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CONCURRENT DIFFERENTIAL THERMAL AND AMPEROMETRIC THERMAL ANALYSIS*

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ABSTRACT

The evolution or absorption of energy in the form of heat that accompanies a transition of a material as a function of temperature has provided the basis for differential thermal analysis. The observation and/or measurement of the changes of other properties of materials can be used also to detect and measure transitions. One such example of this is change in the thermal coefficient of electrical resistance of a material.

A sample holder has been designed which permits amperometric thermal analysis (ATA) and differential thermal analysis (DTA) to be performed concurrently over the temperature range from ambient to 500°C. The DTA portion is performed in the conventional way and the ATA is carried out by measuring the current flow within the sample as a function of temperature. Using ATA, currents as small as 1×10^{-12} can be measured. The thermal analyses of many materials using the concurrent techniques show that the two methods reinforce one another and in some instances ATA is capable of detecting physical changes that are not as readily observable by DTA due to a lack of sensitivity or underlying principle. The thermograms in the following paper illustrate the utility of ATA in detecting the presence of moisture, glass transitions, crystallization, melting, and oxidation. In principle, the thermal coefficient of resistance can be dynamically obtained.

INTRODUCTION

The thermal techniques of differential thermal analysis (DTA), thermogravimetric analysis (TGA), and derivative thermogravimetric analysis (DTG) have become commonplace and accepted methods within the past few years.

These thermal techniques have been applied to a wide variety of organic and inorganic compounds in order to detect, and in many cases, measure, some change in the sample as a function of temperature. Many of these applications have been covered extensively in the literature[1] and in recent monographs[2-5].

Other thermal methods have been in existence for a number of years but have never gained wide acceptance due to certain inherent limitations or difficulty in instrumenting the method itself.

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**Present address: see footnote on p. 273.

Examples of such thermal methods include the use of an inverse heating-rate curve in order to measure changes occurring within the sample as a function of temperature[6], and the measurement of electrical conductivity or the change of the resistance of a material as a function of temperature[1,7-12].

The measurement of the changes in electrical conductivity or resistance as a function of temperature generally requires specialized equipment such as appropriate bridge circuits and voltage supplies.

While these special requirements represent certain inherent limitations, they are by no means limiting factors. The most serious limitation is one of physical sample configuration and ease of handling the sample.

Chiu[13,14] has reported recently on a modified technique of electrothermal analysis that circumvents some of the instrumentation disadvantages of general electrothermal methods. However, there appear to be some problems associated with sample handling still remaining.

As in many of the previously reported thermal methods, Chiu used two platinum electrodes which, in one instance, consisted of inner and outer cylinder foils, and placed the powdered sample between the electrodes[14]. A low DC voltage was applied between the two electrodes (1–2V) and an electrometer was used in series to measure current flow. The signal was displayed as a potential proportional to the logarithm of the current at 0.4 volts per decade.

The present paper describes a sample holder that permits the use of both powdered and solid samples of different physical size and shape, as well as standard electronic components along with a voltage supply adjustable over a wide range.

In the present method, a suitable level of DC voltage from 1 to 1000 V is applied to the sample and the current flow is measured by an electrometer in series with the voltage source. Since this is but one of a number of electrothermal methods and current flow is being measured, it seems more appropriate to refer to this technique as amperometric thermal analysis (ATA).

A differential thermocouple is also present in the sample holder but utilizes a separate sample which permits concurrent DTA–ATA analysis.

INSTRUMENTATION

The sample holder has been designed for use with R. L. Stone LB-202 recorder controller and P-202 furnace platform.

The design of the sample holder, showing the position and spacings of the differential thermocouple, the electrodes, and sample holder thermocouple, is shown in Fig. 1.

The ring-type differential thermocouple, U. S. Patent No. 3,298,220, is the same as that utilized in other Stone sample holders.

The platinum electrodes consist of 20-gauge platinum wire suitably formed. The removable portion of the platinum electrode system in Fig. 1 is coupled to the fixed portion by means of a platinum sleeve (J).

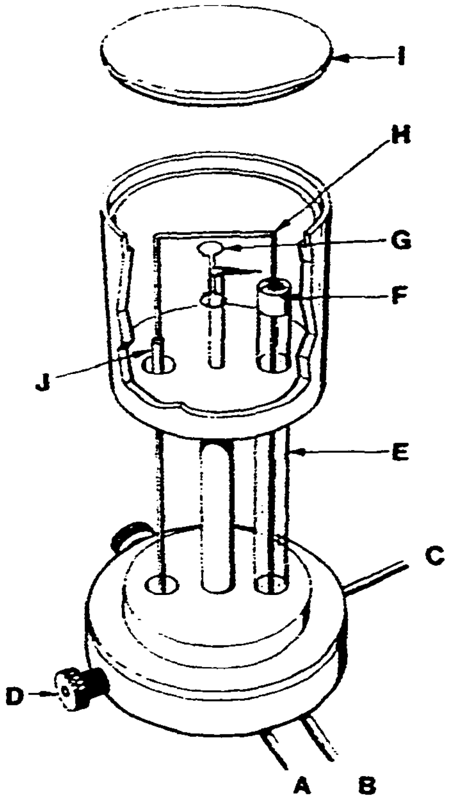

Fig. 1. DTA-ATA sample holder. (A) electrometer input lead; (B) negative voltage input lead; (C) thermocouple leads; (D) cooling water connectors; (E) pyrex capillary voltage insulator; (F) sample-pan container; (G) differential thermocouple; (H) platinum electrode; (I) sample-holder cover; (J) platinum electrode coupler.

Initially, other methods of coupling were tried. These proved to be ineffective since any dissimilarity of metals or oxidation of any metallic components produced anomalous effects in the thermograms.

In addition, a heavy-walled glass insert of capillary ID was used to support the fixed lower electrode. Using this configuration, considerable current leakage from the electrode to ground was experienced at low current settings (1×10^{-12} amps full scale). Consequently, the present system of coupling must be used which provides an air gap between the electrode and sample holder (ground) so that high sensitivities may be utilized.

The second electrode consists of a platinum lead attached to a small platinum cylinder (F). The small platinum cylinder receives the same type of sample cut that is utilized in the ring-type thermocouples, and makes contact with the edge of the cylindrical receiver by virtue of the sample-cup lip.

An R. L. Stone power supply, capable of supplying 0 to 1000 VDC in fixed incremental steps, was used to develop a potential across the sample. A TRACOR solid-state electrometer was used in series with the sample voltage supply to measure the current flow. The output of the electrometer was recorded on a second channel at a chart speed of one-half inch per minute.

For much of the work a Stone LB-202F recorder controller was used. This model has a three-pen strip-chart recorder integral with the unit; thus, two active channels are present which can be used to record the DTA and ATA signals, while the third pen acts as a temperature marker.

The individual conditions under which each thermogram was obtained accompany each figure.

RESULTS AND DISCUSSION

The principle of the method is dependent upon the fact that the thermal coefficient of electrical resistance of a sample changes during a phase transformation because of a change in ionic mobility within the lattice (*i.e.*, fusion); or because of a change in the electronic energy levels, such as occurs in solid–solid transformations[8].

It will be noted in Fig. 1 that the platinum electrode (H) contacting the top of the sample is capable of sliding in the sleeve-contactor. During a phase transformation the upper and lower platinum electrodes will be brought together into closer proximity. This will also result in increased current flow.

The effect of the change of thermal coefficient of electrical resistance, along with the physical movement of the two electrodes during phase transformations of some samples whose densities are not sufficiently great to support the upper platinum electrode, serve to generate a signal which indicates the occurrence of a phase transformation.

While it is a relatively simple matter to fix the geometry of the two electrodes, this approach has serious deleterious consequences. When this approach was tried, the reduction of bulk volume during a first-order phase transformation of some powdered samples resulted in a non-contact condition of the two electrodes.

The technique of ATA should provide an absolutely straight baseline during a programmed run, assuming that the sample is not undergoing a change. However, at high sensitivities and large applied potentials any increase or decrease in resistance, which of course will affect current flow, will be continuously recorded.

In order to establish any current leakage, the electrodes were separated and a blank run was made to 400°C. Fig. 2 shows that no current leakage or anomalous effects were noted at 4×10^{-12} amps full scale (FS) at the highest potential available (1000 VDC). The present sample holder has temperature capability to 500°C.

In the ATA thermograms, Figs. 3–11, sensitivities higher than those that would be employed normally were used to illustrate the character and magnitude of the effects observed by attenuating applied voltage and/or amperage. In routine use, an ATA attenuation setting would be utilized that provides the desired full-scale sensitivity necessary to observe the transition of interest. For qualitative and investigative ATA runs, the use of the highest permissible sensitivities will assist in detecting unexpected transitions that might otherwise remain undetected.

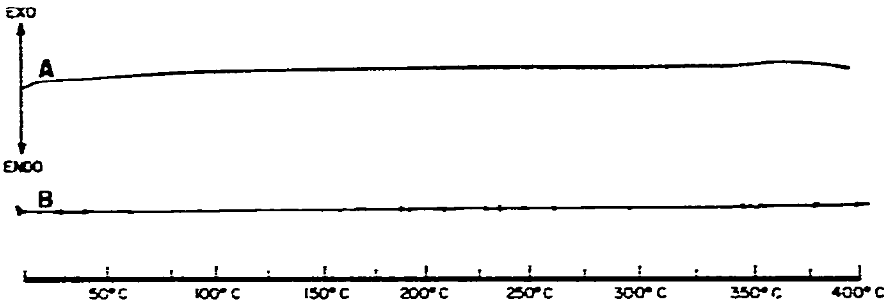

Fig. 2. Thermogram blank run of concurrent DTA-ATA. (A) DTA; sensitivity: 80 μV, approx. 0.26 °C/in at room temperature; atmosphere: static; program rate: 10°/min. (B) ATA; sensitivity: 4×10^{-12} amps FS at 1000 VDC; atmosphere: static; polarity: +; program rate: 10°/min.

A sample of low-density polyethylene was run by concurrent DTA-ATA. The results of this run are shown in Fig. 3. The initial run was made on a "wet" sample of polyethylene and this factor can be seen clearly as the moisture present leaves the sample, as the sample temperature is raised, which results in an increase and decrease of current flow. The second run was made on the same sample which had previously had the moisture expelled. In this case, only the melting of the sample is observed by ATA. The current flow changes abruptly at the peak temperature or when the entire sample is melted. The melting of the polymer is detected easily since the current flow changes over two orders of magnitude.

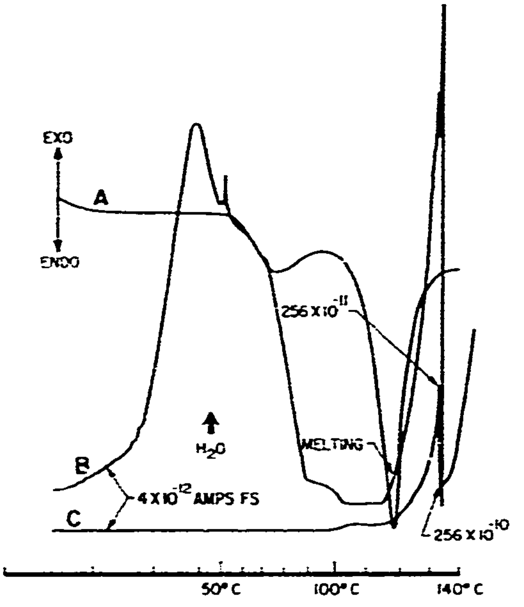

Fig. 3. Thermograms of concurrent DTA-ATA of low densitiy polyethylene. (A) DTA, sample: dry polyethylene (approx. 12 mg); sensitivity: 300 μV, approx. 0.96°/in at room temperature; atmosphere: static; program rate: 10°/min. (B) ATA, sample: wet polyethylene (approx. 25 mg); sensitivity: as shown at 256 VDC; atmosphere: static; polarity: +; program rate: 10°/min. (C) ATA, sample: dry polyethylene (approx. 25 mg); sensitivity: as shown at 256 VDC; atmosphere: static; polarity: +; program rate: 10°/min.

The use of ATA in detecting the glass transition of glassy polymers is shown in Fig. 4. Approximately 8 mg of sample was used for both DTA and ATA. The initial peak is due to moisture, as in the case of polyethylene, since a wet sample was utilized. The two other ATA scans were obtained using separate dry samples at a voltage potential of 512 VDC but at different sensitivities. The highest sensitivity settings permits T_g to be more easily observed.

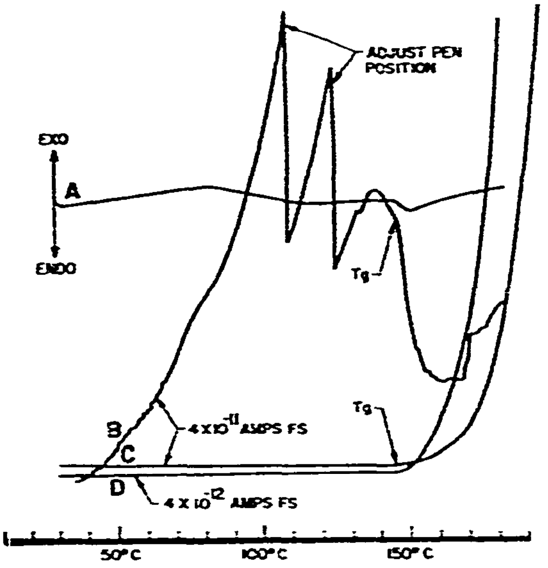

Fig. 4. Thermograms of concurrent DTA–ATA of polycarbonate. (A) DTA, sample: dry polycarbonate (approx. 7 mg); sensitivity: 80 μV, approx. 0.26°/in at room temperature; atmosphere: static; program rate: 10°/min. (B) ATA, sample: wet polycarbonate (approx. 12 mg); sensitivity: as shown at 512 VDC; atmosphere: static; polarity: + ; program rate: 10°/min. (C) ATA, sample: dry polycarbonate (approx. 12 mg); sensitivity: as shown at 512 VDC; atmosphere: static; polarity: + ; program rate: 10°/min. (D) ATA, sample: dry polycarbonate (approx. 12 mg); sensitivity: as shown at 512 VDC; atmosphere: static; polarity: + ; program rate: 10°/min.

After T_g has been reached, the current continues to increase as a function of temperature since the electrical resistance of the sample is changing continuously. Any oxidation or decomposition will also favor a current increase. The absolute current readings are dependent upon: (1) the electrical resistivity of the sample as a function of temperature; (2) residual impurities, such as metals, which can act as charge carriers; and (3) decomposition products present in the original polymer, or formed during analysis, which also affect the ability of the material to conduct a current.

In ATA one has the advantage of both voltage and/or amperage attenuation. In the case of polymers one generally encounters a high electrical resistivity so that relatively high voltage potentials can be used. However, before the programming is begun the voltage is applied in steps while observing the recorder pen. The recorder pen moves and then returns to electrical zero during each successively greater voltage increment until the sample permits some current conduction. This is the limiting voltage and a voltage lower than this limiting value was used to obtain the ATA data presented in these thermograms.

ATA can be especially valuable in cases where there are multiple transitions in the same general region of temperature interest where a transition of interest is being sought. This is the situation that arises in the case of polymethyl methacrylate. The DTA trace exhibits two transitions in the general temperature region of the glass transition which would make it difficult to interpret the thermogram obtained by a single method such as DTA. In this case, the ATA scan in Fig. 5 indicates that the transition beginning at approximately 60 °C is real, as is evidenced by the baseline departure; but the glass transition itself occurs at 100 °C. This is in good agreement with the previously reported glass transformation temperature of 105–110 °C[15,16,17]. In addition, the molecular weight of the sample, as well as thermal history, profoundly influence T_g and the DTA trace[18].

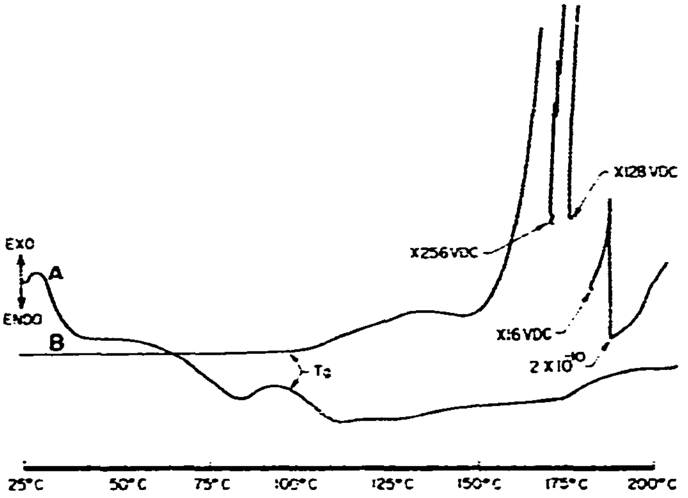

Fig. 5. Thermograms of concurrent DTA–ATA of polymethyl methacrylate. (A) DTA, sample: polymethyl methacrylate (7 mg); sensitivity: 80 μV, approx. 0.26°/in at room temperature; atmosphere: static; program rate: 10°/min. (B) ATA, sample: polymethyl methacrylate (15 mg); sensitivity: 2×10^{-10} amps FS at 512 VDC; atmosphere: static; polarity: +; program rate: 10°/min.

The termination of the effects of one transition and the beginning of additional ones are usually manifested by a change of slope, as is the case with polymethyl methacrylate. Because of the large increase in current, the applied voltage was attenuated to 256, and finally to 16. These large increases in current flow, and the slope change, are indicative of the onset of decomposition.

The concurrent DTA–ATA thermograms of nylon in Fig. 6 show both T_g and T_m. As before, the current changed over two orders of magnitude at T_m. After melting, the signal became appreciably noisy because of the upper electrode sinking into the melted sample. Apparently, some limiting point was reached where there was a large, sudden increase in current; at which point there was constant current-flow. This may be due to electrometer amplifier saturation.

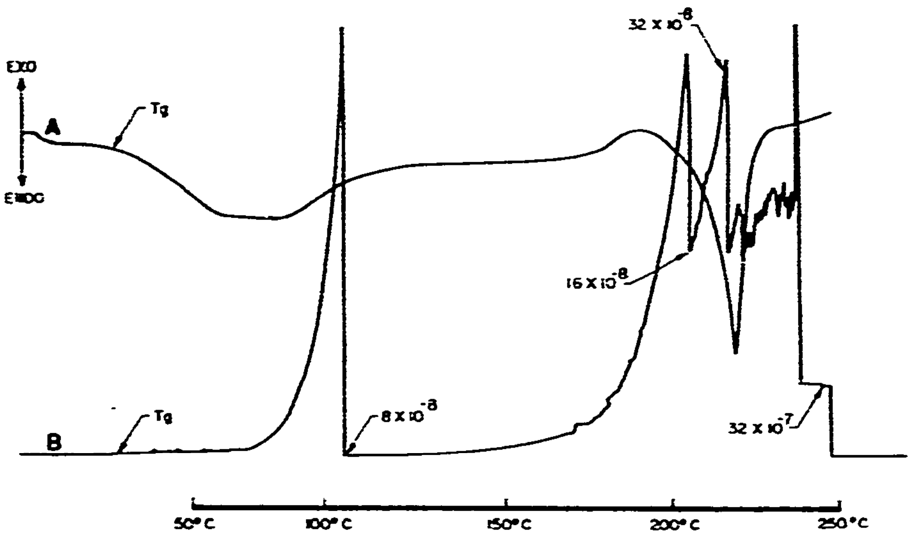

Fig. 6. Thermograms of concurrent DTA–ATA of nylon. (A) DTA, sample: nylon (approx. 10 mg); sensitivity: 150 μV, approx. 0.48°/in at room temperature; atmosphere: static; program rate: 10°/min. (B) ATA, sample: nylon (approx. 10 mg); sensitivity: 4×10^{-11} amps FS at 8 VDC; atmosphere: static; polarity: −; program rate: 10°/min.

We also wished to examine the electrical resistance of materials as a function of the state of the sample. Polyethylene terephthalate was chosen as an ideal material for this purpose. Consequently, approximately 7 and 12 mg of powdered samples were used for the DTA and ATA runs, respectively. The thermograms in Fig. 7 show both T_g and T_m. The current increase at T_m covers over two orders of magnitude.

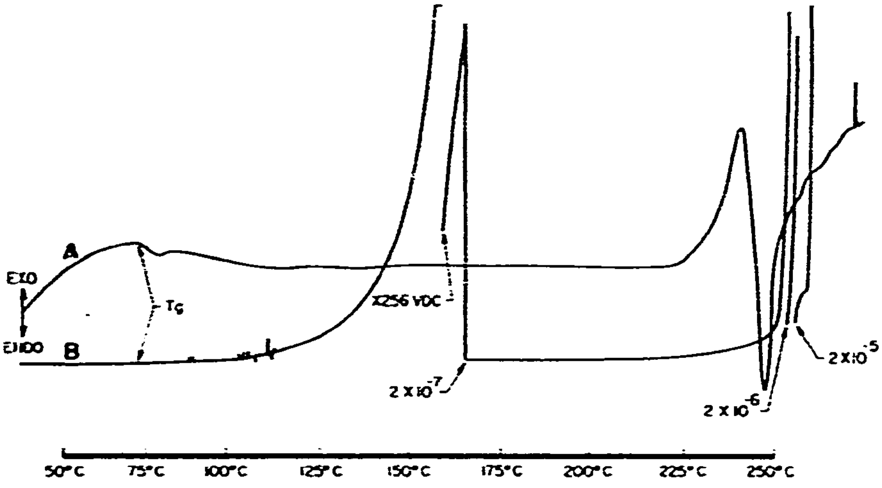

Fig. 7. Thermograms of concurrent DTA–ATA of polyethylene terephthalate. (A) DTA (initial run), sample: powdered polyethylene terephthalate (7 mg); sensitivity: 80 μV, approx. 0.26°/in at room temperature; atmosphere: static; program rate: 10°/min. (B) ATA (initial run), sample: powdered polyethylene terephthalate (12 mg); sensitivity: 2×10^{-10} amps FS at 512 VDC; polarity: +; program rate: 10°/min.

This sample was then air quenched and rerun using the same applied voltage as before. In this case the resistance of the sample is different from the initial run; but on the quenched sample a similar current flow was experienced at 137 °C, which can be seen by comparing Fig. 7 with Fig. 8.

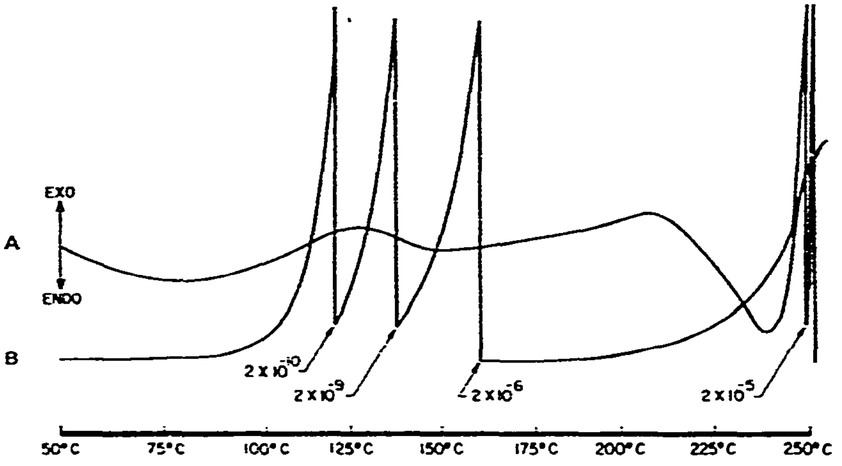

Fig. 8. Thermograms of concurrent DTA–ATA of polyethylene terephthalate. (A) DTA (rerun of sample from Fig. 7), sample: air quenched polyethylene terephthalate (7 mg); sensitivity: 80 μV, approx. 0.26°/in at room temperature; atmosphere: static; program rate: 10°/min. (B) ATA (rerun of sample from Fig. 7), sample: air quenched polyethylene terephthalate (12 mg); sensitivity: 2×10^{-11} amps FS at 512 VDC; polarity: +; program rate: 10°/min.

We have found that the technique of ATA can also be applied to inorganic materials to detect transitions. However, in these cases very low applied potentials must be used for partially conducting materials; or zero applied voltage for materials that are good conductors.

The ATA scan of copper sulfate (Fig. 9) shows that this technique can be used to detect the loss of combined water. The resolution is surprising, considering that

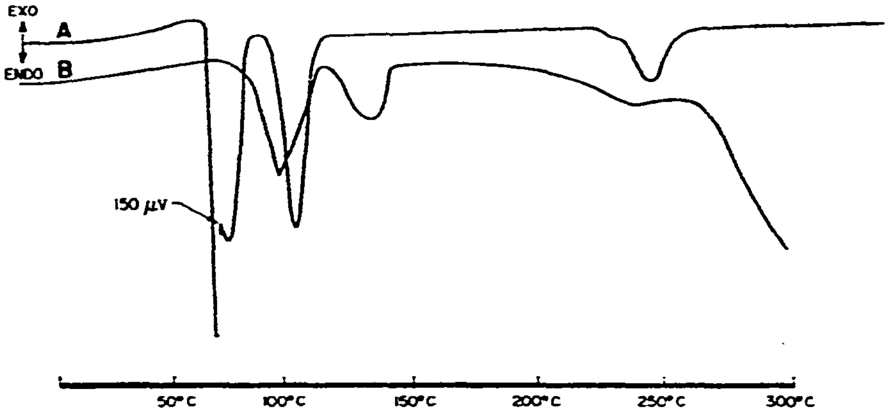

Fig. 9. Thermograms of concurrent DTA–ATA of $CuSO_4 \cdot 5H_2O$. (A) DTA, sample: $CuSO_4 \cdot 5H_2O$ (3 mg); sensitivity: 150 μV, approx. 0.48°/in at room temperature; atmosphere: static; program rate: 10°/min. (B) ATA, sample: $CuSO_4 \cdot 5H_2O$ (10 mg); sensitivity: 2×10^{-11} amps FS at 0 applied VDC; polarity: −; program rate; 10°/min.

a relatively large sample size and static atmosphere were used. Thus, even at zero applied potential, a measurable current flow is generated due to thermal electron transfer within the lattice as chemical composistional changes occur so as to provide easily measurable quantities.

When potassium nitrate was subjected to the same technique, differences between fresh and previously melted samples were observed, as Figs. 10 and 11 show. Differences between runs of potassium nitrate have been observed on numerous occasions, particularly in the temperature region from ambient to 200 °C.

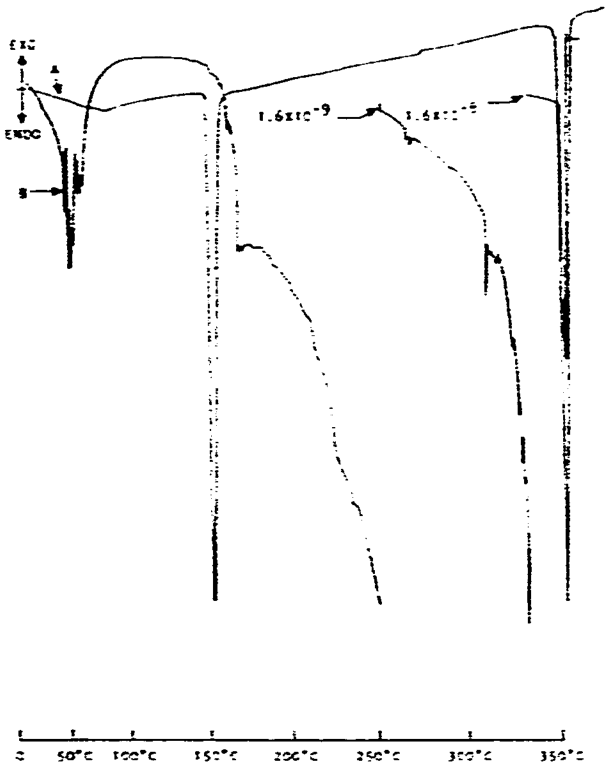

Fig. 10. Thermograms of concurrent DTA–ATA of KNO_3. (A) DTA, sample: reagent grade KNO_3, as received; sensitivity: 150 μV, approx. 0.48°/in at room temperature; atmosphere: static; program rate: 10°/min. (B) ATA, sample: reagent grade KNO_3, as received; sensitivity: 1.6×10^{-10} amps FS at 0 VDC; atmosphere: static; polarity: + ; program rate: 10°/min.

The present thermograms serve to illustrate the complexity of the thermal properties exhibited by potassium nitrate. The ATA transition and DTA endothermic transition between ambient and 100 °C in the fresh sample of KNO_3 are probably due to adsorbed moisture (Fig. 10); and are quite different from those exhibited in the thermogram of the sample reruns (Fig. 11), which shows exothermic activity as in recrystallization. The ATA scans clearly confirm sample activity which might be questioned on the basis of DTA by itself.

The solid–solid transformation of KNO_3 is not exhibited as a distinct peak in the original ATA run; while on the rerun, a distinct peak, followed by a smooth

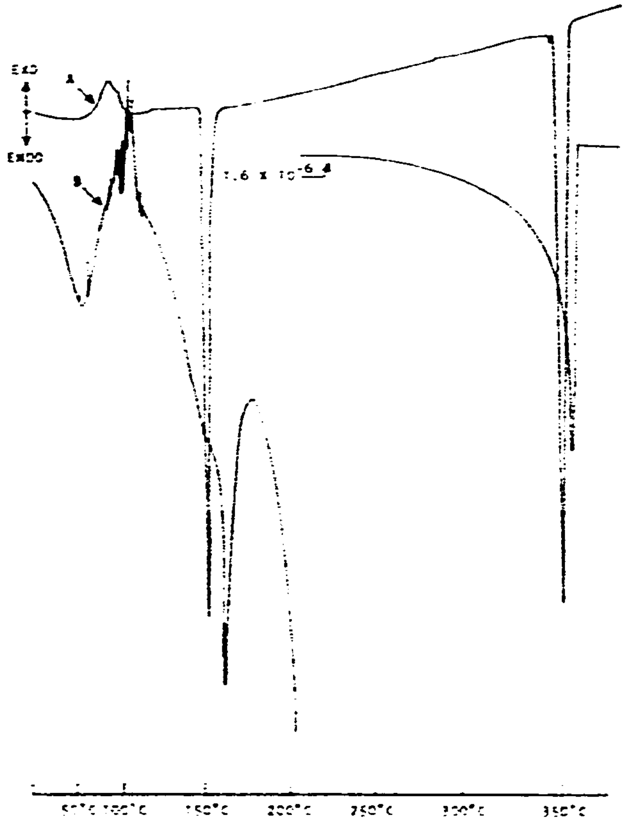

Fig. 11. Thermograms of concurrent DTA–ATA of KNO_3. (A) DTA, sample: previously melted reagent grade KNO_3; sensitivity: 150 μV, approx. 0.48°/in at room temperature; atmosphere: static; program rate: 10°/min. (B) ATA, sample: previously melted reagent grade KNO_3; sensitivity: 1.6×10^{-9} amps. FS at 0 applied VDC; polarity: +; program rate: 10°/min.

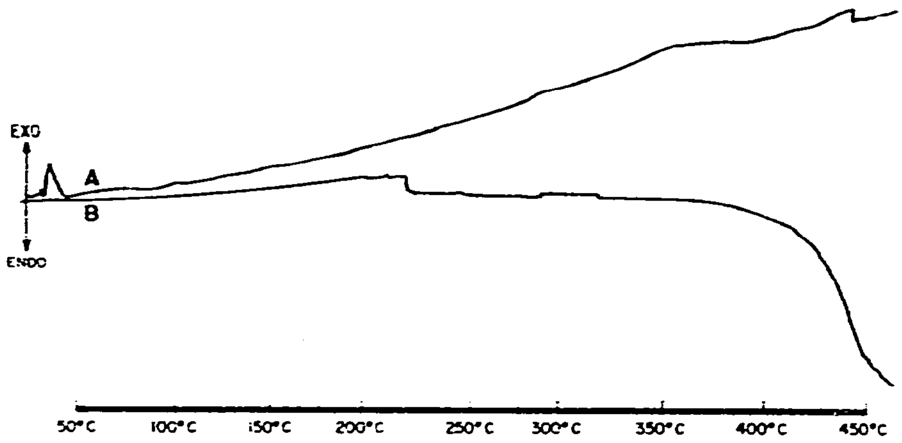

Fig. 12. Thermograms of concurrent DTA–ATA of Fe. (A) DTA, sample: iron filings; sensitivity: 80 μV, approx. 0.26°/in at room temperature; atmosphere: static; program rate: 10°/min. (B) ATA, sample: iron filings; sensitivity: 8×10^{-8} amps FS at 0 applied VDC; polarity: +; program rate: 10°/min.

change in electrical resistance, is evidenced (Fig. 11). One explanation for this is the difference in contact resistance, which may be a problem only in the case of conducting or partially conducting materials. In the case of organics, the resistance of the sample is sufficiently high ($> 10^6$ ohms) that contact resistance is not a problem.

This technique can also be used to study the oxidation of metals. Fig. 12 shows the concurrent DTA–ATA of iron filings. The current flow of the iron filings below 325 °C cannot be accounted for except in a very general way of activity within the sample due to absorption and desorption of gases. The DTA trace appears to follow the ATA trace in all respects.

However, at a temperature of approximately 350 °C, active oxidation begins to occur; as is evidenced in both the DTA and ATA scans. The standing current flow becomes less which would indicate an increase in resistance which would be explained by $4Fe + 3O_2 \rightarrow 2Fe_2O_3$ or $2Fe + O_2 \rightarrow 2FeO$.

This technique has been used in the case of polymers to quantitatively measure the amounts of trace metals present since, in the same set of polymers, the area in coulombs (ampere seconds) was found to be proportional to the quantity of charge carrier[19].

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