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THE USE OF DATA CENTER RECORDERS IN THERMAL ANALYSIS *

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ABSTRACT

The application of a Data Center recorder to the thermal analysis techniques of TG, DTA and dilatometry is described. The recorder used is essentially an eight-channel data acquisition system that multiplexes and converts up to ±10 V analog data into 12-bit digital data which are stored on a floppy disk. The stored data can be recalled at the convenience of the operator and mathematically manipulated before they are replotted on the integral X—Y or Y—time plotter.

INTRODUCTION

In the history of thermal analysis, the type of recording system employed has had a marked influence on the development of the techniques of thermogravimetry (TG), differential thermal analysis (DTA) and others. In one of the first thermobalances, Honda [1] used the point-by-point manual recording of temperature and mass of a sample. This method, though laborious, gave excellent results especially if slow furnace heating rates were employed. In DTA, because of the faster heating rate and/or greater rate of temperature change, photographic recording techniques of various types were generally employed [2—5]. This method had the disadvantage that the experimental run had to be completed and the photographic image developed before the entire recorded curve could be examined.

The first application of a modern potentiometric recorder to a DTA apparatus was by Kulp and Kerr [6] and Kauffman and Dilling [7]. The use of this type of recording system for TG and DTA led to greater accuracy, precision and ease of operation of the apparatus employed.

At the present time, three types of recording systems are employed [8]. They are: (a) X—Y or X—Y_1, Y_2 plotters; (b) single or multiple channel Y-time strip-chart recorders; and (c) multipoint—multichannel strip-chart recorders. The most popular recorders are probably types (a) and (b) although this author prefers the former. This preference is because of the convenient form of data presentation obtained; the apparatus variable Y is plotted directly as a function of temperature, X.

Recently, a new type of recording system has been introduced, one in

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which the transient data are stored in digital form on a floppy disk, and at the conclusion of the experiment can be recorded on an integral X—Y or Y—time recorder. Not only can the data be retrieved at the leisure of the operator, but he can also mathematically manipulate the data or change the data coordinates (expand or contract, etc.). This type of recorder is called a Data Center and appears to have numerous applications in thermal analysis as well as in other instrumentation areas. This brief report describes the application of this recorder to the thermal analysis techniques of TG, DTA and dilatometry, although other techniques may also be employed.

EXPERIMENTAL

Data Center recorder

The recorder employed was the Model 8110 system, equipped with an X—Y/Y—t plotter, manufactured by Bascom—Turner Instruments, 111 Chapel St., Newton, MA 02158.

Thermobalance

A Model TGS-2 thermobalance manufactured by the Perkin-Elmer Corp., Norwalk, Conn., was employed. For purposes of comparison, the mass and temperature data were also recorded on a two-channel potentiometric strip-chart recorder. In order to use the 0—1 V input of the Data Center recorder, the mass data signal was led into a digital voltmeter which had a 0—1 V analog output voltage. The temperature data signal from the thermobalance was in the 0—1 V range so it was connected directly to a recorder channel. A twisted pair of input leads was used for connections to each channel, following the recommendations of the manufacturer [9].

DTA apparatus

The DTA apparatus consisted of a DuPont DSC cell, microvolt DC amplifier, X—Y plotter and a temperature programmer. To interface the (T_s—T_r) and T_s signals to the recorder, digital voltmeters with 0—1 V analog outputs were again employed. Since the (T_s—T_r) signal is 0 ± 5 mV from the microvolt amplifier, a variable millivolt source (Pedersen Inst., Walnut Creek, CA) was employed in this circuit so that the 0—1 V input range could be utilized. An offset voltage of about 5 mV was used so that the (T_s—T_r) "zero" voltage was at mid-range of the recorder scale. It should be noted that all of the input channels must use the same input voltage range as the recorder [9].

Dilatometer

The dilatometer used was similar to that previously described [10]. It employed the same type of digital voltmeter interfaces as in the DTA apparatus.

RESULTS AND DISCUSSION

Data Center recorder

The Bascom-Turner Data Center recorder is illustrated in Fig. 1. The recorder is essentially an eight-channel data acquisition system which multiplexes and converts up to ±10 V analog data into equivalent digital data of 12-bit resolution at throughput sampling rates of 30 kHz. The analog section consists of a multiplexer which samples at periodic intervals any or all of eight input channels by electronically switching the input terminals of an instrument amplifier to the channel to be sampled. The amplifier is connected to a sample-and-hold circuit which tracks the instantaneous voltage value. When the sample/hold circuit receives a command to hold, it ceases tracking (in a few nanoseconds) and the voltage value is held constant while the analog-to-digital converter circuit makes the conversion to a digital number. These digital data can be stored in a plot buffer (one record is 500 points) or they can be plotted directly on the plotter. The digital data are numbers ranging from 0 to 4000 and when outputed to the plotter, they are percentages of full scale ranging from 0 to 100%. Data runs longer than 500 points can be acquired and stored on the disk. Such runs are constituted by stringing together a number of records which are automatically identified as belonging to the same sequence of data.

The specifications of the recorder are given in Table 1. The recorder has a far greater capability of data acquistion than is required for routine thermal analysis techniques. Hence, only those functions that are used for these

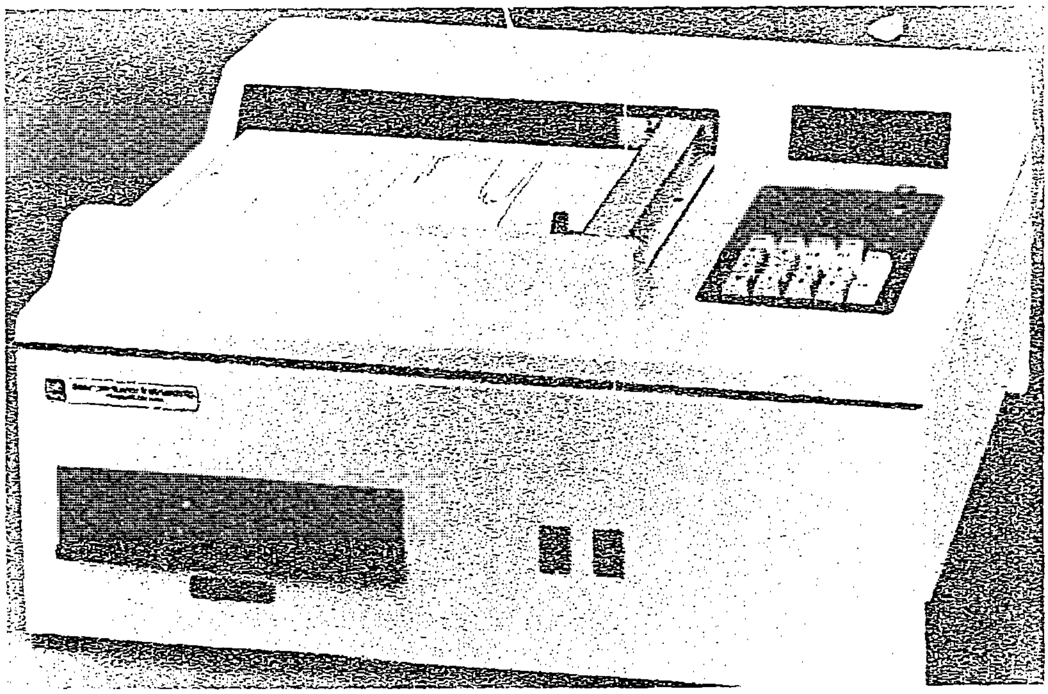

Fig. 1. Bascom—Turner Model 8110 Data Center recorder.

TABLE 1

Partial specification of Bascom—Turner Recorder [9]

Data acquisition	
Number of channels	Eight analog, differential input channels
Input ranges	12 input ranges 0 to 10 mV, −5 to 5 mV, −10 to 10 mV 0 to 100 mV, −50 to 50 mV, −100 to 100 mV 0 to 1 V, −0.5 to 0.5 V, −1 to 1 V, 0 to 10 V, −5 to 5 V, −10 to 10 V
Input impedance	100 megohm, 10 pF OFF 100 megohm, 100 pF ON
Resolution	12 bits (0.025% full scale)
Accuracy at 25°C (% full scale)	0.1% for 10 V, 1 V, 100 mV 0.35% for 10 mV
Sampling rate	Variable from one reading per 999 sec to 500 readings per sec for multichannel acquisition
Common mode rejection	100 dB at line frequency
Channel cross-talk	80 dB at 2 kHz from OFF channel to ON
Storage	
Volatile memory	20 kilobytes RAM
RAM data storage capacity	4000 data readings
RAM-to-disk transfer time	20 msec for transfer of 250 data points
Storage resolution	16 bits
Disk capacity	146 000 data points
Disk format	Hard sectored, special format for Series 8000; four-track program, 73 data tracks per disk, 4000 bytes (2000 data readings) per track
DVM display	
Number of digits	3
Display format	Percent full scale
Accuracy	0.1% full scale
Plotting	
Resolution	0.1% full scale
Accuracy at 25°C	0.3% full scale
Pen resolution	0.25 mm (0.01 in.)
Display size	18 × 25 cm (7 in. × 10 in.) for X—Y
Display format	Y—t graphs (data vs. time) X—Y graphs (data vs. data) (data vs. transformed data) (Y vs. log t, $1/t$, t^2, etc.)
Calculating functions	
Mathematical functions	Add, subtract, multiply, divide, average any two curves (500 points each), point by point, differentiate, integrate, logarithm, reciprocal, normalize, smooth any curve (500 points), point by point
Plotting functions	Offset, scale, expand, compress, shift X-axis

techniques will be described here; further details concerning the recorder's extensive capabilities can be found in ref. 9.

In a typical thermal analysis experiment, two data channels are normally required: temperature, and the function unique to the experiment such as mass, differential temperature or length or volume changes. Data can be acquired at a relatively large sampling interval (the order of seconds) due to the fairly slow furnace heating rates employed, 5—20°C min^{-1}. At these heating rates, the thermal analysis experiment can continue over a time period of 50—200 min (maximum temperature of 1000°C). Thus, data sampling rates of 0.5—2 sec are convenient to employ, far above the capabilities of the recorder's minimum sampling interval of 3—12 msec.

There are a number of functions of the Data Center that are useful for the thermal analysis experiment. They are: (a) multichannel recording of up to eight channels; (b) permanent storage of the data from one to eight channels on a floppy disk; (c) recall of the stored data at the convenience of the operator; (d) convenient plotting of data in various formats such as X—Y, Y—time, etc.; (e) data can be scaled or offset as required; (f) mathematical treatment of the stored data, i.e., differentiate or integrate, subtract one curve from another, etc., (g) smooth the raw data; and (h) output data to an external computer. To illustrate the use of most of the above functions, data from TG, DTA and dilatometry instruments will be recorded and their manipulation for each technique will be described.

Thermogravimetry (TG)

In thermogravimetry (TG), two channels of data are required: (a) mass (0—10 mg), and (b) temperature (0—1000°C). Using the Data Center, both of these data channels are recorded as a function of time, as shown in Fig. 2 (curves C and F) for the compound $CaC_2O_4 \cdot H_2O$. The two well-known mass-loss transitions are illustrated on the TG curves; they are

$$CaC_2O_4 \cdot H_2O(s) \rightarrow CaC_2O_4(s) + H_2O(g)$$

$$CaC_2O_4(s) \rightarrow CaCO_3(s) + CO(g)$$

Using the calculation modes of the Data Center, the time-based TG curve is scaled and offset to produce curve A. The TG curve is then replotted as a function of temperature (curve D) and then scaled and offset, as shown in curve B. Using the derivative function, the first derivative (after multiplication by a factor of 15) curve is obtained (curve E). In normal practice, the derivative of the TG curve requires an external derivative circuit or outboard device, plus another channel on the recorder (three-channel potentiometric strip-chart or two-channel $Y_1 Y_2$—X plotter). In the Data Center, the derivative of the curve can be obtained by simply depressing the appropriate keyboard code.

To illustrate the expansion mode of the Data Center on a TG curve, the curves for the dehydration of $NiSO_4 \cdot 6\ H_2O$ are shown in Fig. 3. While no definite horizontal mass plateaus are shown in the curves, the mass-loss transition is probably due to the reaction

$$NiSO_4 \cdot 6\ H_2O(s) \rightarrow NiSO_4(s) + 6\ H_2O(g)$$

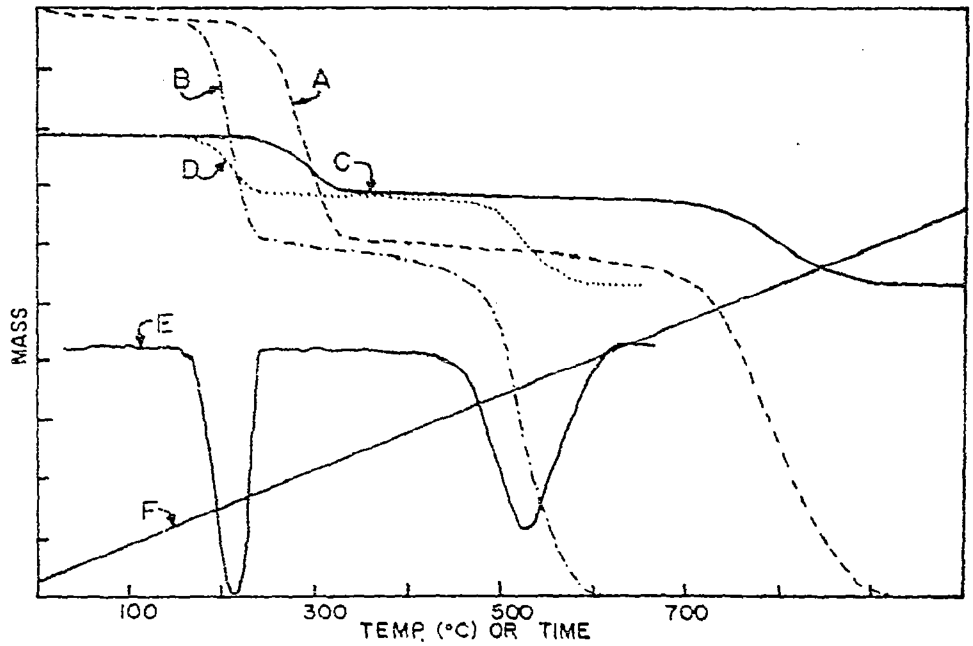

Fig. 2. TG curves of $CaC_2O_4 \cdot H_2O$. Heating rate of 10°C min^{-1} in N_2. Data sampling rate was 1.0 sec. A, Mass—time, scaled and offset; B, mass—temperature, scaled and offset; C, mass—time; D, mass—temperature; E, first derivative—temperature; F, temperature—time.

The original data curve (curve X1) contains little useful information concerning the dehydration reaction. By means of the expansion mode of the recorder, this curve is multiplied by X2, X4, X8, and X16. The X16 curve

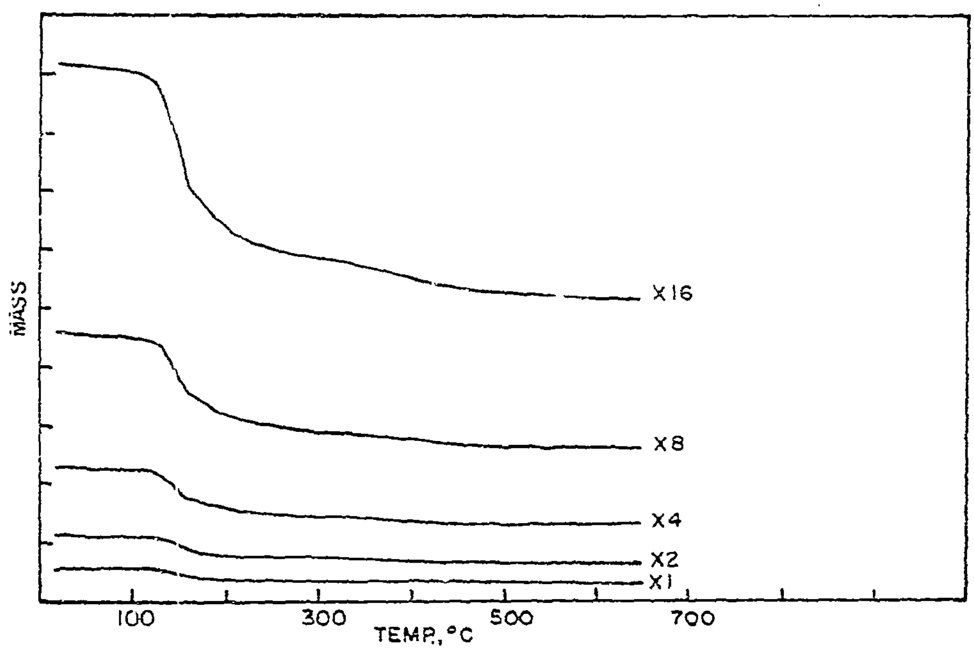

Fig. 3. TG curves of $NiSO_4 \cdot 6\ H_2O$. Amount of amplification on mass axis indicated on each curve.

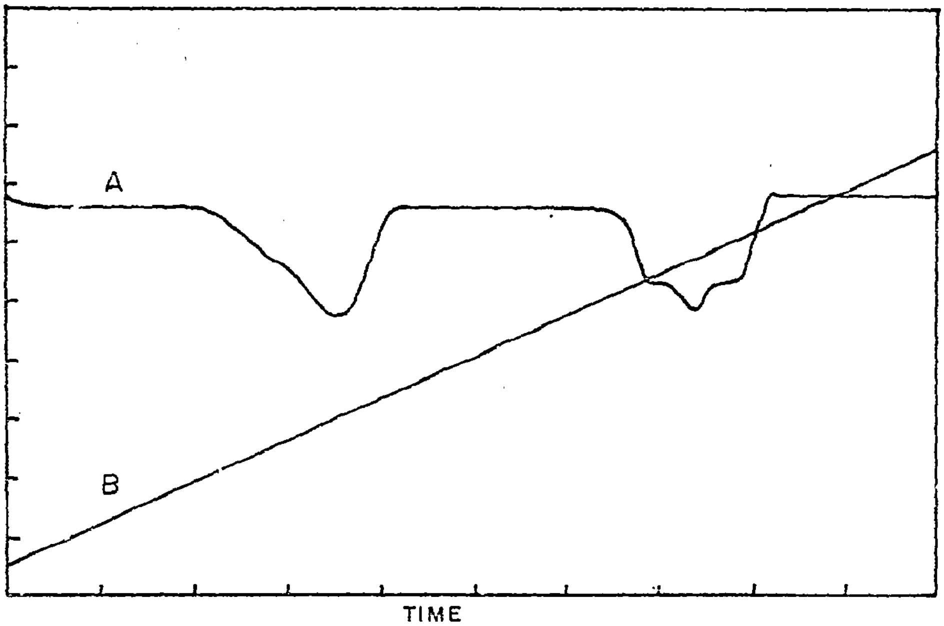

Fig. 4. DTA curve of $Cu(C_2H_3O_2)_2 \cdot H_2O$. Heating rate of 10°C min^{-1} in nitrogen. A, (T_s-T_r)—time; B, T_s—time.

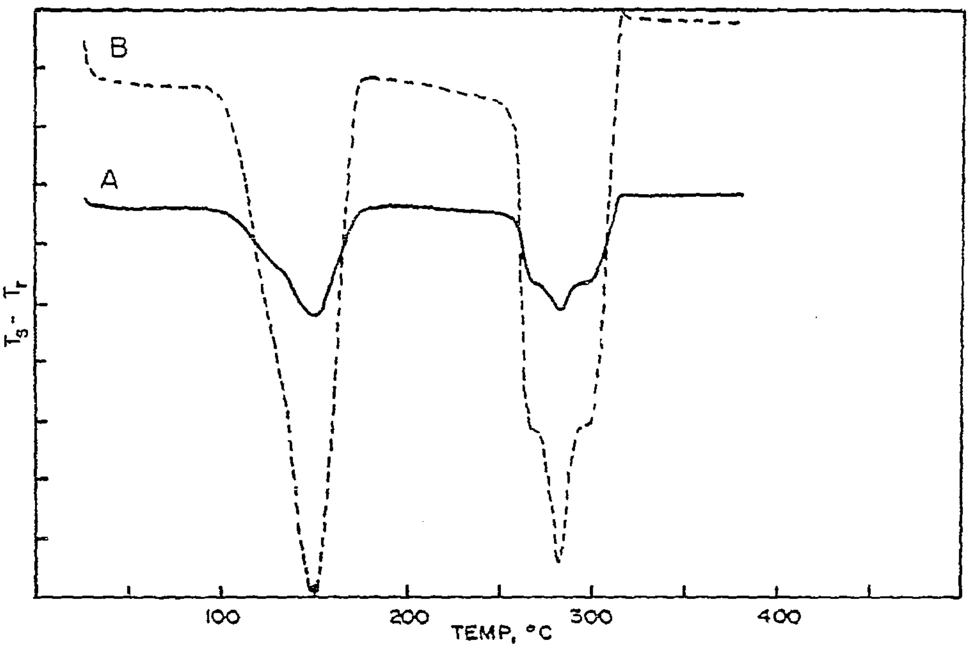

Fig. 5. DTA curves of $Cu(C_2H_3O_2)_2 \cdot H_2O$. A, (T_s-T_r)—T_s; B, (T_s-T_r)—T_s, scaled and offset.

reveals that perhaps intermediate hydrates of various thermal stability do exist.

Differential thermal analysis (DTA)

In the technique of DTA, two channels of data are also required; they are the differential temperature (T_s—T_r), which is proportional to the enthalpic change of the reaction, and the sample temperature, T_s. A typical DTA curve, such as that for $Cu(C_2H_3O_2)_2 \cdot H_2O$, is illustrated in Fig. 4. The raw data consist of the (T_s—T_r) and T_s curves, both plotted as a function of time. A replot of these data as (T_s—T_r) vs. T_s (Y—X) is given in Fig. 5. (curve B). To amplify the enthalpic features of the DTA curve, the curve is scaled and offset, again as (T_s—T_r)—T_s (Y—X) (curve B).

Dilatometry

The two channels of data required in dilatometry are change of length (or volume) of the sample, ΔL, and temperature, T. These are illustrated for sodium tartrate · 2 H_2O in Fig. 6. These date are replotted in Fig. 7 where the ΔL curve is recorded as a function of temperature (Y—X) and is scaled and offset to completely fill the Y-axis coordinates. The first derivative $d(\Delta L)/dt$ is also given in Fig. 7, scaled and offset.

In the dilatometry of compounds that have small ΔL transitions, the recorder data may still be quite useful. This is illustrated by the dilatometry curve of $Cu(C_2H_3O_2)_2 \cdot H_2O$ in Fig. 8. The ΔL curve obtained from the

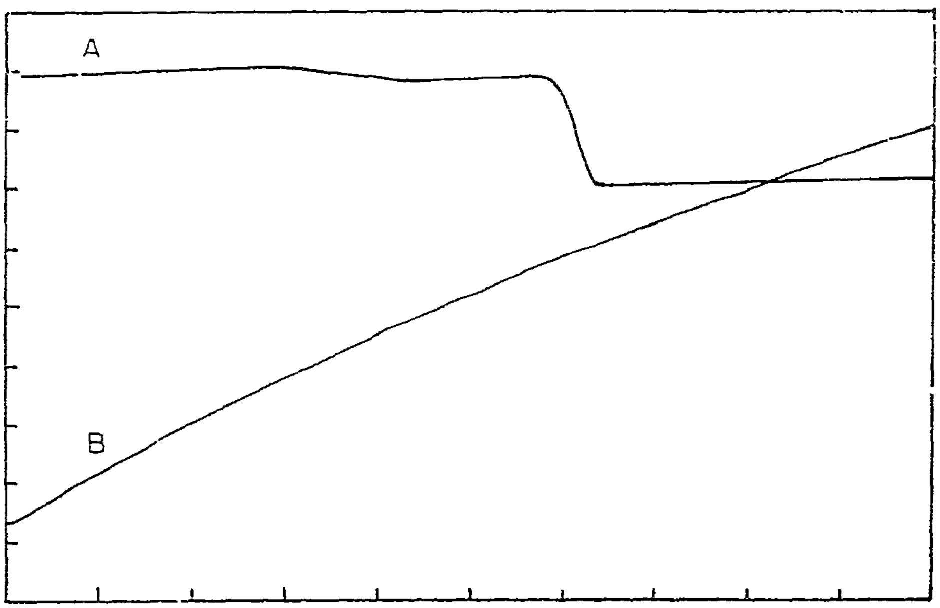

Fig. 6. Dilatometry curve of sodium tartrate · 2 H_2O. Heating rate of 10°C min^{-1}. A, Dilatometry curve, ΔL—t; B, temperature curve, T—t.

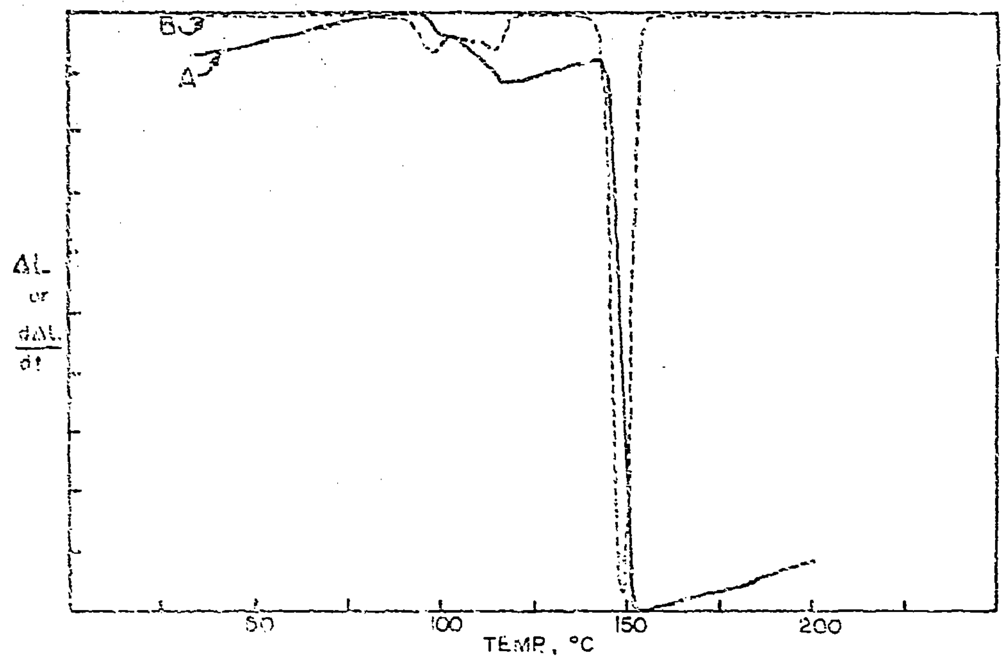

Fig. 7. Dilatometry curves of sodium tartrate · 2 H_2O. A, ΔL—T, scaled and offset; B, first derivative, $[(d\Delta L)/dt]$—T, also scaled and offset.

instrument indicates no pronounced transitions and for all practical purposes is a curve that increases linearly with temperature. On replotting the ΔL curve with scaling and offset, several transition or discontinuities are revealed. Full-scale response is 0.001 in on the expanded curve.

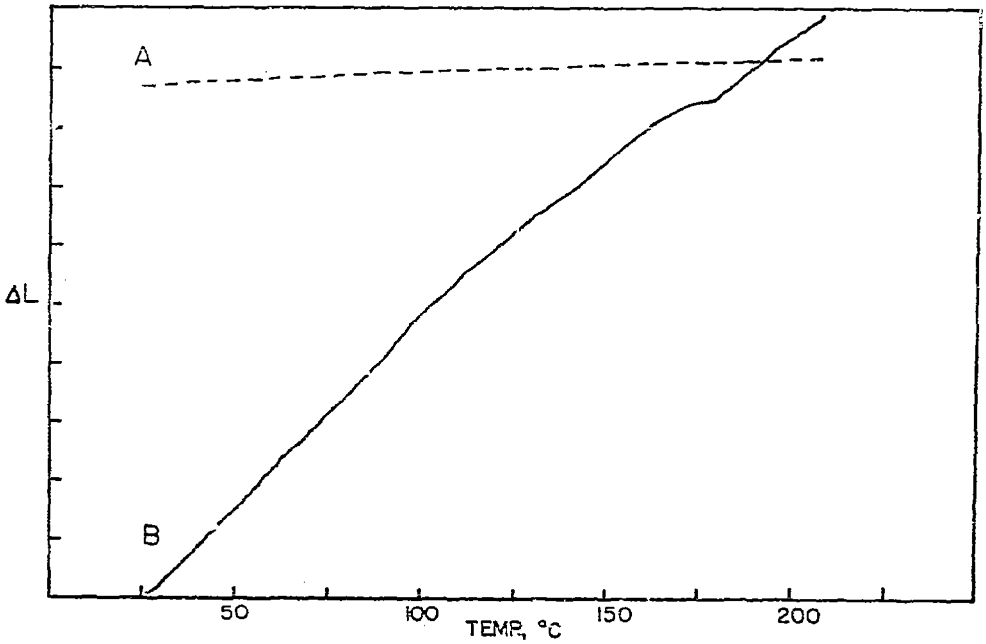

Fig. 8. Dilatometry curves of $Cu(C_2H_3O_2) \cdot H_2O$. A, ΔL—T as original data; B, ΔL—T, scaled and offset. Full-scale response on the ΔL axis is 0.001 in.

CONCLUSIONS

The Data Center recorder described here can prove to be very helpful in thermal analysis data presentation. The ability to accumulate and store eight channels of data would permit four different thermal analysis techniques to be carried out simultaneously. The recorder would also be useful for simultaneous or concurrent techniques on the same instrument, such as DTA—TG—DTG—T, etc. Also, the ability to perform various mathematical operations, such as differentiation and integration, on the accumulated data is also convenient. No longer will thermal analysis data be "lost" because of the recording device running off-scale or exceeding its limits of presentation. Small, subtle changes in the data curves can be amplified and expanded for ease in their detection or interpretation.

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