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INTRODUCTION OF A NEW SIMULTANOUS SYMMETRICAL AND DIGITAL TG-DTA THERMOANALYZER

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A completely new simultaneous digital and symmetrical TG–DTA thermoanalyzer, called TAG 24, has been designed.

The instrument is built around a very sensitive microbalance and one or two high-temperature furnaces (maximum limit: 2400 °C). When the TAG 24 is used in the symmetrical version (two furnaces), the buoyancy effect is eliminated and more sensitive thermogravimetric measurements can be achieved.

The controller controls the furnace temperature, the positions of 8 electrovalves for vacuum and gas sweeping, and the taring of the balance, calculates the DTG value, and also amplifies and processes the analog signals (temperature, TG and DTA). Still higher performance is produced by coupling the controller with a scientific computer through a serial interface.

Whereas the DSC and TG methods are widely used in industrial laboratories, the TG-DTA method has not had such success. However, it provides much information on materials, especially in the high-temperature field: raw material transformations, ceramics investigations, catalyst or zeolite characterizations, etc.

TG-DTA instruments are probably more complicated to use, and not too readily automated. Taking account of these limitations, SETARAM has designed a completely new digital TG-DTA thermoanalyzer, which is easy to manipulate and to operate, called the TAG 24 (Fig. 1). Simultanous symmetrical and digital features are the main characteristics of the TAG 24.

TAG 24 thermoanalyzer: one or two furnaces?

The TAG 24 is built around a very sensitive microbalance (minimum detectable weight change: 1 microgram), and one or two high-temperature furnaces (maximum temperature limit: 2400 °) (Fig. 2). The choice of the number of furnaces depends on the type of applicaton.

Why use a symmetrical design? The answer to this question is given in Fig. 3. Two tests run with empty crucibles in the TG-DTA configuration are compared: one with the one-furnace configuration, and the second with the two-furnace or symmetrical configuration.

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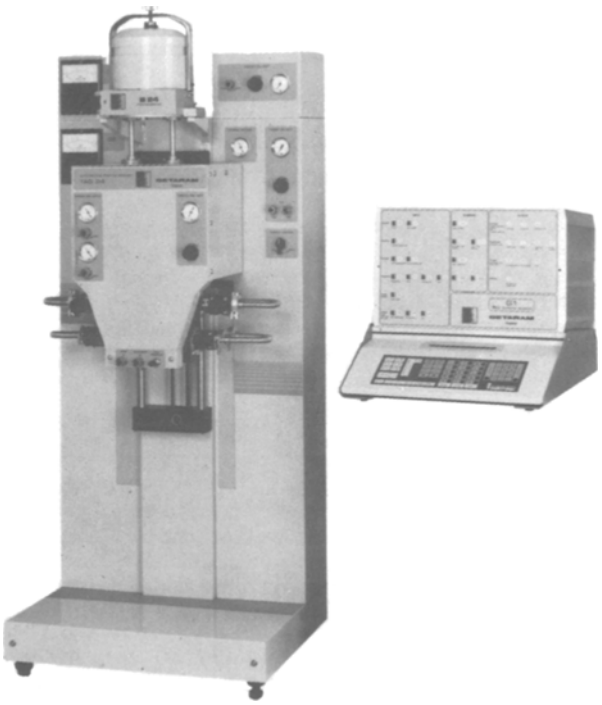

Fig. 1 – TAG 24 thermoanalyzer

During the first test (one furnace), a relatively large drift of the thermogravimetric base line is recorded. It corresponds to about 1.5 mm at 1000°. This drift is mostly due to the buoyancy effect on the crucible and the suspension. When the instrument is used in the symmetrical mode, the gas flow rates are equally adjusted in the two furnaces, and the buoyancy effect is compensated. In such a situation, practically no drift of the thermogravimetric base line is recorded. With the computerized instrument, it is possible to store and subtract the base line in the first case, in order to correct the data for the buoyancy effect. However, the precision of the data is affected by the reproducibility of the base line. In the symmetrical mode, no numerical correction is needed, except for the detection of very low mass changes (some micrograms). More sensitive thermogravimetric measurements can be achieved. This is particularly interesting for gas interaction studies (adsorption, catalysts, corrosion, etc.), for small vapour

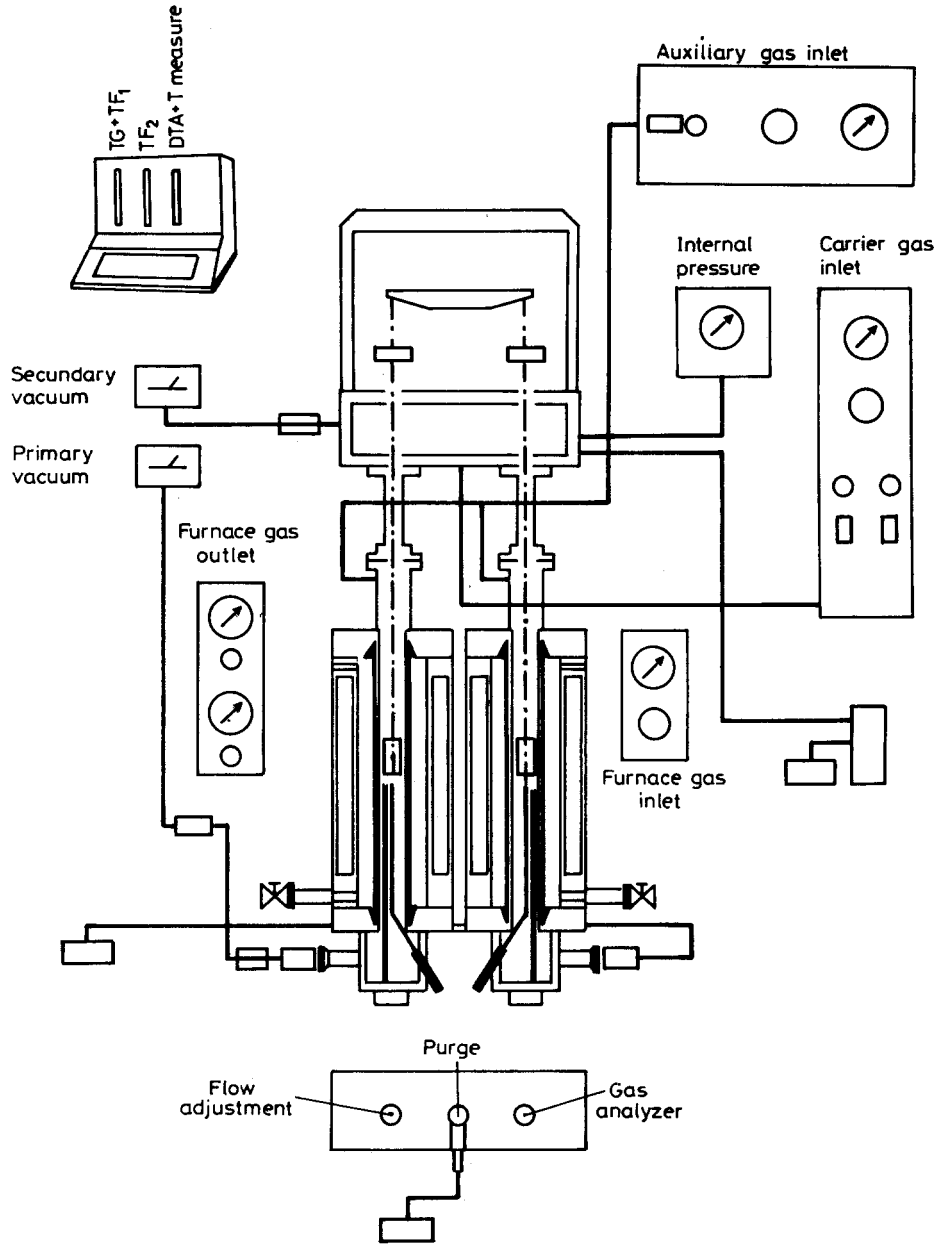

Fig. 2 – TAG 24 cross-section

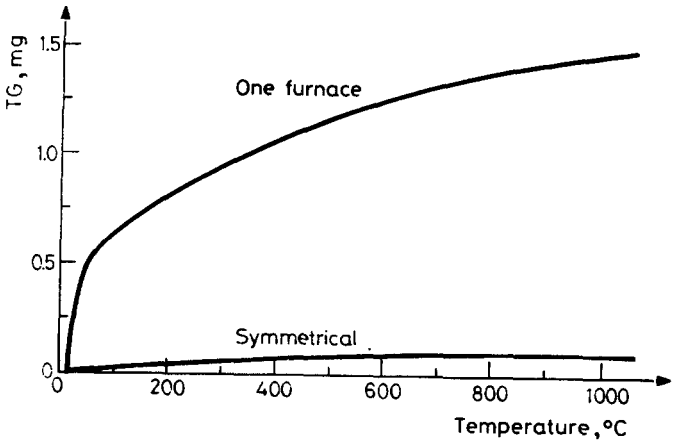

Fig. 3 – One furnace and symmetrical configurations: base line

escapes (desorption, vaporization, etc.) and for the investigation of very small amounts of samples. This unique capability of the TAG 24 thermoanalyzer provides symmetrical thermogravimetric and DTA measurements up to very high temperatures. Either with one or with two furnaces, two types of measurements can be run:

– TG only: in this case, the smallest detectable mass variation is 1 microgram.

– TG-DTA with a multicouple (3 thermocouples) DTA detector which hangs on the microbalance. This provides very good thermogravimetric and DTA measurements on the same sample.

Control and automation of TAG 24

The largest improvement in this new instrument relates to the temperature, gas and signal control with the new G1 microprocessor controller. Most of the operations are performed automatically through the keyboard of the controller. Only the handling of the crucible with the sample is done manually.

The controller (Fig. 4) accurately and automatically sets:

– the programming and regulation of one or two furnaces according to 10 different heating sequences (temperature, scanning rate, and isothermal delay);

– the automatic taring of the balance;

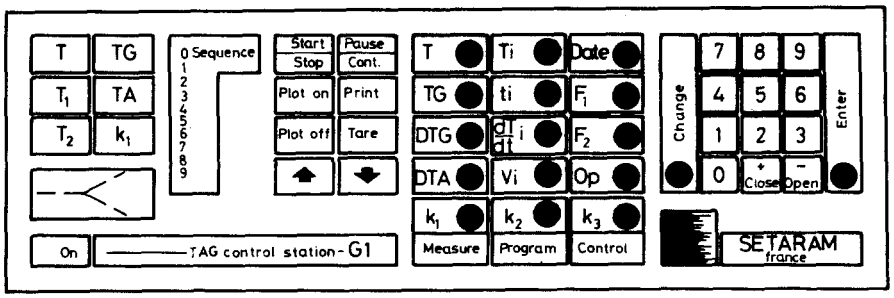

Fig. 4 – G1 keyboard

– the situation of 8 programmable electrovalves for automatic gas switching (vacuum, inert gas or active gas);

– the acquisition and amplification (DTA) of the analog signals (temperature, TG and DTA), their processing and the determination of the DTG signal;

– the transfer of the numeric signals (T, TG, DTG and DTA) to a computer through an RS 232 serial interface;

– the control of a printer for printing the digital signals;

– the display of experimental parameters and signals.

Through the G1 controller, it now becomes easy to run a TG-DTA test with good accuracy and reproducibility. A complete cycle of heating, cooling, and isothermal period with various gas switching can be programmed and memorized through the keyboard of the G1 controller and automatically run without any special caution. The G1 controller can be coupled to a computer. In this situation, all the experimental inputs are entered through the keyboard of the computer, using different menus. The monitoring of the thermoanalyzer is done from the computer through the G1 controller.

For one experimentation, different heating sequences have to be defined, building up a procedure. 48 different procedures can be programmed by the computer and stored on disks. A catalog of the procedures is displayed on the screen in order to make a choice, or to define a new procedure.

During the experimentation, the digital signals (T, TG, DTG and DTA) are continuously displayed on the screen versus time and stored. At the end of the test, data can be expended or plotted versus time or temperature, and the number of curves (TG, DTG and DTA) can be chosen. Different treatments can be applied to the different data: mass variation determination with the corresponding temperatures, DTA peak integration, calculation

of the DTA derivative (DDTA), transition temperature determination, base line correction for TG and DTA curves, substraction of different curves, etc.

Experimentation on TAG 24 thermoanalyzer

The TAG 24 thermoanalyzer is built around a basic unit, and many different options, especially the gas and vacuum control, are available. The gas control, particularly important when a thermoanalyzer is used, is fully automatic. Different operations can be run:

– Carrier gas sweeping (mostly inert gas) for the protection of the sample during the heating.

– Active gas sweeping can also be used, e. g. with oxygen or hydrogen, if the gas is not corrosive towards the balance.

– If there is a risk of reaction between the gas and the metallic parts of the balance, the gas is introduced at the upper part of the furnaces.

– If a primary vacuum has to be applied, two procedures are available: a purge (1 mbar) or a forced primary vacuum (10^{-2} mbar).

– For high-vacuum experimentation, a diffusion pump is used to obtain a secondary vacuum in the thermoanalyzer.

For evolved gas analysis, a special gas outlet is provided for collection of the gases evolved during the heating, and connected to a gas chromatograph or a mass spectrometer (by means of a capillary tube).

Applications of TAG 24 thermoanalyzer

The new TAG 24 operates in a very broad range of temperature (up to 2400°). Thus, it can be used for various types of applications or for different purposes:

– a better knowledge of raw materials before their transformation, a better knowledge of the reactions and transformations in the materials during the heating process for optimization of the industrial conditions of transformations;

– better determination of the decomposition and degradation of mineral and organic compounds;

– investigation of the behaviour of materials in various gaseous conditions (oxidizing, reductant, etc.);

– the study of gas-solid interactions (catalysis, adsorption, etc.).

Industrial research is increasingly interested in the information provided by the simultaneous TG-DTA method. The new TAG 24, with its different options and its automation, is particularly well adapted for this new mode of research and control.

Zusammenfassung – Ein völlig neues, digitalisiertes und symmetrisches Gerät "TAG 24" wurde für simultane TG–DTA entwickelt. Es enthält eine sehr empfindliche Mikrowaage und einen oder zwei Öfen (Temperaturgrenze 2400 °C). Wenn es in der symmetrischen Version (mit 2 Öfen) benutzt wird, wird der Auftriebseffekt unwirksam, so dass empfindlichere TG-Messungen möglich sind. Der Regler steuert die Ofentemperatur, die Stellung von 8 elektrischen Ventilen für Vakuum und Gasspülung und die Waagentarierung, er berechnet das DTG-Signal und verstärkt und verarbeitet die analogen Signale von Temperatur, TG und DTA. Über ein serielles Interface kann ein wissenschaftlicher Rechner zur Erhöhung der Leistungsfähigkeit angeschlossen werden.

РЕЗЮМЕ — Создан совершенно новый тип одновременно цифрового и симметричного ТГ-ДТА термоанализатора ТАГ 24. Прибор построен на основе высокочувствительных весов и одной или двух высокотемпературных печей с максимумом температуры 2400°. При использовании ТАГ 24 в симметричном режиме(две печи) устраняется эффект подъемной силы и тем самым достигается большая чувствительность термогравиметрических измерений. Регулятор контролирует температуру печей, положение 8 электроклапанов для вакуума и газа, извешивание, вычисление ДТГ значений, усиление и обработку аналоговых сигналов температуры, ТГ и ДТА. Более высокая производительность аппаратуры достигается за счет соединения контролирующего устройства с ЭВМ посредством стандартного интерфейса.