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Note

A MODIFICATION TO DUPONT 951 TGA-1090 THERMAL ANALYSIS SYSTEM FOR CONCURRENT THERMOGRAVIMETRY AND DIFFERENTIAL THERMAL ANALYSIS

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Differential thermal analysis (DTA) is essentially a qualitative method for studying thermal changes in a particular sample while being heated or cooled at constant rates. Thermogravimetry (TG), on the other hand, is a quantitative method to detect changes in the sample mass as a function of temperature (dynamic thermogravimetry) or as a function of time (isothermal thermogravimetry). Together, DTA and TG constitute a powerful combination for providing valuable information about the thermal behaviour of materials under various conditions. Correlating results from the two techniques, however, has always been questionable due to unavoidable differences in experimental conditions. Ideally, both techniques should be applied to the same sample at the same time (simultaneous thermal analysis) except in cases where optimum results are only attainable if a different experimental procedure is administered in each technique. Only a few thermal analysis systems designed to perform simultaneous measurements are available on the market and they are relatively expensive due to the complexity of their construction necessary to achieve sensitivities comparable to those of the individual techniques.

A viable and simple alternative to simultaneous thermal analysis is concurrent thermal analysis in which DTA and TG are conducted, at the same time, on two separate samples placed close to each other in the reaction tube of the TG equipment. Although the measurements are done on two individual samples, correlating the results in this case is more acceptable since both samples (with the same geometry) are subjected to the same thermal program and are exposed to the same conditions in the furnace.

Some successful attempts to modify existing TG equipment to perform concurrent thermal analysis were published by Chiu [1] and Wendlandt [2]. In both cases, however, certain internal alterations or external additions had to be made to accommodate other measuring probes and to amplify, record and display the additional signal. By using the DuPont 1090 thermal analyser, the modification proposed here is simple and requires minimum additions and no alteration to the existing 951 TGA system.

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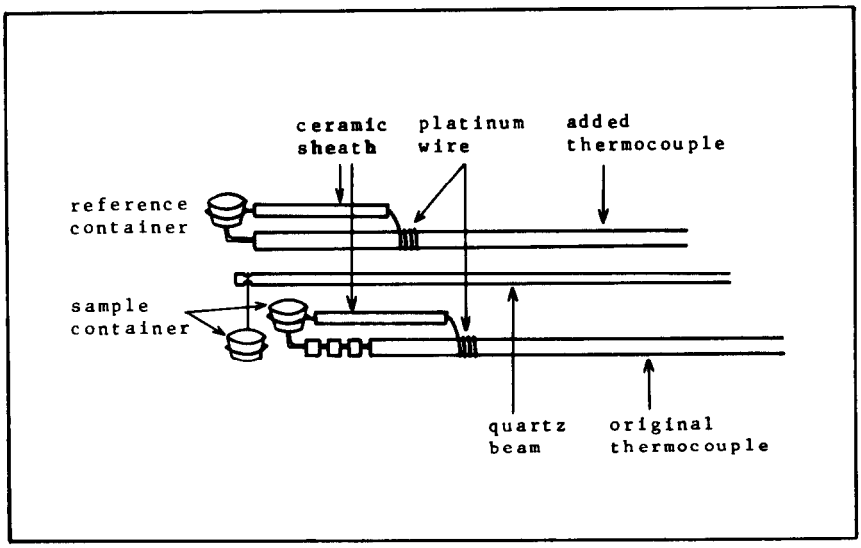

Fig. 1. Schematic diagram of thermobalance modification.

Connected to the TG module, the 1090 unit receives, records and, when desired, displays simultaneously four signals, namely time (t), temperature (T), mass (w) and the derivative ($\Delta w/\Delta t$), DTG. The latter signal is provided by an analog circuit built into the module. This circuit is practically unused when using the 1090 unit since the derivative ($\Delta w/\Delta t$) is computed from the digital values of w and t stored by the microprocessor. Hence, a port to the 1090 unit becomes available and can be used to introduce any external signal within the specified limits of the original signal; 7.5 mV to 3.5 V [3]. The external signal in this case is accepted, recorded and displayed as the Auxilliary Signal B in millivolts.

A chromel–alumel thermocouple, identical to that of the TG module, was mounted on the other side of the quartz beam as shown in Fig. 1. Two relatively heavy-gauge platinum wires, each shaped like a ring at one end and wound around the thermocouple sheath at the other end, supported two platinum crucibles for the DTA assembly. The crucibles, made with indentations at the bottom, rested on the beads of the two thermocouples. The original and added thermocouples were used to accommodate the sample and reference crucibles, respectively. This arrangement provided a more accurate measurement of sample temperature during TG runs than in the original design where the sample thermocouple was located a few millimeters away from (in no contact with) the sample [4]. The chromel wire of the added thermocouple was attached to that of the original thermocouple at the thermocouple block. The differential signal was taken from the alumel wire of the added thermocouple and that of the original thermocouple and amplified using a low-noise DC amplifier (Type LA-1 from Bailey Instru-

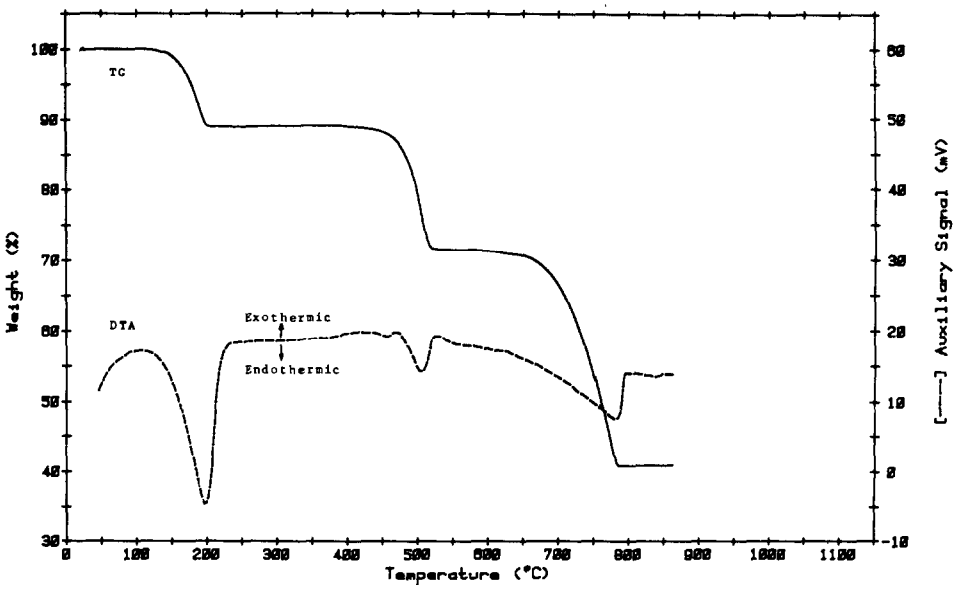

Fig. 2. Concurrent TG–DTA diagrams for calcium oxalate monohydrate in argon.

ments, NJ, U.S.A.). The output of the amplifier was connected to pins E and H of the umbilical connector at the output of the TG module. The signal from the analog derivative circuit board to the 1090 unit also passes through

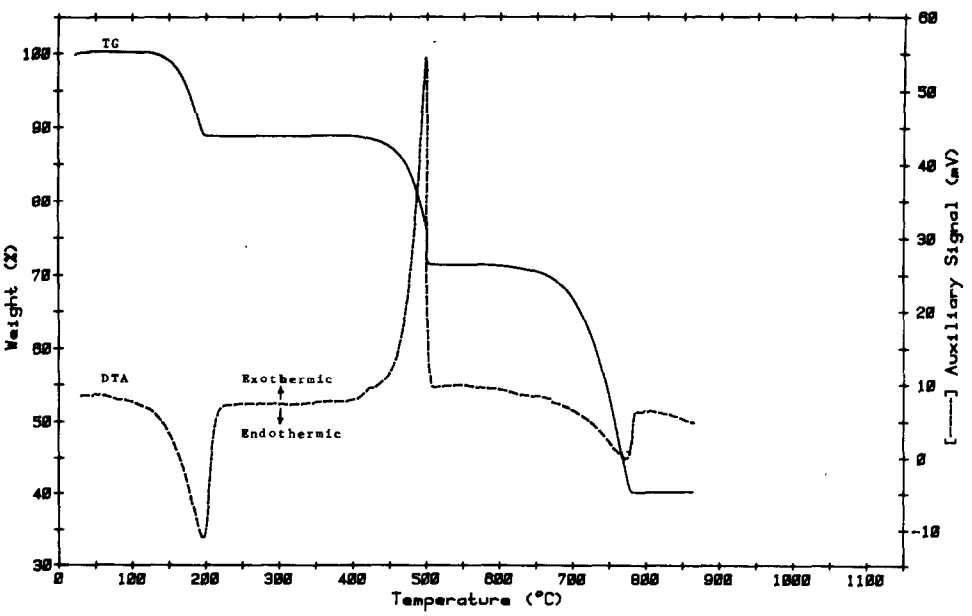

Fig. 3. Concurrent TG–DTA diagrams for calcium oxalate monohydrate in air.

pins E and H of the umbilical connector [5]. Therefore, when the amplified DTA signal is to be transmitted to the 1090 unit, the "Derivative" switch on the front of the module should be in the "Off" position and when the analog DTG signal is required, the switch should be in the "On" position and the external amplifier switched off.

Figures 2 and 3 show concurrent TG/DTA diagrams for calcium oxalate monohydrate ($CaC_2O_4 \cdot H_2O$) in argon and air atmospheres, respectively. A good correlation between the changes in weight and the corresponding thermal effects is apparent. It can be seen that while there were no noticeable differences between the TG diagrams generated in the different atmospheres, the DTA diagrams were different. The three stages of weight loss correspond to the following reactions

$$CaC_2O_4 \cdot H_2O \rightarrow CaC_2O_4 + H_2O \quad (1)$$

$$CaC_2O_4 \rightarrow CaCO_3 + CO \quad (2)$$

$$CaCO_3 \rightarrow CaO + CO_2 \quad (3)$$

The three reactions are endothermic as shown on the DTA diagram generated in argon atmosphere (Fig. 2). When the sample was heated in air, however, the CO generated by reaction (2) reacted immediately with oxygen as follows

$$2CO + O_2 \rightarrow 2CO_2 \quad (4)$$

The overlapping thermal effects of reactions (2) (slightly endothermic) and (4) (exothermic) resulted in a net exothermic effect, represented by the second peak on the DTA diagram in Fig. 3.

To obtain meaningful data using the TG/DTA concurrent technique, it is essential to maintain the same sample geometry for the TG and DTA measurements. In the early stages of this work, it was found that using different geometries resulted in noticeable differences in both temperature and duration of thermal effects and weight changes.

ACKNOWLEDGEMENT

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