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# INTRODUCTION TO A NEW SIMULTANEOUS TG-DSC 111

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## ABSTRACT

The combination of DTA, with thermogravimetric analysis is a method widely used in a wide range of temperature. However DTA measurements are qualitative and sometimes are issued from investigation of a sample different from the thermogravimetric one. On the other hand, if the sensor is supported by the balance - simultaneous measurement - the thermogravimetric sensitivity becomes very poor.

A real improvement is obtained when combining the Differential Scanning Calorimeter SETARAM DSC 111 with the very sensitive symmetrical microbalance B 111 (limit of detection : 1 µg). The crucibles hanging on the balance are centered without mechanical contact in the DSC tubes crossing the calorimeter.

## INTRODUCTION

The combination of thermal measurement with thermogravimetric analysis gives a better understanding of the physical or chemical transformation of the sample.

The combination of DTA with TG is widely used. Sometimes the DTA sample is different from the TG sample but both are located in the same experimental chamber - combined measurement. Sometimes only one sample is set in the DTA detector hanging on the balance - simultaneous measurement. But in this case, the thermogravimetric sensitivity becomes very poor.

A real improvement of such a combination supposes the use of a quantitative detection unit, like a DSC. The original structure of the DSC 111 SETARAM with its open experimental tubes (1) is particularly attractive for a combination with a balance. This gives today the new simultaneous TG-DSC 111 : TG and DSC on the same sample.

## DESCRIPTION OF THE SIMULTANEOUS TG-DSC 111

The DSC 111 (2) is built around two open refractory tubes crossing the heating furnace. The detection unit, designed according to the Calvet principle, is located in the medium part of the tubes : two heatflux transducers are like crowns around the tubes. With such a design, the sample contained in a cylindrical crucible is entirely surrounded by the detector, which measures all

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heat exchanges. This particular detection gives very accurate measurements. The calibration is independent of the gas around the sample or the nature of the crucible containing the sample.

The calorimeter works either in vertical or horizontal position. The vertical work is obtained by hanging crucibles in the DSC tubes, with or without contacting the walls of the tubes. Both horizontal and vertical work give similar results. This was the starting point for the balance combination above the DSC 111.

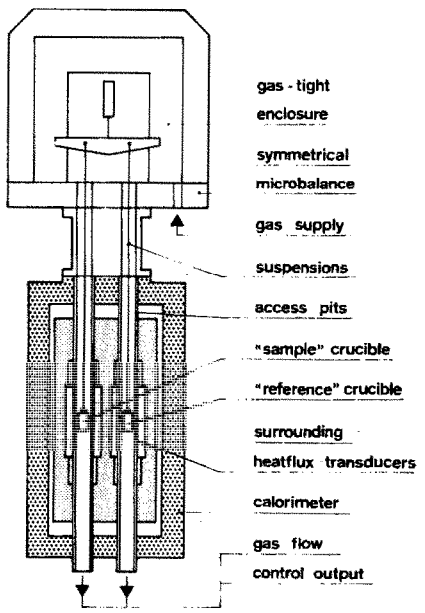


Fig. 1. TG-DSC schematic cross section

The calorimetric block is fixed on a vertical stand, and a symmetrical balance is set above. The suspensions of the balance are brought into line with the axis of each experimental tube. The crucibles, hooked at the ends of the suspensions,are driven in the detection zone of the DSC by sliding the balance.

So, DSC and thermogravimetric detections are mechanically separated instead of DTA attached on the thermogravimetric rod for most of the TG-DTA instruments. These features give the full sensitivity to the balance. Though the crucibles have no contact with the walls of the DSC tubes, the structure of the calorimetric detector, surrounding completely the sample, makes possible a good integration of the heat exchanged by the sample with the surrounding.

The balance and the DSC are gas tight, making easy the work under gas flow. The gas (inert or active) is introduced below the balance and flows downstream in the DSC tubes. At their lower ends the evolved gases can be collected or sent directly in a gas analyzer. Before any investigation under gas flow control, a vacuum purge of the instrument is possible.

CHARACTERISTICS

The new instrument combines the well known characteristics of the DSC 111 with the qualities of a symmetrical balance of very high precision and stability ; the temperature range is from -123° C up to 827° C. Different heating functions are available : isothermal, step heating, scanning (from $1°C.h^{-1}$ up to $30°C.min^{-1}$ )The limit of detection of the DSC 111 combined with the balance is about 15 microwatts. The DSC 111 is calibrated according to the Joule effect method. The limit of detection of the thermobalance is about 1 µg that allows very sensitive thermogravimetric measurements. Due to the symmetrical set-up of the balance, the perturbations generated by the heating (buoyancy effect) or by the gas sweeping in the two tubes are cancelled. The original thermogravimetric signal shows practically no significant drift that is very interesting for the detection of small mass changes.

Open crucibles of various types (aluminium, platinum, alumina) are used. The diameter of the crucibles is 5 mm (DSC tube diameter : 7 mm) with 10 mm length.

The TG-DSC 111 is combined with a high performance computer for data acquisition and treatment. The temperature programmed can be conducted by the computer, giving many different possibilities of scanning. The data, after storage, are simultaneously treated according to different softwares : heats and mass changes are correlated. The DTG curve can be numerically calculated (differential thermogravimetry).

OTHER CONFIGURATIONS

Though the main interest of the instrument is the simultaneous thermogravimetric and calorimetric measures on the same sample, the thermobalance can be used alone, the DSC 111 block acting only as a furnace.

The DSC 111 block can also be disconnected and set on a special horizontal stand. In this position the DSC 111 has a wide range of applications and various types of crucibles can be used : open alumina crucible for gas-sample reactions, standard crucibles (aluminium, platinum, alumina) for powdered or solid samples, high pressure crucibles (more than 100 atmospheres), controlled high pressure crucibles (3).

Using the vertical stand, the DSC 111 can also work alone in the vertical situation. This is very convenient for gas-solid reactions when using special silica reactor tubes (2).

APPLICATIONS

The TG-DSC 111 is especially designed for all investigations relative to interactions between gases, and solid or liquid samples : physisorption at low temperature, chemisorption , heterogeneous catalysis, oxidation, reduction, surface reactivity... It is also interesting for the experimentations on non homogeneous samples in order to have the TG and DSC measures on a really identical sample, heated under strictly identical conditions, e. g. : thermal stability of powders, organic products,... Actually, two main types of applications can be distinguished : analysis with evolved gas and analysis with gas interaction.

Among the known experimentations with evolved gas under controlled atmosphere, dehydration, dehydroxylation, decomposition, pyrolysis are the most often investigated. An example is given by the decomposition of $CuSO_4.5H_2O$ from 20° C up to 820° C (Fig. 2). Successive mass losses ($H_2O$, $SO_2$ , $O_2$) with the corresponding heats are measured.

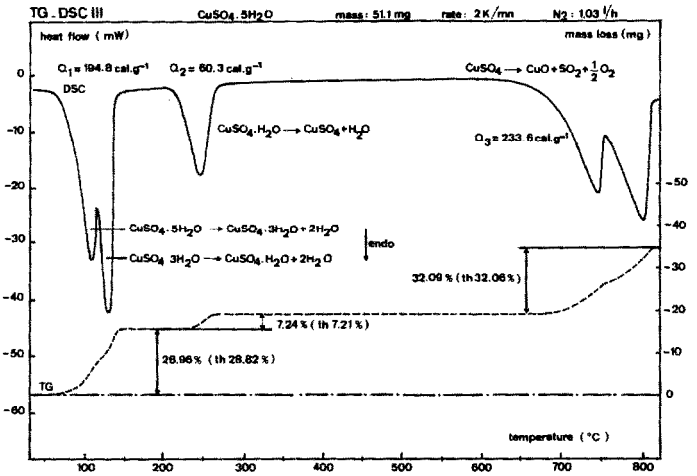


Fig. 2. $CuSO_4$ 5 $H_2O$ decomposition

Interactions between gas and sample are the most interesting applications of thermogravimetry and calorimetry. For example it is possible to measure accurately the amount of the gas adsorbed on a sample, and the corresponding heat of adsorption, even in the case of slow rate of adsorption.

Gas adsorption is very often correlated with catalysis. As an example, a sample of nickel oxide NiO deposited on a silica support is reduced in a mixture of hydrogen (20 %) and nitrogen (80 %) (Fig. 3). For this experimentation , a quadrupole mass spectrometer was combined to the TG-DSC 111. When heating, a first mass loss corresponding to the evaporation of adsorbed water is recorded. The endothermic DSC peak shows that two distinct effects are present. A second mass loss, due to the reduction of the nickel oxide and the formation of water is detected, corresponding to an exothermic DSC peak. The curve of $H_2O^+$ on the mass spectrometer proves that water is first evaporated, then formed during the reduction.

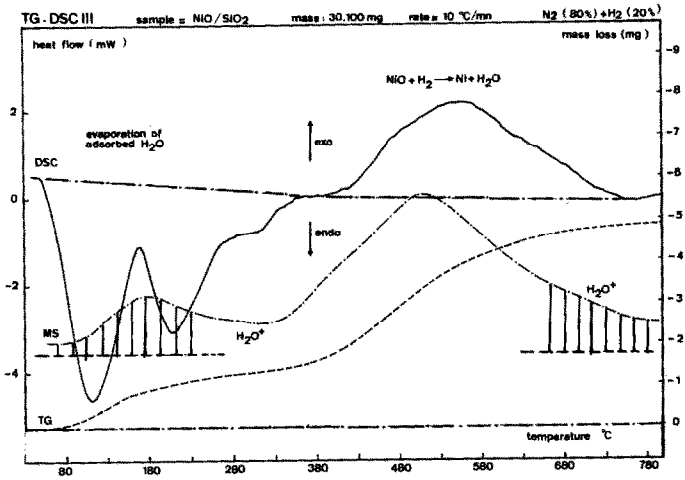


Fig. 3. Nickel oxide reduction

## CONCLUSIONS

With the capabilities of the DSC 111 and the high performances of a symmetrical balance, the TG-DSC 111 is an instrument which is a very useful tool for laboratories involved in gas-solid reactions, surface reactivity and materials stability.

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