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CONCURRENT DTA, ELECTROTHERMAL ANALYSIS AND TG USING DUPONT THERMAL ANALYSIS EQUIPMENT*

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ABSTRACT

Concurrent TG–DTA and TG–EC measurements were performed using a modified DuPont thermobalance and control console. The DTA and EC sample probes, which were inserted into the furnace tube, permitted DTA and EC measurements to be made in conjunction with TG data. The TG curve was recorded on the DuPont control console plotter while the DTA or EC curves were recorded on an outboard *X–Y* plotter. The use of the combined techniques is illustrated by TG–DTA and TG–EC curves of $CuSO_4 \cdot 5H_2O$, $(NH_4)_2C_2O_4 \cdot H_2O$, and NH_4NO_3.

INTRODUCTION

The use of simultaneous thermal analysis techniques is a well established procedure in thermal analysis today. Simultaneous measurements, such as TG–DTG, TG–DTA, TG–DTG–DTA, TG–DTA–EGD, and so on, are easily made using commercially available equipment from several manufacturers. The advantages of this approach over simple technique measurements are numerous, with the most important being (a) time-saving convenience of two or more measurements at the same time; (b) exposure of the sample to identical conditions of furnace atmosphere and temperature environment; (c) identical sample characteristics, such as packing density, particle size, surface area, and so on; and (d) preparation and instrument loading of a single, rather than multiple samples. There are, as expected, some disadvantages of simultaneous techniques also, the most important of which is that certain thermal analysis techniques require different conditions of furnace heating rates or sample characteristics for optimum results. However, the advantages of the simultaneous measurement technique almost always outweigh the disadvantages so that this approach is widely used in many areas of thermal analysis.

The purpose of this report is to describe the modification of DuPont thermal analysis equipment, basically the Model 950 thermobalance and Model 900 control unit, for *concurrent* thermal analysis measurements. The distinction between simul-

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taneous and concurrent measurements is that the former employs multiple technique measurements on a single sample, while the latter uses an individual sample for each technique employed. As might be expected, the latter approach is easier to carry out in modified commercially available equipment, hence its use in this investigation.

EXPERIMENTAL

Sample probes

The sample probes for the concurrent DTA–TG and EC–TG measurements are shown in Fig. 1.

Two sample probes are employed: probe A for DTA–TG measurements and probe B for EC–TG measurements. The sample probe is inserted into the outboard end of the furnace tube (see Fig. 2) and positioned so that the sample holder is located as close as possible to the thermobalance sample container. The DTA sample probe consists of two inconel cups, each 6 mm in diameter by 1 mm in height, to which is spot-welded the chromel and alumel thermocouple wires. These wires are contained in a 3 mm diameter 4-hole ceramic insulator tube whose length in the furnace may be adjusted by a set-screw on the machined aluminum holder. This holder, which is inserted in the furnace tube, is held firmly in place by the "O"-ring. The electrothermal probe consists of two ceramic insulator tubes, the lower one of which contains a cavity which holds a 6 mm diameter gold cup. The sample is placed in the gold cup and is held in place by the spring-loaded upper ceramic rod, which is capped on the end with a platinum metal disk. Electrical contact with the sample is provided by the wire attached to the gold cup and the wire spot-welded to the spring-loaded platinum disk. The overall length of the probe within the furnace chamber can

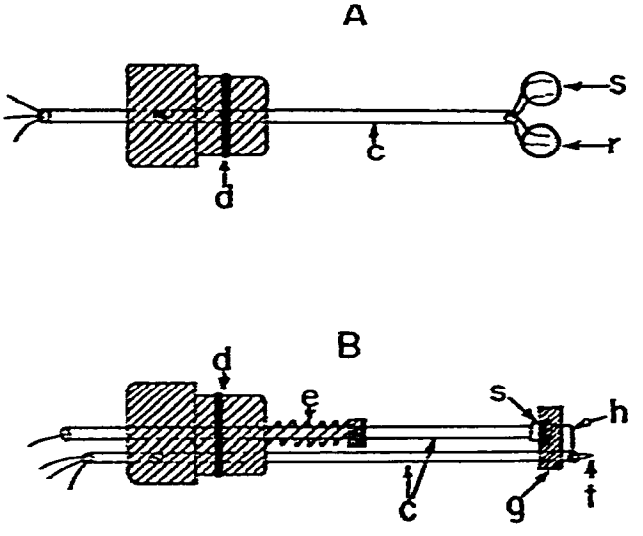

Fig. 1. Sample probes for (A) DTA and (B) electrothermal measurements. c, Ceramic insulator tubes; d, "O"-ring; e, spring; r, reference sample holder; s, sample holder; t, thermocouple; g, sample block; and h, contact wire.

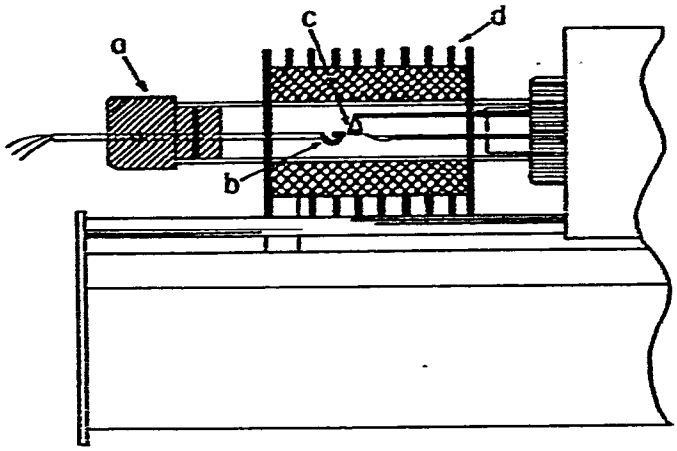

Fig. 2. Sample probe configuration in thermobalance. a, DTA sample probe; b, DTA sample holder; c, TG sample holder; and d, furnace.

be adjusted by means of a small set screw on the machined aluminum holder.

The positioning of the sample probe into the thermobalance furnace is shown in Fig. 2.

The furnace tube hose coupling is cut off and the tube extended about 2.5 cm so that the aluminum holder of the probe can be inserted into the furnace chamber. A tight fit is provided by the rubber "O"-ring, which is fitted in a machined grove in the holder. A small hole is drilled in the holder to permit the effluent gases to be discharged into the atmosphere.

TG–DTA system

A schematic diagram of the TG–DTA system is illustrated in Fig. 3.

The system components consist of the following components: the DuPont Model 900 control console (A); a DuPont Model 950 thermobalance (B); a Leeds and Northrup Model 9835B microvolt amplifier (C); and a Hewlett-Packard Model 7035B *X–Y* function plotter (D). Mass-change data is obtained on the control console plotter while the DTA curve is recorded on the outboard plotter. The temperature drive for both recorders is obtained from two separate thermocouples; one is located near the thermobalance sample container and the other is part of the DTA sample probe.

TG–EC system

A schematic diagram of the TG–EC system is illustrated in Fig. 4.

The system components consist of the following: (A) DuPont Model 900 control console; (B) DuPont Model 950 thermobalance; (C) Heath Model 1G-1B variable frequency oscillator; (D) Hewlett-Packard Model 7035B*X– Y* function plotter; (E) Keithley Model 171 digital multimeter; and (F) Southwest Technical Products frequency counter. As in the case of the TG–DTA probe, the temperature drive on both of the recorders is obtained from two separate thermocouples. The

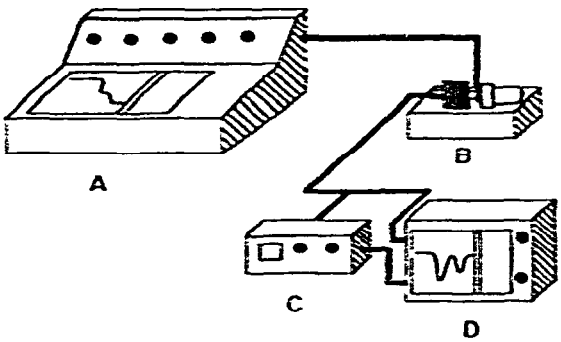

Fig. 3. TG–DTA system. A, DuPont control console; B, DuPont thermobalance; C, microvolt amplifier; and D, *X–Y* plotter.

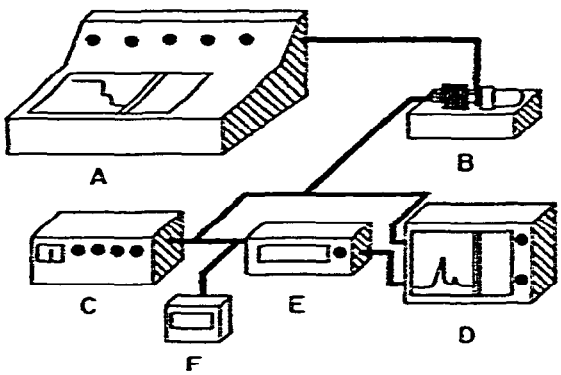

Fig. 4. TG–EC system. A, DuPont control console; B, DuPont thermobalance; C, Heath oscillator; D, *X–Y* plotter; E, digital multimeter; and F, frequency counter.

mass-change curve is recorded on the DuPont control console while the EC (A.C. current) is recorded on the Hewlett-Packard *X–Y* plotter.

Procedure

The experimental procedure for the concurrent TG–DTA measurements is basically the same as for the individual techniques. Two identical samples are used, each weighing 5–20 mg, with one placed in the DTA sample probe and the other in the TG sample container. The furnace chamber is flushed with nitrogen gas, using a flow-rate of about 50 ml min^{-1}, while the furnace heating is maintained at about 10°C min^{-1}. Both of the plotters are activated; one records the resultant TG curve, the other the DTA curve.

The procedure for the TG–EC is somewhat more complex, since the EC curve is dependent on more experimental variables. The A.C. voltage applied to the sample electrodes can be varied from 1 to 10 V at a frequency of 100 Hz. A digital multimeter, set on the A.C. current mode, was used to detect the current flowing through the sample. This current, usually in the 0–100 μA range, was recorded on the *Y*-axis of the plotter. A digital frequency counter was used to monitor the frequency of the excitation voltage. It was found that best results were obtained if the sample was pressed in the form of a disk using a homebuilt piston and die[1]. Either the pure

sample could be employed or the sample suspended in a KBr matrix and then pressed into a disk. The disk diameter was 5 mm with a thickness of about 1 mm. For all measurements, a nitrogen gas flow-rate of 50 ml min^{-1} was used. The TG curve was recorded on the control console plotter while the EC (current) was recorded on the outboard plotter, both as a function of temperature.

RESULTS AND DISCUSSION

Chiu[2], in 1967, described a technique for the concurrent measurement of TG, DTG, DTA and electrothermal analysis (ETA), using the same type of DuPont equipment as is described in this study. His approach was somewhat more complex than that used here although he did employ separate samples for the TG, DTA, and ETA measurements. The TG sample was placed in a 2 mm diameter quartz capillary tube and suspended on the balance beam while the DTA and ETA samples were placed in 4 mm diameter quartz tubes located parallel to the TG sample container. All four measurements could be obtained simultaneously using four separate *X–Y* plotters, one for each parameter.

The data obtained here could only be obtained in a TG–DTA or TG–EC sequence due to the configuration of the two sample probes employed. However, it is a relatively simple procedure to change from one mode to the other.

The use of the TG–DTA mode is illustrated by the curves in Figs. 5 and 6.

In Fig. 5, the well known TG and DTA curves for the dehydration of $CuSO_4 \cdot 5H_2O$ are illustrated. Both curves show the following dehydration reactions, all of which have been previously described[3].

$$CuSO_4 \cdot 5H_2O(s) \rightarrow CuSO_4 \cdot 3H_2O(s) + 2\,H_2O(l) \quad (1)$$

$$2\,H_2O(l) \rightarrow 2\,H_2O(g) \quad (2)$$

$$CuSO_4 \cdot 3H_2O(s) \rightarrow CuSO_4 \cdot H_2O(s) + 2\,H_2O(g) \quad (3)$$

$$CuSO_4 \cdot H_2O(s) \rightarrow CuSO_4 + H_2O \quad (4)$$

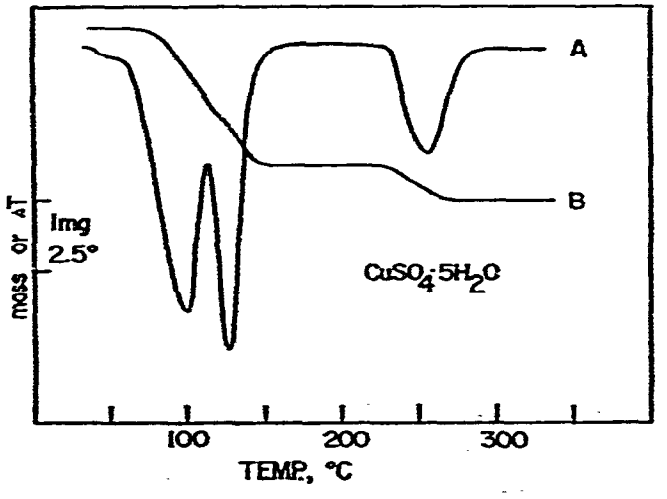

Fig. 5. Concurrent TG–DTA curves of $CuSO_4 \cdot 5H_2O$. (A) DTA curve; (B) TG curve.

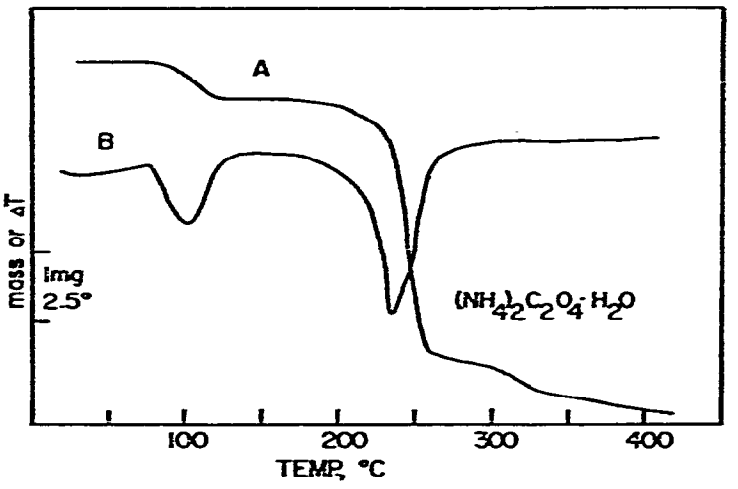

Fig. 6. Concurrent TG–DTA curves of $(NH_4)_2C_2O_4 \cdot H_2O$. (A) TG curve; (B) DTA curve.

The first three reactions take place below 150°C while the last one occurs over the temperature range 225–300°C.

The thermal decomposition of $(NH_4)_2C_2O_4 \cdot H_2O$, which is not as well known as the dehydration reactions of $CuSO_4 \cdot 5H_2O$, is illustrated by the TG–DTA curves in Fig. 6. Liptay[4] has previously described the TG, DTG and DTA curves of this compound, using data obtained on the derivatograph. He noted that at a slow heating rate, 1°C min^{-1}, the dehydration reaction involved some type of intermediate compound which is not present at the faster 3°C min^{-1} heating rate. Only a single-step dehydration reaction is noted here but there appears to be a shoulder on the decomposition curve peak. The stoichiometry of the decomposition reaction is not known but if it is similar to the thermal decomposition of other ammonium salts, it must involve simultaneous sublimation as well as decomposition.

The results of the TG–EC studies are illustrated in Fig. 7 and 8.

The TG–EC curves of $CuSO_4 \cdot 5H_2O$ in a disk form[1] are shown in Fig. 7. The TG curve is, of course, similar to that of the powdered sample given in Fig. 5. In the EC curve there is an increase in the current passing through the sample starting at about 100°C. This increase, as previously described[5], is due to the formation of the quadruple point in the $CuSO_4 \cdot 5H_2O$ system. The presence of the liquid water, as given in reaction (2), forms a saturated solution, which permits an increase in current flowing through the sample. As this water vaporizes, the current decreases to the level of the original substance. As discussed previously[5], EC measurements can be used to detect quadruple points in metal salt hydrate systems[6, 7].

The TG–EC curves of ammonium nitrate, in a KBr disk, are given in Fig. 8. As indicated by the TG curve, decomposition of the NH_4NO_3 in the KBr disk began at about 170°C and continued to about 300°C. The EC curve indicated a large increase in current also in this region. Ammonium nitrate has a melting point of 169.6°C in the pure state but the presence of a KBr matrix may enhance its decomposition.

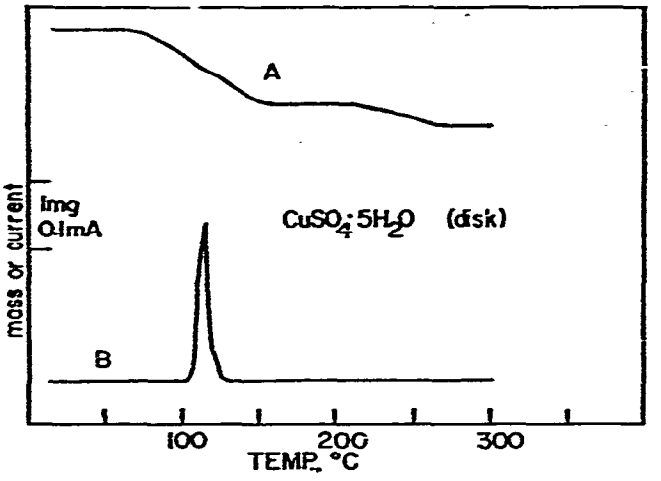

Fig. 7. TG–EC curves of $CuSO_4 \cdot 5H_2O$ in disk form. (A) TG curve; (B) EC curve.

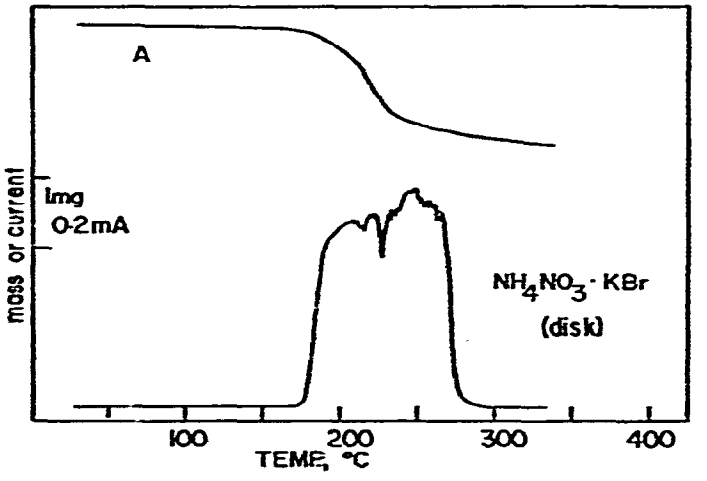

Fig. 8. TG–EC curves of NH_4NO_3 (12%) in a KBr disk. (A) TG curve; (B) EC curve.

ACKNOWLEDGMENT

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