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AN AUTOMATIC DATA ACQUISITION SYSTEM FOR SIMULTANEOUS OPERATION OF TWO METTLER THERMOANALYZERS

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ABSTRACT

An automatic data acquisition system was developed for two Mettler Vacuum Recording Thermoanalyzers, Model TA-I, using a Hewlett-Packard 9825S calculator. The interface with the thermoanalyzers is unique in the way that it is independent of and has a wider dynamic range than the six-channel strip chart recorder supplied with the instrument. The data acquisition system permits data from two TA-Is simultaneously in operation to be collected and stored in a magnetic tape cartridge.

To facilitate rapid analysis of the acquired data, five computer programs were also developed for use with a Hewlett-Packard 9872A plotter. This data reduction system would (1) plot the thermograms (DTA, TG, DTG) including the % weight changes as a function of temperature or time, (2) label the thermograms, (3) record the experimental conditions, (4) correct the thermogravimetric data for effect due to buoyancy, if desired, (5) locate and mark the peak minima and maxima on DTA and DTG curves, and (6) tabulate the % weight change between two temperatures or time.

INTRODUCTION

With the field of thermal analysis growing rapidly during the last decade, instruments which are capable of doing differential thermal analysis or thermogravimetric analysis have become plentiful in the marketplace. Among those commercially available systems, the Mettler Recording Vacuum Thermoanalyzer, Model TA-I, is one of the few which can perform differential thermal analysis (DTA), thermogravimetry (TG), and derivative thermogravimetry (DTG) simultaneously on one sample in one single experiment. The instrument uses a six-channel recorder to record the thermograms, the temperature profile, and the total pressure of the system (if the test run is made under vacuum) as a function of time. Wendlandt [1] has described the Mettler thermoanalyzer in some detail and called it a most elaborate, versatile and universal research instrument.

The usefulness of the Mettler TA-I is often offset by the time and effort needed to reduce the recorded data. Since the raw data are printed in different color dots, and temperatures are recorded in mV, data reduction is a slow and tedious process. In order to improve this disadvantage, Stuk et al. [2] developed an automatic data acquisition and recording system with which data could be processed off-line using a PDP-11 computer and plotted with a Honeywell 6000 system.

In this paper we will describe an on-line computer system which we developed to automate data collection from our two Mettler thermoanalyzers (TA-I) simultaneously. Data reduction is also accomplished subsequently on the same system.

EXPERIMENTAL

Data acquisition

The central element of our data acquisition system is an HP 9825S desktop computer equipped with real time clock and HP—IB interface options. The computer has 23k bytes of random access memory (RAM) for user program and data storage and approximately 42k bytes of read-only memory (ROM) containing the HPL (similar to BASIC) interpreter and monitor firmware.

Other elements of the system include an HP 59500A I/O interface, an HP 6940B multiprogrammer and an HP 9872A four color plotter. The HP 59500A unit converts bidirectional byte oriented HP—IB information to the 16 bit parallel format required by the multiprogrammer. The multiprogrammer can accommodate up to 15 user selected circuit cards and provides for the communication necessary between selected input/output cards and the computer. A 12 bit analog to the digital converter, relay output cards, a digital input card and a custom designed dynamic range expansion circuit are used with the multiprogrammer unit in our system. The plotter, which is coupled to the computer via the HP—IB interface, is used to plot data which have been previously collected and stored on the computer's tape cartridge. Figure 1 shows a block diagram of the major components and how they are interconnected.

The data acquisition system is designed to collect up to six channels of analog information, as a function of time, from each of two TA-I thermoanalyzers. The logging operation for each TA-I may be started independently; however, the data rate for both units must be the same as the collection is alternated between units. The nominal collection rate is one data set of six channels logged alternately from each instrument every 5 s for a per instrument rate of six sets per min. This is more data points per min than the Mettler supplied recorder system provides and is more than adequate for normal analyses. For very long experiments, the data rate may easily be changed to reduce storage requirements. The maximum data rate is limited to 15 sets per min because of selected delays to allow settling time for the dynamic range expansion and analog to digital converter cards.

The six-channel multipoint strip chart recorder system supplied by Mettler makes use of separate offset circuits located in temperature, TG, and DTA units to effectively expand the recorder scale. These offset circuits are controlled by microswitches near the recorder's high and low limits. This imposes constraints on any data acquisition system connected to the recorder

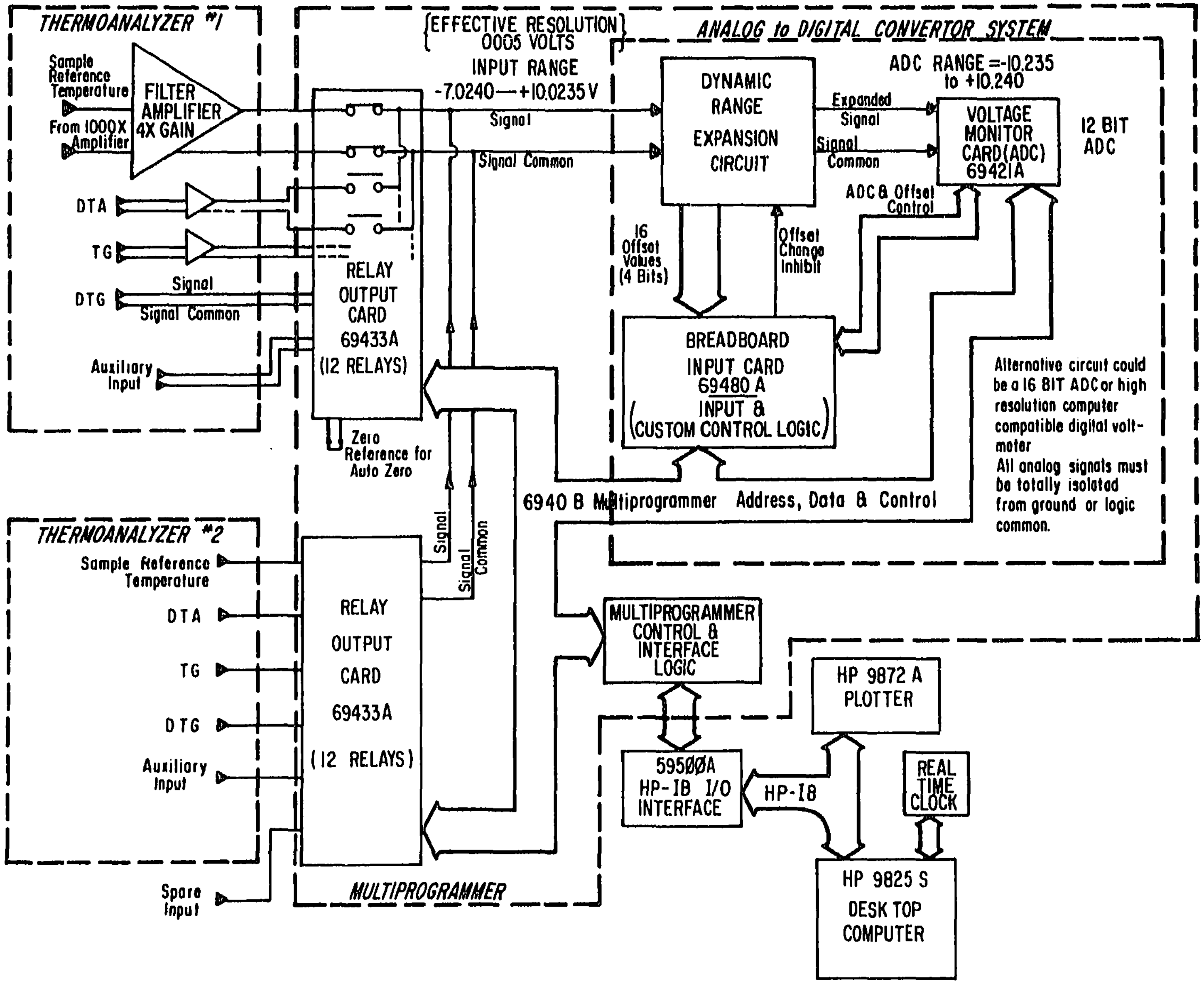

Fig. 1. A block diagram showing the major components of the data acquisition system.

outputs, as in this case, the system must be synchronized with the multipoint recorder [2].

In our system, in order to increase reliability and facilitate simultaneous data acquisition from two instruments, the signals from TA-I electronic units are taken ahead of the recorder divider and offset circuits. In addition, custom designed filter/amplifier circuits are added to the temperature control, TG, DTA and DTG chassis to condition the signals as well as to enhance the dynamic range of each channel. For instance, the data system has typically about twice the weight range capability as the Mettler recorder with the accuracy of that portion beyond calibration better than 1%. The signals going into the data system are not affected by the electrical tares on the TG chassis, the zero-adjust control of the DTA, the shift and zero-adjust of the DTG or the offset circuitry of the multipoint recorder.

Data acquired from the two thermoanalyzers are converted to actual units, such as temperature in °C, and stored in two arrays of 100 data sets, with one array being assigned to each instrument. The conversion of the thermocouple EMF into temperature is based on two polynomials, one for the PtRh10%—Pt system and the other, NiCr—Ni, stored in the data acquisition program. When the two data arrays are filled, they are automatically recorded on tape, verified, and in the unlikely event of a read error, rewritten on the next file. With both TA-Is in operation, data are recorded on alternate 6200 byte files. The tape has the capacity to store up to 5.8 h of data from the two instruments running simultaneously at the nominal rate of six data sets per instrument per minute. Data acquisition from each instrument will terminate automatically as the upper temperature limit of that unit is reached.

The scaling factors used to convert the acquired data are entered prior to the starting of the run. The program inquires about which thermoanalyzer is to be used, the thermocouple type, the range settings on the various units, initial sample weight and other information to be later printed on the plot. When starting a run the first instrument has the option of reading in all input parameters from either a tape cartridge or from direct keyboard entry. Parameters for the second instrument started while data acquisition is in progress must be entered by having the program read the previously recorded information from a tape cartridge.

The data acquisition program uses a real time clock to generate interrupts that time the data collection intervals. In order to avoid any program induced accumulative error, the time recorded with each data set is read from separate buffered clocks that are part of the real time clock unit.

Data reduction

The data acquisition system as described above stores all the data including the system temperature and the time of testing on a magnetic tape cartridge. Data reduction at the end of the sample run is handled by five separate programs. The functions of these programs are discussed below.

(1) Weight off program. This program is developed to automatically compensate any change in the thermobalance setting during a sample run. Since

samples of completely unknown thermal behaviors are ordinarily analyzed, there are occasions when the initial TG sensitivity setting is not sufficient to accommodate the total weight change the sample may have experienced. Under this condition, the analyst may wish to change the tare weight on the balance in order to have continuous display on the strip chart recorder. This results in a discontinuity of 10 mg, 100 mg or 1000 mg in the TG data depending on which tare weight is adjusted. The weight off program identifies discontinuities of this type and corrects the data, if they occur within 30 s.

(2) Buoyancy correction program. This optional program is developed so that buoyancy changes with respect to temperature and the initial offset effect (i.e. when the sample is first being heated) can be corrected from the TG data. Although this program is written for the following test conditions: (a) furnace, quartz mid range; (b) Pt/Rh sensor, DTA/TG micro (DT-21) or macro (DT-20) sample holder; (c) crucible, 3 mm × 10 mm or 8 mm × 20 mm alumina; (d) atmosphere, air; (e) flow rate, 5.72 l h^{-1} (i.e. 10 divisions on flow meter); (f) heating rate, 10° C min^{-1}, it can easily be modified for other conditions. The buoyancy change is calculated according to the change an

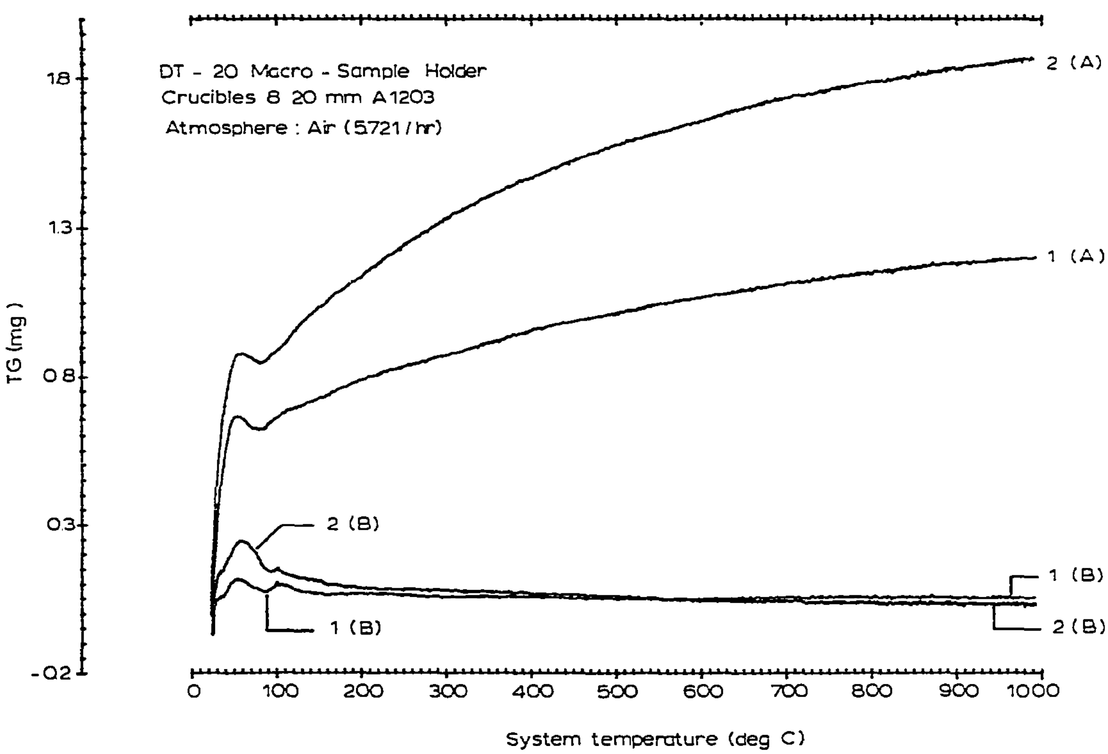

Fig. 2. Buoyancy effect of DT-20 macro-sample holder with the 8 mm × 20 mm alumina crucibles filled with alundum. Uncorrected TG curves: 1 (A) sample height = 0.39 cm, reference height = 0.59 cm; 2 (A) sample height = 1.84 cm, reference height = 1.84 cm. 1 (B) and 2 (B), TG curves of 1 (A) and 2 (A), respectively, after correcting for buoyancy change.

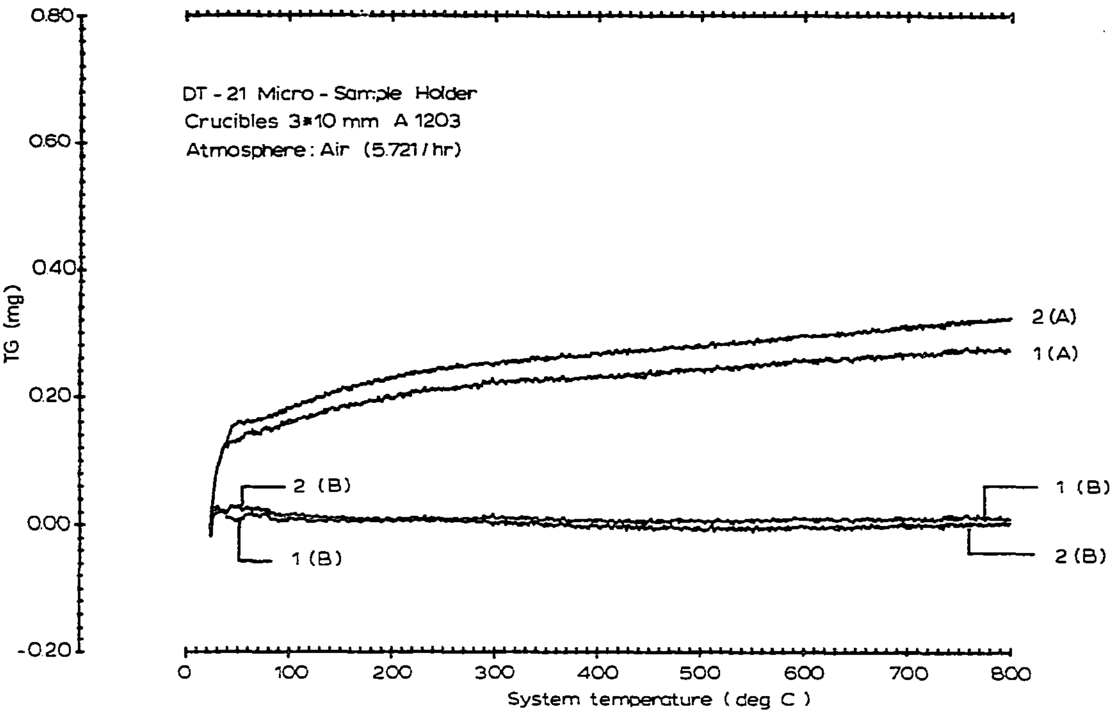

Fig. 3. Buoyancy effect on DT-21 micro-sample holder with the 3 mm × 10 mm alumina crucibles filled with alundum. Uncorrected TG curves: 1 (A) sample height = 0.45 cm, reference height = 0.50 cm; 2 (A), sample height = 0.95 cm, reference height = 0.90 cm. 1 (B) and 2 (B), TG curves of 1 (A) and 2 (A), respectively, after correcting for buoyancy change.

equal volume of alundum will experience under similar conditions. The height of the sample and that of the reference are the two parameters that need to be entered when the program is used. The buoyancy correction for the DT-20 and DT-21 sample holders is illustrated in Figs. 2 and 3, respectively. In both cases, the alumina crucibles are either partially or completely filled with the alundum which is supplied with the instrument to be used as reference material for DTA analysis.

(3) Plotting program. This program is used to plot the collected data on an HP 9872A plotter. The size of the plot is optional with the nominal size set at 11 in. × 14 in. The initial dialogue with the HP 9825S computer consists of answers to the following questions: (a) which of the two thermoanalyzers was used, (2) on which track and file the data was first stored, (3) plot as a function of time or temperature, and (4) lower and upper limits for time or temperature. With this information, the program will examine the stored data associated with the DTA, TG, DTG and temperature channels and determine the most convenient scales to plot the data. The program also provides the operator with the option to specify his/her own scales. In this case, the computer determined scale will be printed out on the printer to facilitate the operator in making up his/her decision. In addition to DTA, TG, DTG, and temperature, the program will also convert the TG data into

% weight change and plot the final results either as a function of time or temperature. If the TG data have been corrected for buoyancy change, the plot is automatic once it is called for; otherwise the operator has to enter the time or temperature for 0% weight change. The entry here is independent of the type of plot being made provided that the computer is informed about its identity, time or temperature. The program will plot the above mentioned thermograms in four different colors, at the end of which it also permits the operator to label each curve in words, add his/her comment text and print out the experimental conditions used.

(4) Find peak program. This program is chained to the plotting program. When used, the computer will examine the DTA or DTG data and locate the minima and maxima on the thermogram. The information which includes the temperature and time at which the minimum or maximum occurs is printed out on the printer. The marking of the peaks on the thermogram is then achieved by instructing the computer the index of the minimum or maximum one chooses to label. If the plot is against temperature, the peak will be marked in °C. If it is a time plot, an option is provided to mark the peak in minutes followed by the temperature in °C in parentheses.

(5) Percent weight change tabulation program. This program prints out the % weight loss/gain between any two temperatures or time entered into the computer. It therefore enables this information to be retrieved readily and accurately without reference to the curve generated by the plotting program.

RESULTS AND DISCUSSION

As described previously, our data reduction system permits data to be analyzed rapidly. The normal slow process of analyzing the data from the instrument's six-channel strip chart recorder, which involves joining the printed color dots and measuring the temperatures with a special ruler, is eliminated completely. A time saving of 70—80% has been experienced. Illustrated in Fig. 4 are the results obtained on a sample of calcium oxalate monohydrate under an atmosphere of helium. As is obvious, the plot is remarkably clear and includes a curve of % weight change as a function of temperature. The latter curve which normally requires hours to draw manually is now achieved in a matter of seconds. The same results plotted as a function of time are shown in Fig. 5. In both cases, the data are graphed in presentation and publication quality without the help of an artist. The same quality plot (in multicolors) can also be made directly on clear transparency for conference use if desired. This special feature is particularly advantageous as previously, a half decent transparency of the Mettler data would mean the necessity of multiple reductions by a Xerox machine, taping sections of the data together and finally coloring the thermograms individually.

We have mentioned that our automatic data acquisition system has a wider dynamic range than the instrument's recorder. In Fig. 6, the original recorder

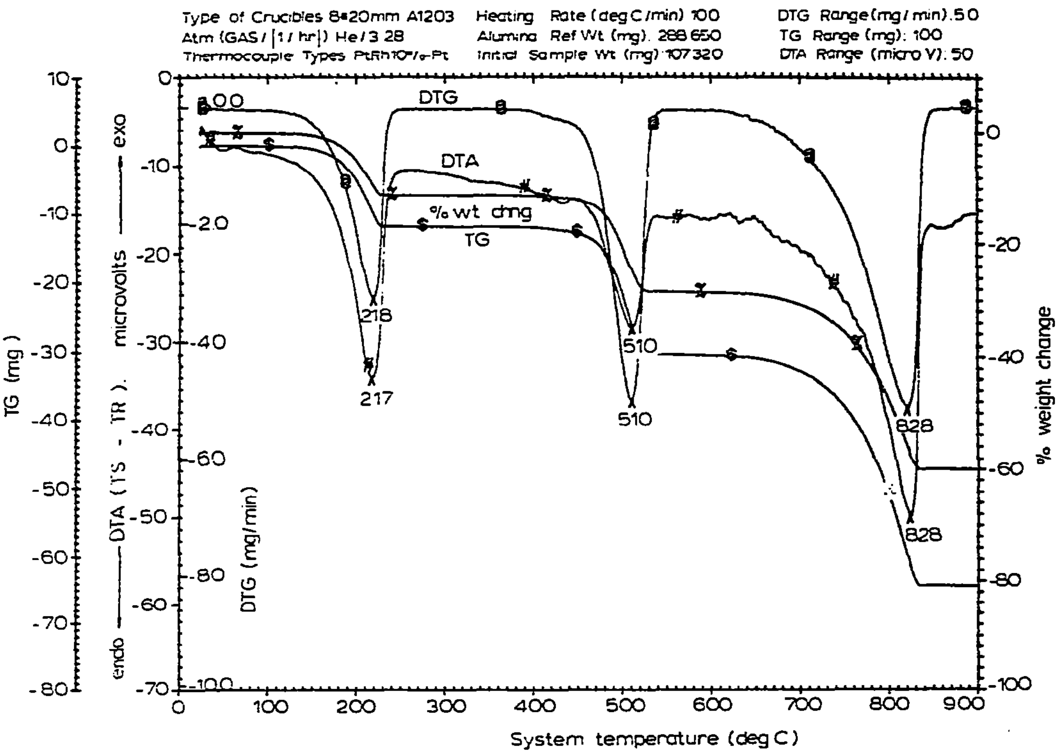

Fig. 4. Thermograms of calcium oxalate monohydrate ($CaC_2O_4 \cdot H_2O$) obtained under a helium atmosphere with a DT-20 macro-sample holder and plotted as a function of temperature.

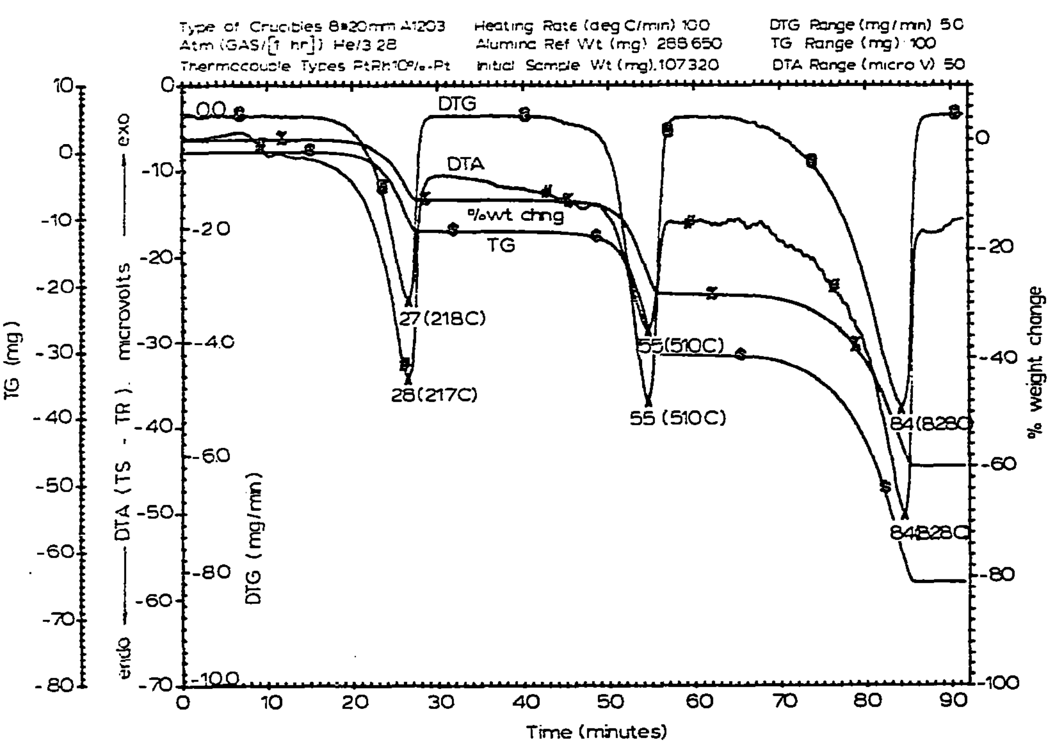

Fig. 5. Thermograms of the calcium oxalate monohydrate ($CaC_2O_4 \cdot H_2O$) shown in Fig. 4 plotted as a function of time.

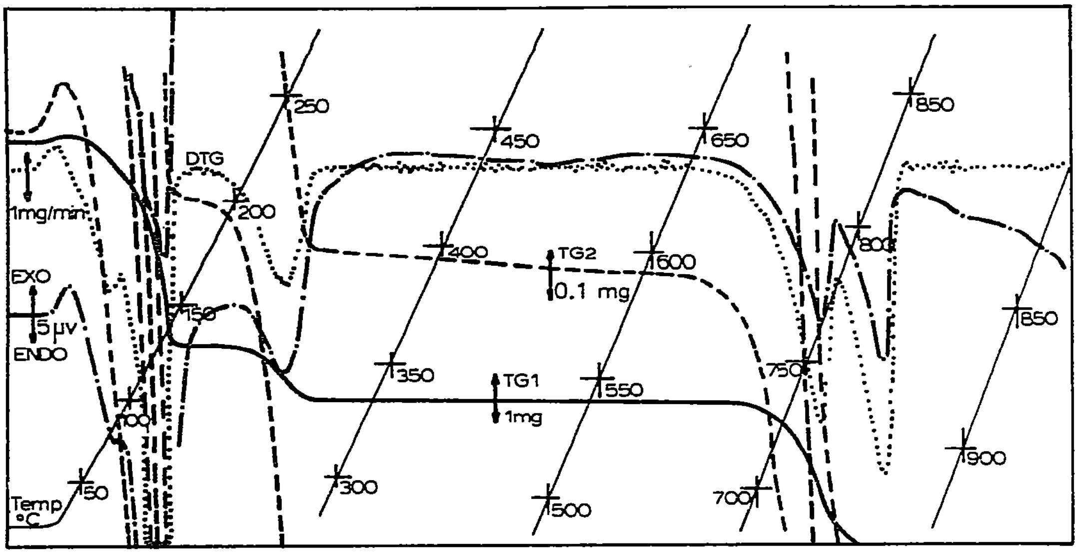

Fig. 6. Thermograms of copper sulfate pentahydrate ($CuSO_4 \cdot 5\ H_2O$) obtained under air using a DT-21 micro-sample holder. A reproduction of the original recorder traces ·—·—·, DTA; ———, TG1; — — —, TG2; · · · · · ·, DTG.

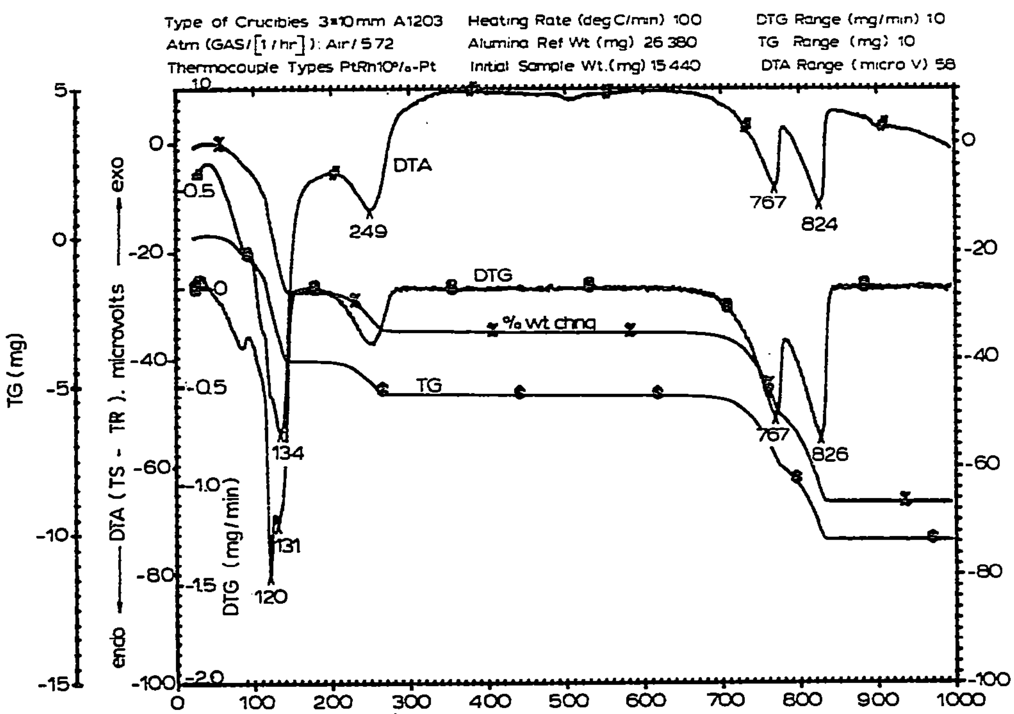

Fig. 7. Computer plot of the thermograms of copper sulfate pentahydrate ($CuSO_4 \cdot 5\ H_2O$) shown in Fig. 6.

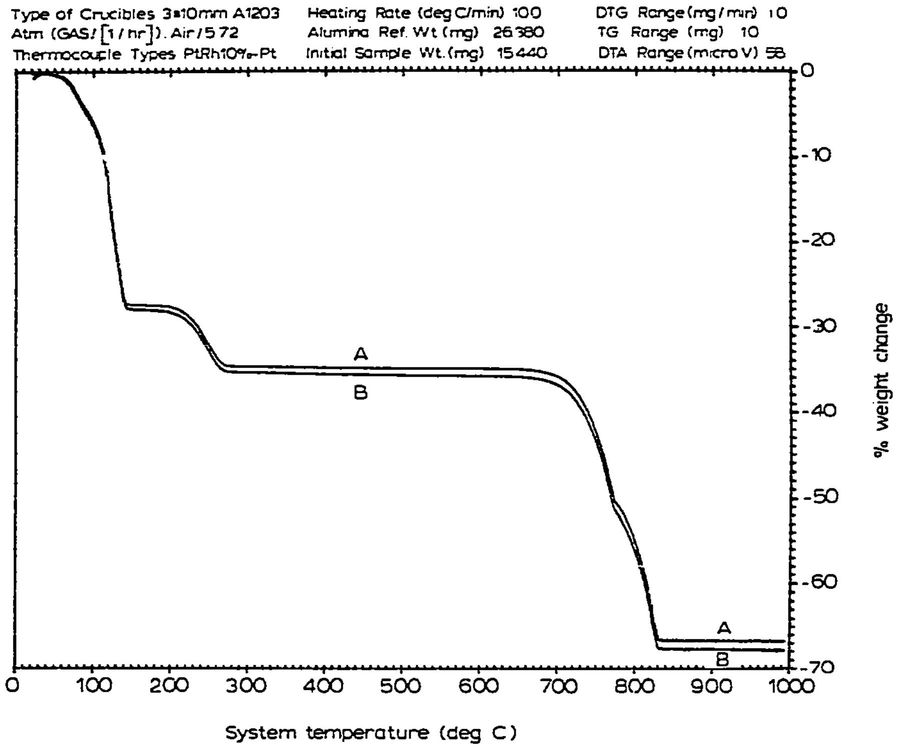

Fig. 8. Comparison of the % weight change curve before and after buoyancy change correction of copper sulfate pentahydrate ($CuSO_4 \cdot 5\ H_2O$) shown in Fig. 7: A, before correction; B, after correction.

trace of an analysis of copper sulfate pentahydrate ($CuSO_4 \cdot 5\ H_2O$) under air is reproduced. It can be seen that the DTG and the TG curves are out of scale during dehydration and decomposition of the compound, respectively. While the required information is lost on the recorder, it is preserved by our computer system. This is illustrated in Fig. 7.

The buoyancy correction program is especially useful when only small weight changes are detected over the temperature range studied or when highly accurate TG information is needed. In the former case, if buoyancy correction is not made, the computer, while magnifying the weight change by plotting the data against a narrow scale, will also magnify the buoyancy effect. This undoubtedly will lead to an awkward looking and undesirable TG plot. If the weight change is positive and gradual, the buoyancy correction program will also help to identify if the change is real or just an artifact. The % weight change curves of the copper sulfate penthahydrate before and after correcting for buoyancy are compared in Fig. 8.

REFERENCES

1 W.W. Wendlandt, Thermal Methods of Analysis, Wiley-Interscience, New York, 2nd. edn., 1974.
2 G. Stuk, L.E. Stillwagon and L.F. Thompson, ACS Preprints, Organic Coating and Plastic Chemistry, Vol. 38, March 1978, p. 147.