

The high-sensitivity microthermobalance reported by us sometime ago[4] ensures such high performances as (1) free selection and easy control of atmosphere, (2) minimized influence of convection and buoyancy, (3) long-term stability, and (4) high-precision temperature control. But its upper temperature limit was as low as 1000 °C.

In inorganic chemistry and metal industry, there is a strong demand for an instrument that ensures these high performances described above 1500 °C. We have recently developed an instrument that meets these requirements.

## 2. CONSTRUCTION

### 2.1 *Outline*

Figure 1 shows the external view of the instrument, which consists of a thermobalance, a weight–current conversion unit, a temperature programmer, and a two-pen recorder. Figure 2 shows the principle and performance schematically.

The temperature is sensed by a Pt–PtRh (10%) thermocouple placed close to the sample. The output of this thermocouple is compensated automatically for the ambient temperature and is then fed to the temperature recorder and also to the temperature programmer to facilitate temperature control. The temperature programmer is designed to accept a chromel–alumel thermocouple besides the Pt–PtRh (10%) thermocouple, the change-over being done by a switch. For both of these two thermocouples, the temperature programming rate can be changed over in 11 steps from 0.5 °C $\text{min}^{-1}$ to 80 °C $\text{min}^{-1}$, and the programming mode can be changed over in four steps of UP, HOLD, DOWN, and CYCLE.

The thermobalance is a symmetrical balance, in which a sample is suspended from one end of the beam (light alloy pipe) and a counter-weight on the other end. The position of the tip of the beam in the counter-weight side is detected by a light source and one pair of photocells. The output of the photocells, after amplified, is fed back to the coil located at the center of the beam. The feed-back current, in combination with a permanent magnet placed externally, gives a rotating momentum to keep the beam in a balanced state; since the feed-back current is proportional to the weight change of the sample, the record of this current directly indicates the weight loss or

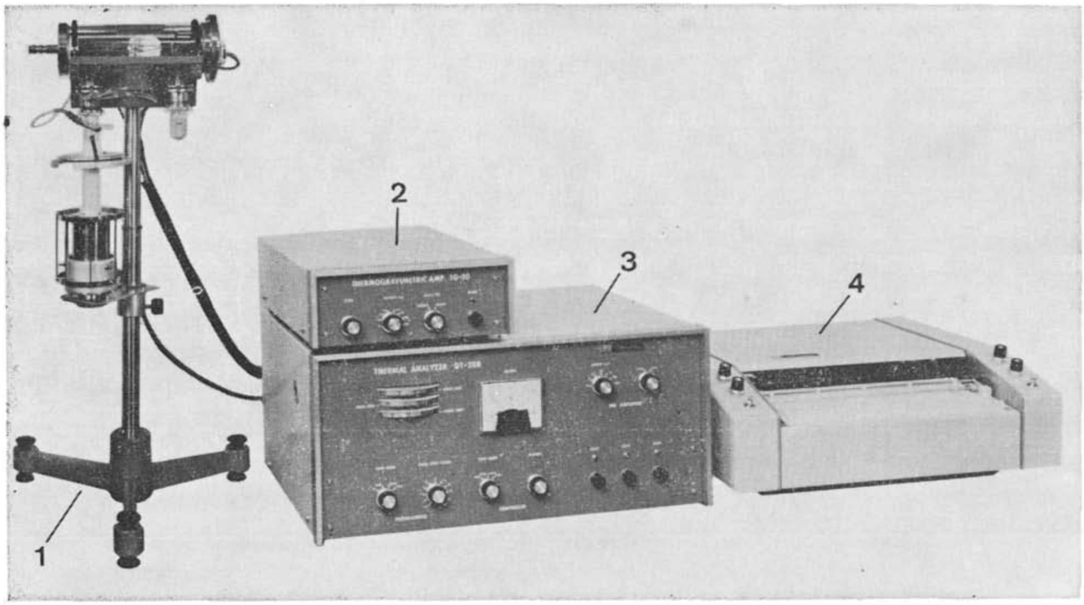

Fig. 1. External view of high temperature micro-thermobalance. 1 = Thermobalance; 2 = amplifier (weight-current conversion unit); 3 = temperature program-controller; 4 = 2-pen recorder.

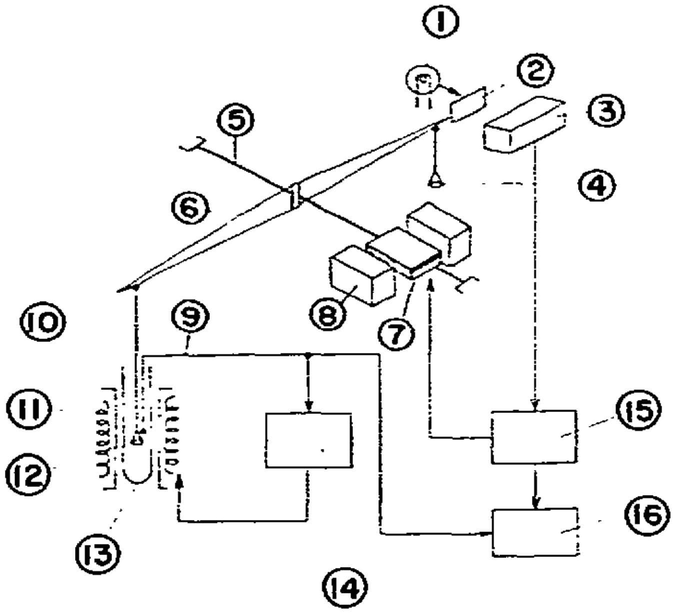

Fig. 2. Schematic diagram of high temperature micro-thermobalance. 1 = Lamp; 2 = shutter; 3 = pair of photocells; 4 = counter weight; 5 = taut band; 6 = beam; 7 = coil; 8 = permanent magnet; 9 = thermocouple; 10 = suspension wire; 11 = furnace; 12 = sample cell and cell support; 13 = alumina mantle; 14 = temperature program controller; 15 = weight-current conversion unit; 16 = 2-pen recorder.

weight gain of the sample. The temperature and the weight change are continuously recorded on the two-pen recorder simultaneously.

### *2.2 Performances of thermobalance*

*2.2.1 Sensitivity and maximum sample size.* This thermobalance gives an output of 20 mV for a weight change of 1 mg. If the sensitivity is considered from the viewpoint of S/N ratio alone, it may be concluded that the detection limit will be 0.1 $\mu$g or better in weight change. Since a long term stability is necessary in practical thermogravimetry, we decided the sensitivity (detection limit) to be 1 $\mu$g, which is easily attainable in an installation without a shock-absorber. Up to one gram of sample can be held by the sample suspension wire. But if a sample cannot be held by the wire, a sample cell is used, and the maximum sample size will be that much smaller.

The maximum range for measurement of weight change is 200 mg. The measuring range can be changed in eight steps from 1 mg to 200 mg. The output in each of these ranges is 20 mV.

*2.2.2 Selection and control of atmosphere.* Figure 3 shows the construction of the sample holder which is designed to facilitate control of the atmosphere surrounding the sample. The mantle is made of alumina of high purity, and the mantle support is made of silica glass. The joints of the mantle and the support have tapered, ground surfaces, so that the silica glass mantle used for operation in the temperature range

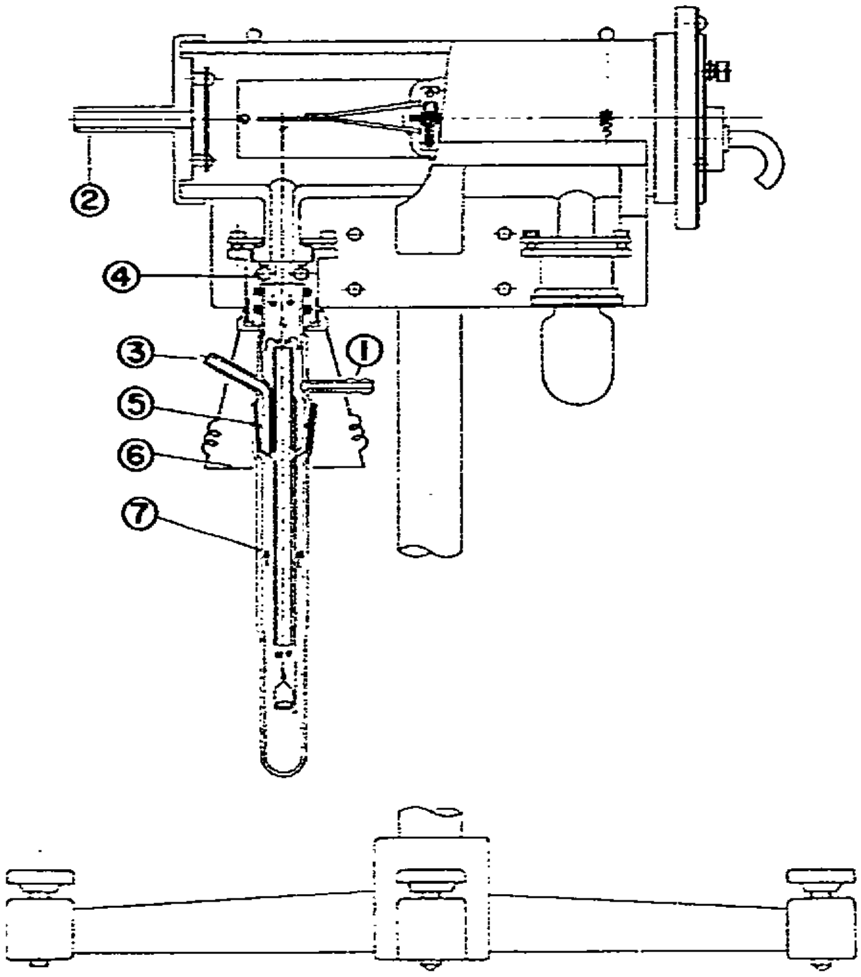

Fig. 3. High temperature micro-thermobalance. 1 = Gas inlet (1); 2 = gas inlet (2); 3 = gas outlet; 4 = water cool; 5 = O-ring; 6 = thermal shield plate, 7 = alumina mantle.

upt to 1000 °C can be mounted interchangeably. The sample holder can be evacuated without any other sealing material. But, since the coefficient of expansion of alumina is larger than that of silica glass, the mantle may not come off easily after heating. To prevent this inconvenience, we cut a groove on the tapered surface and put an O-ring in it, so that the joint may become leak-proof and the mantle can still easily be detached. The mantle is pressed against the support by springs in the direction of the casing of the balance, via an aluminum heat insulating plate. As for the flow line of the gas used as the atmosphere, two inlets and one outlet are provided.

When air or an inert gas is allowed to flow during measurement, the flow-controlled gas is allowed to flow into the casing via inlet (1) or (2) and travels downwards as shown by the arrows in Fig. 3 coming into contact with the sample suspended by the wire, and is then exhausted from the vent (3) at the top.

When it is required to allow a corrosive gas of a known concentration to react with the sample, it is necessary to prevent the corrosive gas from flowing or diffussing to the balance unit so that the balance might not be corroded. Allow a small flow-rate of air or an inert gas to flow into the casing via inlet (2) and introduce the corrosive gas via the vent. Thus, the corrosive gas flows upwards (in the opposite direction of that shown by the arrows) after coming into contact with the sample, and is then exhausted out of inlet (1) together with the air or inert gas introduced via inlet (2). We successfully made thermogravimetry using corrosive gases such as $SO_2$, $H_2S$, $NH_3$ and $Cl_2$.

When it is necessary to remove oxygen completely, evacuate the casing completely and introduce the desired gas without delay. This method, however, is not recommended for a corrosive gas, because it may damage the balance unit.

*2.2.3 Furnace.* The furnace is compact which is a little expensive but ensures an excellent long-term stability through a temperature range reaching up to 1500°C. It employs a resistor wire or ribbon made of platinum alloy, which can be coiled compact and in non-inductive manner and hence, the induction noise is minimized.

The heat capacity of the furnace is minimized so that a rapid heat response can be expected, only a little power is required through efficient heating, and cooling can be done rapidly. Figure 4 shows the construction of the furnace.

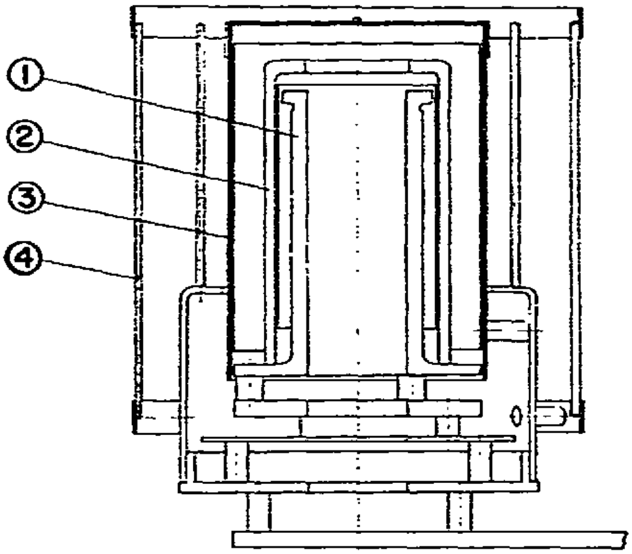

Fig. 4. Construction of a high temperature furnace. 1 = Alumina furnace-tube; 2 = alumina heat insulator lined with platinum foil; 3 = nickel heat insulator lined with pure gold; 4 = guard.

The furnace tube is made of high-purity alumina porcelain and has two grooves cut on the outer surface. The platinum alloy wire is coiled in these grooves in a non-inductive manner.

When the sample is heated to 1500°C, the temperature of the heater wire naturally rises above 1500°C. If the heater wire is left uncovered, the platinum may vaporize gradually at these temperatures. To prevent the vaporization of the platinum and to improve the service life of the heater, high-purity alumina cement is coated on the furnace tube on which the heater wire has been coiled. The furnace tube is then heated at 1500 ~ 1550°C for a few hours in another furnace to sinter the cement.

This cement coating proved to have an effect not only to prevent the vaporization of the platinum of the heating element but also to place the heater wire in closer contact with the furnace tube and hence, improve the heat response.

The cylindrical heat insulator made of alumina porcelain, placed just around the furnace tube is lined with platinum foil, and the nickel heat insulator placed outermost is lined with pure gold. Between these heat insulators is a space, which serves as a heat insulator in a low temperature range. In a high temperature range, the platinum and gold liners effectively reflect the thermal radiation. Thus, the heat insulation is so complete that the power necessary for heating to 1500°C is only 600 W.

This furnace can be used for heating to 1700°C, but such a high-temperature operation is not recommended because it would drastically shorten the service life of the furnace.

Since the temperature on the surface of the nickel heat insulator rises very high, a guard frame is placed on it for safety.

The furnace can be cooled from 1500°C to ambient temperature in 30 ~ 40 min, when cooled to 800°C spontaneously and then forcibly by means of a blower. Such a rapid cooling is attributable to the use of air layers and noble metals as heat insulator and to the compact design, hence small heat capacity of the furnace.

*2.2.4 Errors attributable to leakage current.* In thermal analysis, in general, when the apparatus is heated to a very high temperature, the electrical insulation of the unit decreases and a leakage current may cause errors in measurement. In the experiments with our prototype instrument, it was observed that, when the temperature had exceeded 1200°C, the TG curve began to drift in one direction, and that, when the temperature rose to 1400 ~ 1500°C, the drift was big enough to correspond to about 10 mg in change of weight. It was confirmed that the error was caused by a current leaking along the sample suspension wire which is made of platinum, and the balance beam, and reaching the amplifier of the feedback system.

Various measures were discussed to prevent this error. In conclusion, we used a silica wire, which is a good insulator, as a part of the sample suspension wire: the silica wire was hooked to the balance beam and then the platinum wire was connected to this silica wire. Thus, the leak was stopped.

The influence of the current leak on the system of temperature measurement and control is completely removed by a filter. No noise and no error were observed when the heater was turned on and off in a 1500°C operation.

*2.2.5 Drift of baseline in blank test.* Since samples of thermal analysis are mostly powdery or will melt during analysis, our instrument is so designed that the cell support is always suspended at the platinum suspension wire and the cell is put on and off the support (See Fig. 5).

In a blank test with only the cell support suspended and with an atmosphere of air (flow-rate 50 ml min$^{-1}$), the apparent weight change when the furnace was heated from ambient temperature to 1500°C at 10°C min$^{-1}$ was 10~20 μg. The drift remained almost the same when the heating rate was changed to 30°C min$^{-1}$. The reproducibility was better than 10 μg.

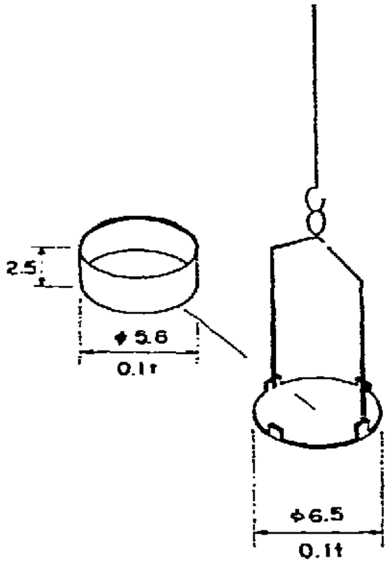

Fig. 5. Sample cell and cell support.

*2.2.6 Errors attributable to evaporation of platinum.* Though the sample cell, cell support, and sample suspension wire are made of platinum, it is necessary to know in advance the degree of errors caused by the evaporation of the platinum.

A platinum foil (20 × 10 mm, 116.66 mg, and about 4 cm$^2$ in surface area) was suspended and heated at 1500°C for about 5 h, and then heated in a cyclic manner from 1100 to 1480°C at 10°C min$^{-1}$, twelve times.

The weight loss measured by a micro-balance was 0.63 mg.

Meanwhile, the amount of evaporation at 1500°C, calculated from Langmuir's equation about the rate of evaporation, is about 0.89 mg, which agrees rather well with our test result. The vapor pressure of platinum at 1400°C is about 1/10, and that at 1300°C is about 1/100, of that at 1500°C. As shown by the equation about the rate of evaporation, the amount of evaporation is proportional to the vapor pressure.

The total surface area of the sample cell, cell support and suspension wire of our instrument is about 1.7 cm$^2$. When a thermogravimetry is made at 10~30°C min$^{-1}$, the period of time when the evaporation of platinum is large enough to be taken into consideration is as short as about 10 min. The amount of evaporation during this period is, at the largest, 0.005 mg or less, which is almost negligible.

*2.2.7 Other characteristics.* To study the influence of the change in ambient temperature upon the accuracy of the balance, the room temperature was raised from

5 to 30°C at a rate of 0.5°C min$^{-1}$. The drift was 80 μg, hence the temperature coefficient under this condition was as small as 3.2 μg °C$^{-1}$.

Moreover, since such a great and rapid change in room temperature will not occur in practice, it may be concluded that the change in room temperature does not cause any drift of baseline.

It is possible that some errors are caused by the influence of the heat from the furnace upon the balance system. To check the errors, the temperature of the furnace was raised to 1500°C at 10°C min$^{-1}$, with the cell support and suspension wire removed to eliminate the influence of buoyancy and convection. No change in weight was observed. It can be concluded that the heat from the furnace is completely stopped by the heat insulators.

When the pressure in the sample holder is depressed, the increased mean free path of the particles may result in some apparent change in weight due to increased chances for the particles to collide with the cell support and suspension wire. This thermal transpiration effect cannot be neglected in high-sensitivity thermogravimetry.

In the case of our instrument, the thermal transpiration effect becomes biggest at 0.5~1 Torr, reduces to zero at atmospheric pressure, and is negligibly small at a pressure lower than $10^{-4}$ Torr. The effect becomes larger with the rise in temperature.

The stream of the atmospheric gas has no influence upon the results, provided that the flow-rate is controlled to be smaller than 50 ml min$^{-1}$.

As for the accuracy of temperature measurements, the curie points of pure nickel and iron were measured in $N_2$ and He gas atmosphere, with the heating rate varied from 1 to 40°C min$^{-1}$. The error was better than ±5°C.

## 3. SOME EXAMPLES OF ANALYSIS

The main purpose of this paper is to report the performances of our trial-produced instrument, but we would like to refer to some of the results of actual thermogravimetry with this apparatus.

Figure 6 shows the TG curve of $CaCO_3 \rightarrow CaO + CO_2$, the temperature being raised to 1300°C. The weight loss stops at 880°C after a loss of 43.7%, which agrees very well with the theoretical value of 43.0%.

Figures 7 and 8 show the TG curves of a quick lime and a byproduct lime, the temperature being kept in isothermal state at 1500°C to confirm that the weight of the samples becomes constant. The total weight losses were 44.1 and 1.13%, respectively.

## 4. CONCLUSIONS

A high-sensitivity thermobalance, which permits use of air, inert gas, corrosive gas, or vacuum as atmosphere has been developed. The performances are as follows.

(1) Sensitivity was better than 1 μg.

(2) The mantle is designed for convenient use of corrosive gases.

(3) In a blank test up to 1500°C, the drift was less than 30 μg and the reproducibility was better than 10 μg.

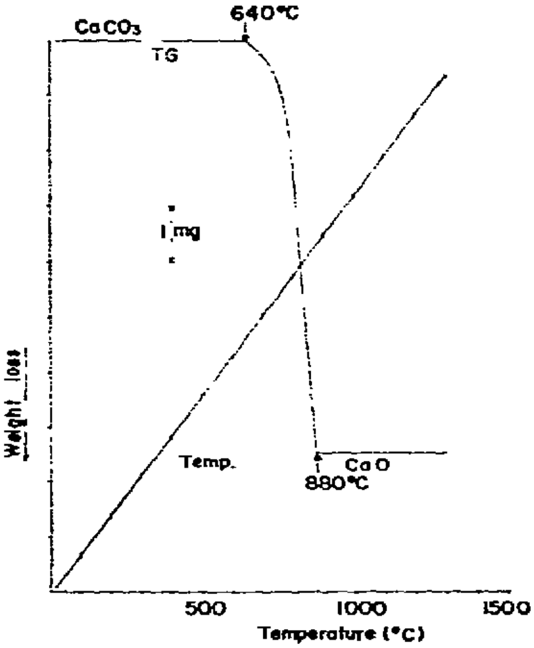

Fig. 6. Thermogravimetry of $CaCO_3 \rightarrow CO_2 + CaO$. Sample weight 17.000 mg; heating rate 15°C min$^{-1}$; atmosphere air flow 50 ml min$^{-1}$.

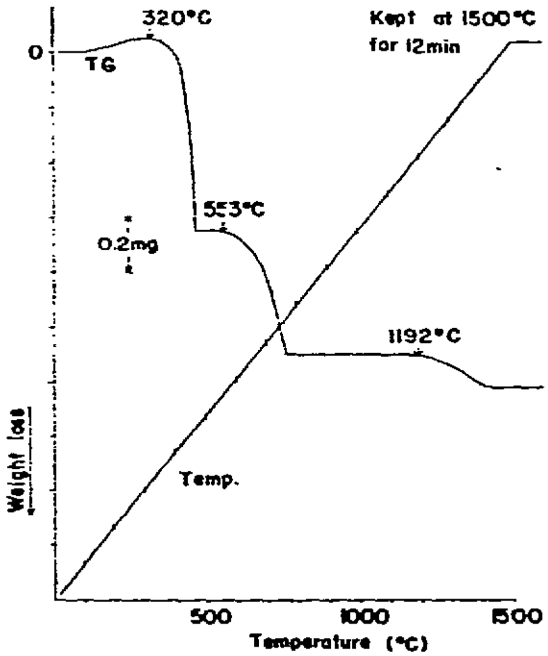

Fig. 7. Thermogravimetry of a quick lime. Sample weight 102.000 mg; heating rate 20°C min$^{-1}$; atmosphere air flow 50 ml min$^{-1}$.

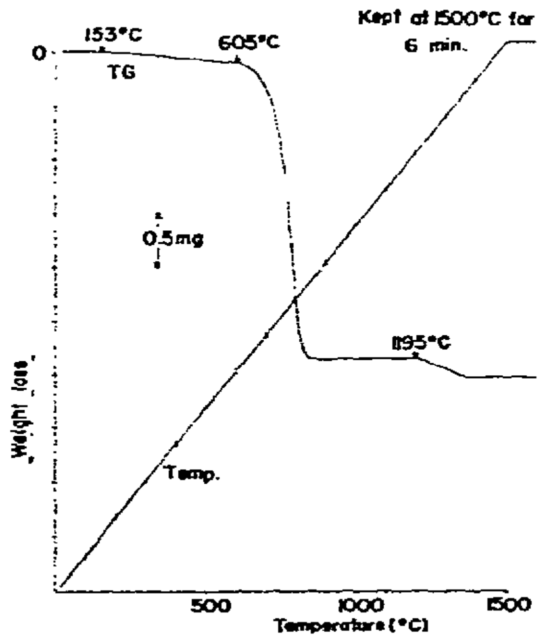

Fig. 8. Thermogravimetry of a by-produce lime. Sample weight 6.890 mg; heating rate 20°C min$^{-1}$; atmosphere air flow 50 ml min$^{-1}$.

(4) The preferable flow-rate of a gas that comes into contact with the sample is less than 50 ml min$^{-1}$.

(5) The evaporation of platinum used for the sample cell, cell support and suspension wire, was less than 5 μg when the temperature was raised to 1500°C at 10°C min$^{-1}$.

(6) No errors attributable to change in room temperature and to the heat from the furnace were observed under practical conditions.

With these performances, the thermobalance will be effectively used in high-temperature analysis of inorganic samples. We obtained satisfactory results in the thermogravimetry of metal materials for heat and corrosion resistancy. The test was performed in various atmospheres, where the temperature was being kept constant at several points below 1200 ~ 1300°C for a few continuous days.

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