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THERMOVOLTAIC DETECTION. II. PRINCIPLES, APPARATUS AND APPLICATIONS *

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ABSTRACT

The new thermal analysis of thermovoltaic detection (TVD) is described and its application to various substances is presented. Basically, the technique consists of recording the EMF curve generated by the thermally decomposing sample in contact with two dissimilar metal electrodes (usually Al–Pt). The general shape of the curve, in reference to the temperature axis, enables it to be used for the qualitative identification of the substance. The curves are reproducible to within about ±3–4% of each other. TVD curves of $CuSO_4 \cdot 5\ H_2O$, $[Co(NH_3)_6]Cl_3$, various polymers, organic acids, coal, tobacco, water, and ethanol are presented.

INTRODUCTION

It was recognized by Wendlandt [1] that the technique of thermovoltaic detection (TVD) could be developed into a general thermal analysis technique. The technique, which consists of studying the thermal decomposition or phase change reaction of a sample placed between two dissimilar metal electrodes (Al–Pt, Zn–Cu, etc.), can be applied to a wide range of substances. These include inorganic metal salt hydrates, transition metal ammine coordination compounds, organic acids, polymers, amino acids, clays, coal, tobacco, and many others. Very few compounds that have been investigated failed to yield an EMF curve—the notable exceptions include non-polar organic compounds such as naphthalene, phenanthrene, and so forth. The physical state of the sample may be a liquid, paste or solid, although solids are the most commonly used form at this time.

The instrumentation employed is very simple, usually consisting of the two electrode sample holder (Fig. 1) and furnace, a furnace temperature programmer, a digital multimeter with a DC analog output, and a recording system (two channel T–Y or X–Y recorder). The sample can be in powdered

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* For Part I, see ref. 1.

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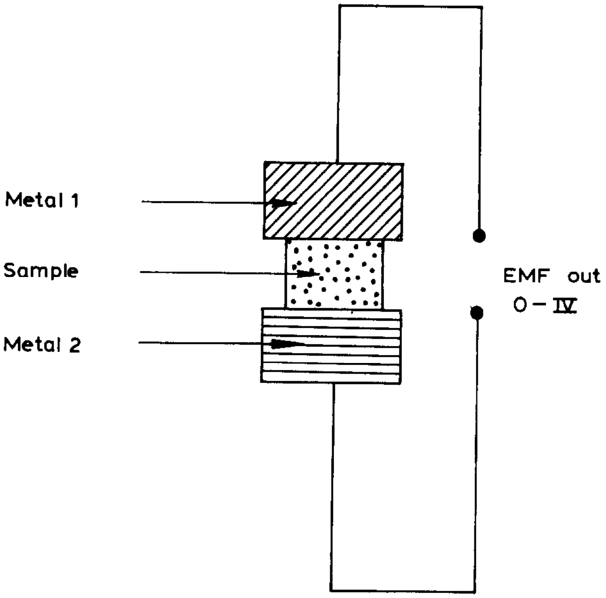

Fig. 1. Schematic diagram of electrode holders for TVD.

or pelletized form, and in certain cases, a liquid. The TVD curve, generally from 0–1 V, is most conveniently recorded as a function of temperature on an X–Y recorder. During the thermal decomposition or phase change of the sample, an EMF signal is generated which is indicative of the reaction being investigated. The temperature axis location and EMF amplitude of the curve, like other thermal analysis data [2], can be used to qualitatively identify the substance being studied. At the present time, it is difficult to quantify the data because of the experimental variables involved.

An attempt is made here to present examples of the types of substances that can be investigated by TVD. Although the list is limited here, it illustrates the broad applicability of the technique to a wide variety of materials. Further studies are continuing on specific classes of substances that are of interest.

EXPERIMENTAL

Apparatus I

This apparatus was identical to that previously described [1] except that a data center recording system was employed [3] instead of a conventional X–Y recorder. This modification made possible the storage of data records as well as the mathematical modification of the stored data before plotting.

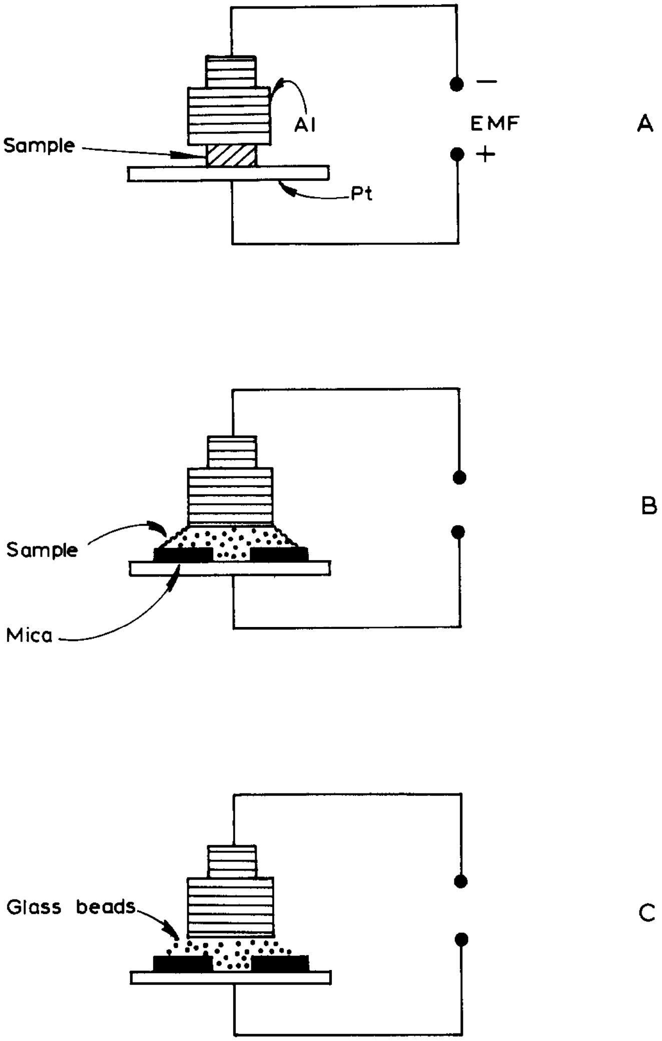

Fig. 2. Sample holder configurations for TVD for A, disk samples; B, powdered samples; and C, liquid samples.

Modification of sample holder

In order to use samples in the form of powders, liquids and pastes, the modified sample holder shown in Fig. 2 was used in both apparatus A and B. In Fig. 2A, the sample was in the form of a disk (1 mm thick × 6 mm diameter), while Fig. 2B permitted the use of powdered samples. Due to the sample melting and thus permitting electrode contact, a mica washer was placed between the electrodes. If the electrodes contacted each other during the experiment, the resultant EMF dropped to zero and hence provided no further useful information concerning the reaction. To study liquid samples, the arrangement in Fig. 2C was employed. Glass micro-beads, which were

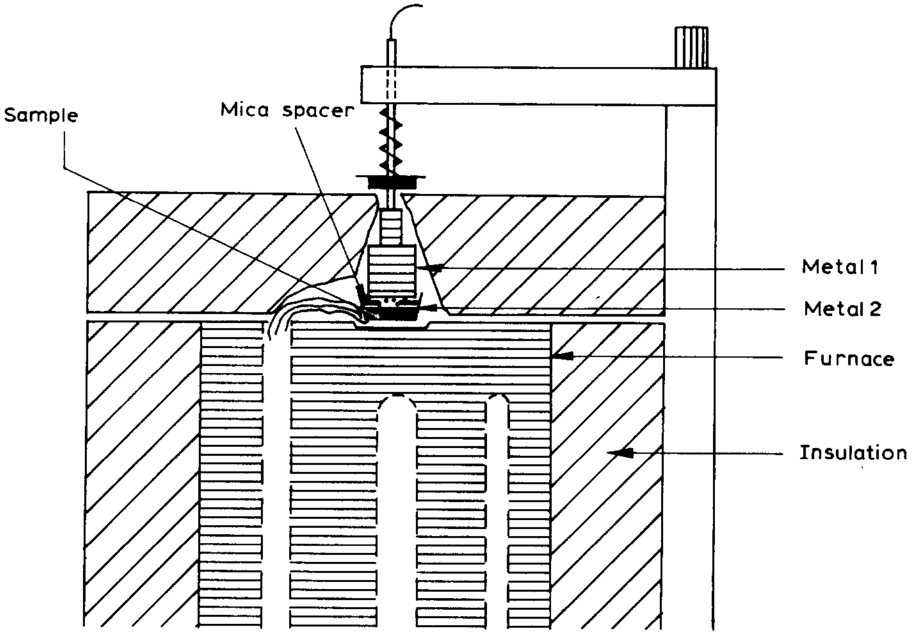

Fig. 3. Schematic diagram of furnace and sample holder for apparatus II.

placed on a mica washer, were saturated with the liquid sample. An EMF was observed until the liquid vaporized.

Apparatus II

This apparatus is illustrated schematically in Fig. 3. The sample was placed in a metal crucible which served as one electrode. A second metal electrode, which was spring loaded, compacted the sample from the top. A mica washer was again employed to prevent electrode contact during fusion reactions. Powdered and disk type solid samples could be investigated as well as liquid samples, which were placed on glass micro-beads. The furnace heating rate, which was generally 5°C min^{-1}, was controlled by a Theall Model TP-2000 temperature programmer. A Keithley Model 177 digital multimeter was employed to process the resultant EMF which was recorded on a Houston Instruments Model 100 X–Y recorder. The temperature of the furnace was detected by a chromel–alumel thermocouple connected through a 0°C reference junction to the X-axis of the recorder. Various electrode pairs were employed such as Mg–Ni, Mg–Cu, Mg–Pt, Al–Ni, Al–Cu, and Al–Pt. The more active metal of the electrode pairs (Mg or Al) was the negative electrode.

Samples

The samples were all obtained from the usual chemical sources. The coal samples were obtained from Exxon Corp., Houston, TX, while the tobacco sample was obtained from the Philip Morris Tobacco Co., Richmond, VA.

RESULTS AND DISCUSSION

Inorganic compounds

The TVD curves of two inorganic compounds are given in Fig. 4. As expected from the TVD curve of $NiSO_4 \cdot 6\ H_2O$ given elsewhere [1], the TVD peaks for $CuSO_4 \cdot 5\ H_2O$ occur during the dehydration reactions. The first peak appears at the $5\ H_2O \rightarrow 1\ H_2O$ dehydration transition. There peaks occur at somewhat lower temperatures than those observed in the DSC or DTA curves. For $[Co(NH_3)_6]Cl_3$, a compound that has been extensively studied thermally [4], the TVD curve indicates a number of peaks

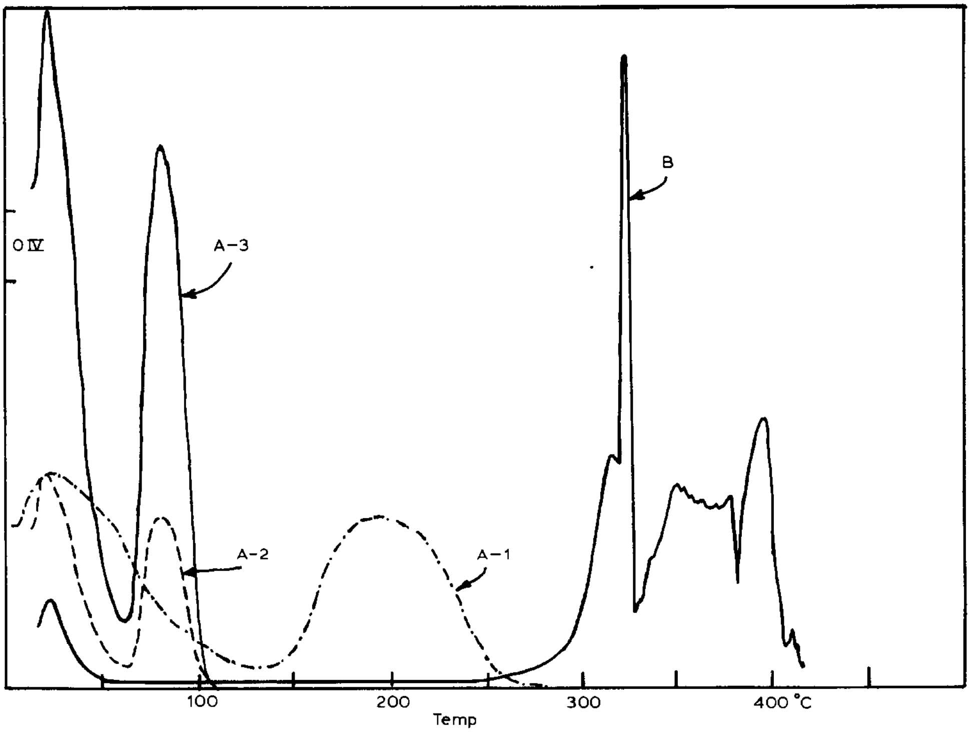

Fig. 4. TVD curves of some inorganic compounds: (A-1) $CuSO_4 \cdot 5\ H_2O$, *Y*–time plot; (A-2) $CuSO_4 \cdot 5\ H_2O$, X–Y plot; (A-3) $CuSO_4 \cdot 5\ H_2O$, Y–time plot normalized; (B) $[Co(NH_3)_6]Cl_3$.

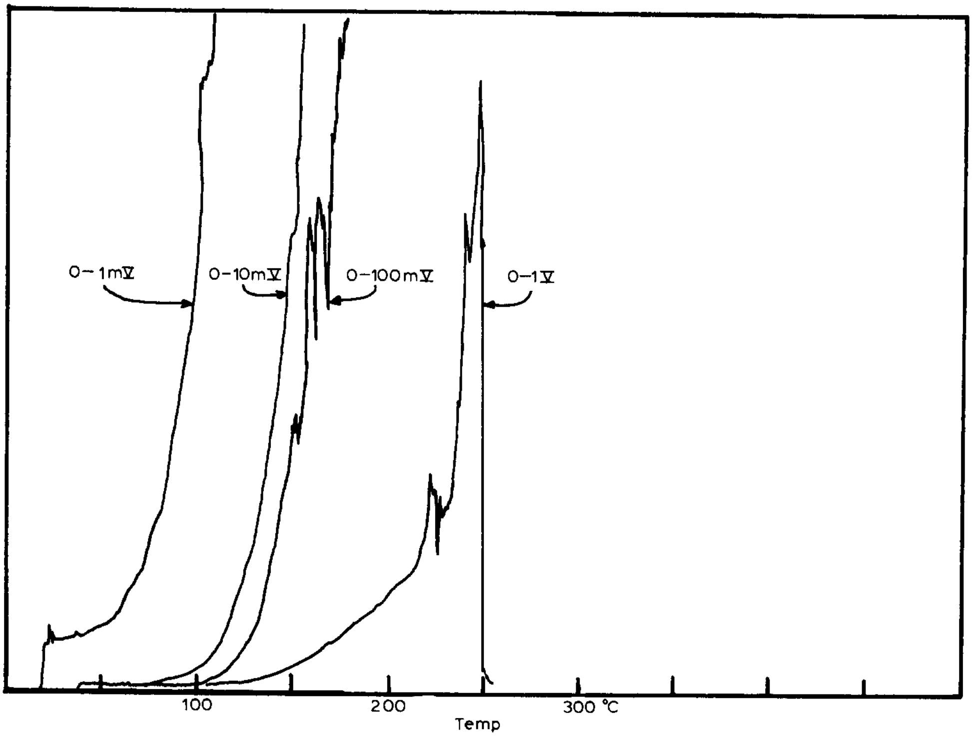

Fig. 5. TVD curves of Nylon 6/10 at different EMF sensitivities (apparatus I).

beginning at about 250°C. The dissociation reaction is complex, involving an oxidation–reduction reaction, changes of state from solid → liquid → gas, and the formation of a number of intermediates. Unfortunately, at this time it is not possible to interpret the origin of the three major peaks found in the TVD curve. The first peak, at a V_{max} of about 320°C, and the last peak with a V_{max} of 400°C, correspond with endothermic peaks found in the DTA curve [4].

Polymers

Most of the polymers investigated by this technique yielded TVD curves of various types. To illustrate the effect of EMF sensitivity on the resultant TVD curves, four curves of Nylon 6/10 recorded at various sensitivities from 0–1 mV to 0–1 V are given in Fig. 5. At the highest sensitivity, 0–1 mV full scale, the curve begins to increase starting at 50°C, while on the 0–1 V scale, no increase in the curve began until about 125°C. At 247°C, the fusion of the polymer permitted electrode contact causing the EMF to decrease to 0 V.

Using the sample holders in Fig. 2A and B, the TVD curves for Nylon 6/6 are given in Fig. 6. The Fig. 2A sample holder allowed contact to be made as the polymer melted and this was evidenced by the drop to 0 V at

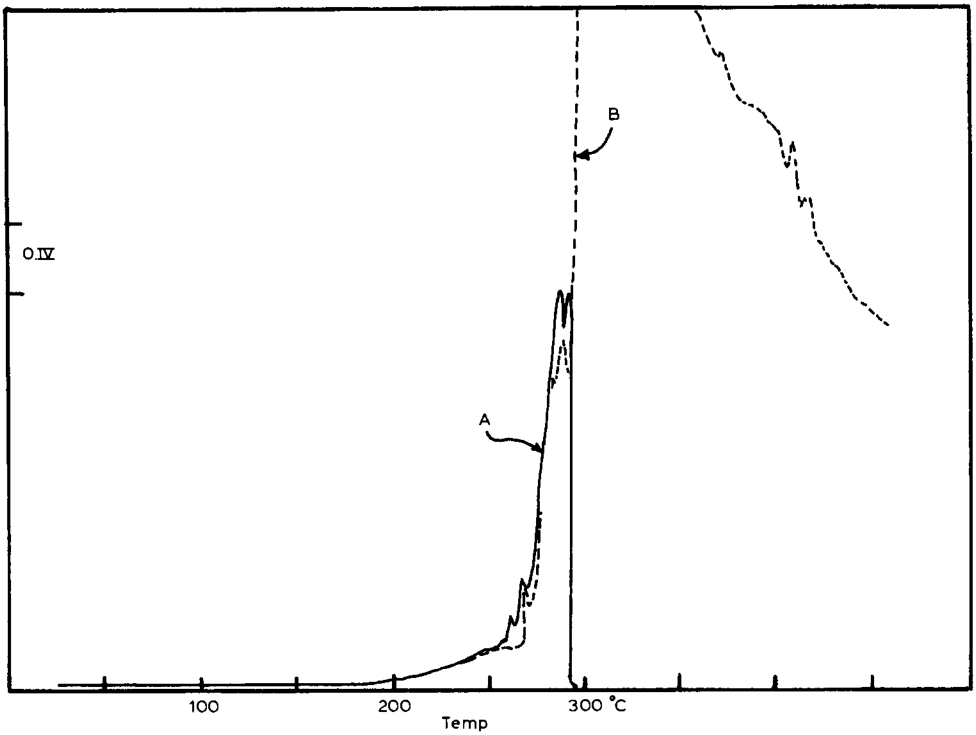

Fig. 6. TVD curves of Nylon 6/6 using various sample holders. A, Sample holder Fig. 1A; B, sample holder Fig. 1B (apparatus I).

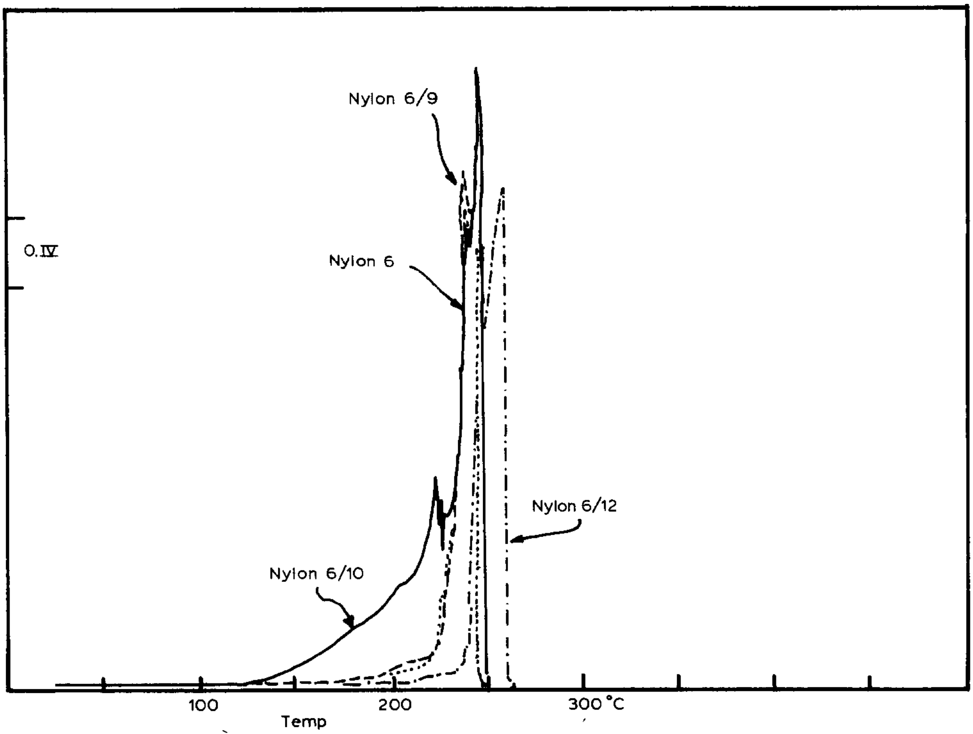

Fig. 7. TVD curves of various Nylon polymers; apparatus I with sample holder Fig. 1A.

about 290°C. With sample holder Fig. 2B, the mica washer prevented electrode contact so that the curve continued beyond 400°C.

It is possible to qualitatively identify four of the various Nylon polymers by the technique of TVD, as shown by the curves in Fig. 7. These curves, recorded with sample holder Fig. 2A, show a sharp drop-off to 0 V in the 200–300°C temperature range due to electrode contact. However, it is possible to distinguish between the various Nylons such as 6/10, 6, 6/9 and 6/12, each of which is made up of different monomers. With the sample holder Fig. 2B, it should be possible to extend the curves to higher temperatures.

Organic acids

A number of organic acids were also investigated by the TVD technique. The first of these acids, malonic acid, is shown in Fig. 8. These data illustrate the reproducibility of the TVD technique, as applied to these compounds. Three curves are illustrated, each of which was recorded under identical conditions. The curves appear to be within 3–4% of each other, with the greatest differences found during the middle region when the acid is in the molten state. The reproducibility may be fortuitous when one considers all the instrumental parameters that must be taken into account. There is the solid sample–electrode interface followed by the liquid sample–electrode

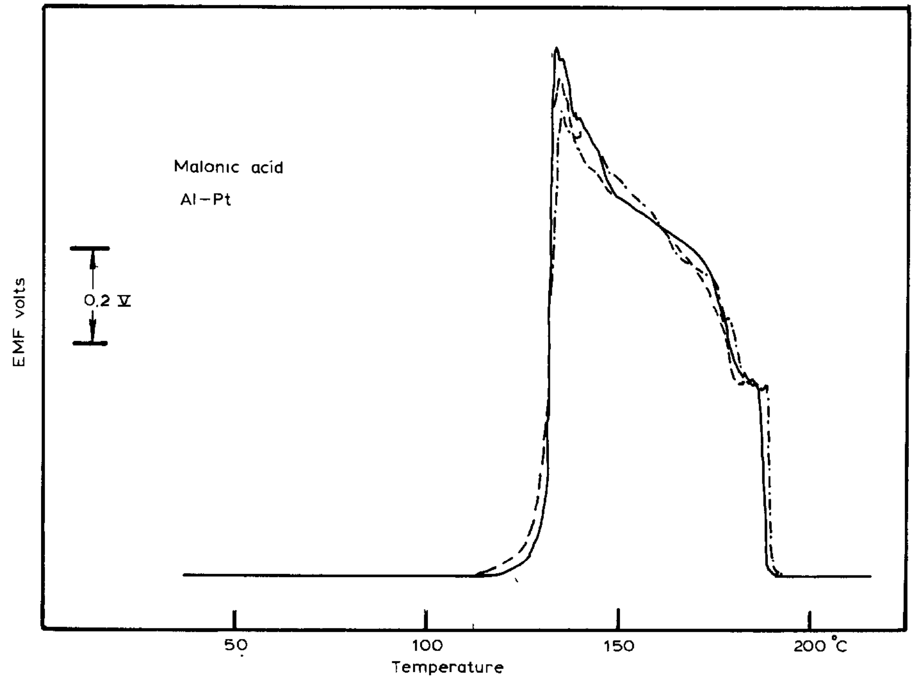

Fig. 8. TVD curve of malonic acid (apparatus II).

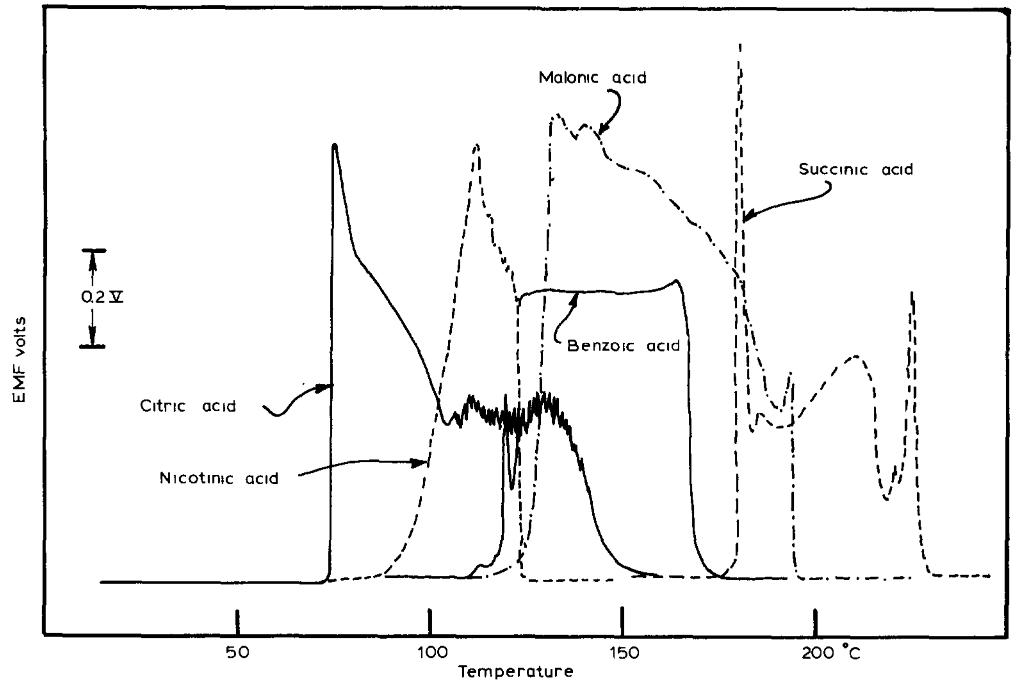

Fig. 9. TVD curves of various organic acids (apparatus II).

interaction. During the latter, the aluminum electrode reacts with the liquid acid, further complicating the acid–electrode interface. With certain other acids, the fusion reaction is followed by decarboxylation and/or decomposition reactions as well, which creates other sample–electrode problems. It is indeed surprising that the curves are as reproducible as they are.

The TVD curves of five organic acids are illustrated in Fig. 9. Each acid gives a characteristic curve which can be used for "fingerprinting" or identification of the individual compound. All of the acids generate their characteristic EMF curve during their fusion and/or decomposition reactions. For these compounds, the probable electrode reactions that occur at the Al–Pt electrode system are:

aluminum electrode (−)

$$Al^0 \rightarrow Al^{3+} + 3\,e^-$$

$$Al^{3+} + 3\,H_nY \rightarrow AlY_3 + 3\,nH^+$$

platinum electrode (+)

$$3\,nH^+ + 3\,ne^- \rightarrow \frac{3n}{2}\,H_2$$

At the end of the run, the aluminum electrode is covered with a deposit from the organic acid, necessitating the polishing of it before the start of the next run. Likewise, the platinum electrode is heated to a red-heat in a Bunsen burner flame before a new run is begun.

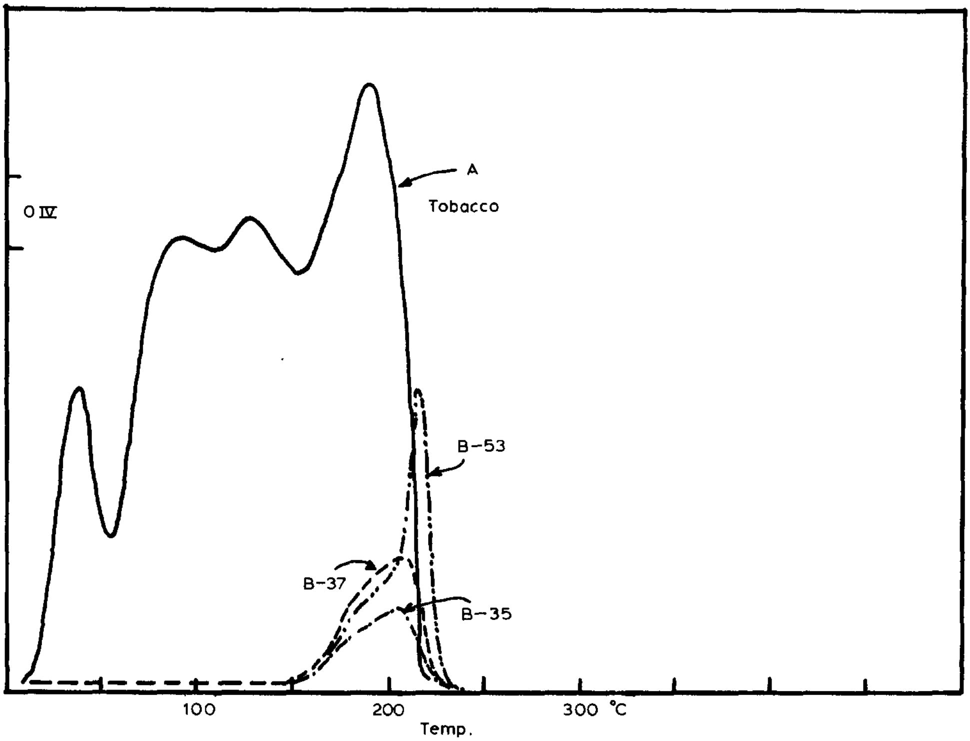

Fig. 10. TVD curves of miscellaneous substances. A, Tobacco; B-35–B-53, coal samples (apparatus I).

Miscellaneous substances

The TVD curves of three coal samples are shown in Fig. 10. The three curves, with peak maxima in the temperature range 210–220°C, are for coal samples with widely different volatile matter, BTU/lb, and carbon and oxygen contents. Sample 53 is for a low volatile matter content (30%), high BTU/lb (15 810), and high carbon content (88.5%). Sample 35 is a high volatile matter (42%), low BTU/lb (13 560) and low carbon content (76.5%) coal. However, the differences between samples 35 and 37 are not that great compared to sample 53.

The TVD curve for tobacco reveals a number of maxima and minima in the temperature range from room temperature to about 200°C. These result from the evolution of water and other volatiles from the tobacco and may be useful in differentiating the various grades of tobacco. However, it is not possible to interpret their origin or correlate them with the composition of tobacco at this time.

The last TVD curve of this series is for two liquid samples, as shown in Fig. 11. These two samples, water and ethanol (95%), were placed on glass

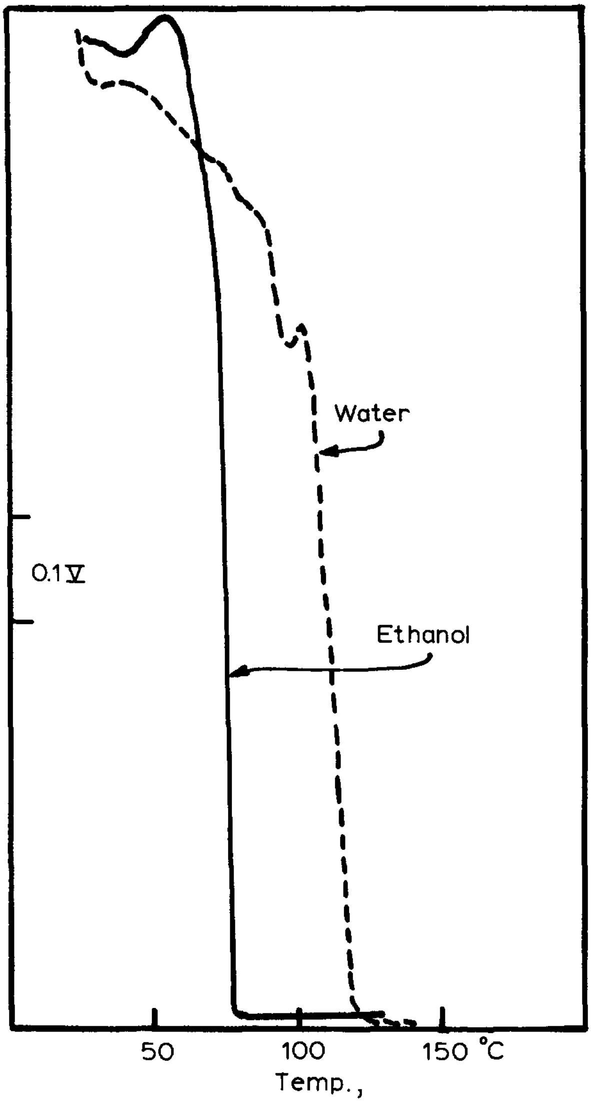

Fig. 11. TVD curves of miscellaneous substances. Sample holder Fig. 1C.

micro-beads contained on the Fig. 2C sample holder. The curves start out at an EMF maxima and as the liquids vaporize, the EMF decreases to a value of zero. Ethanol, due to its lower boiling point, has a curve which falls off to 0 V at a lower temperature than water. Thus, it should be possible to distinguish qualitatively liquids with different boiling points.

ACKNOWLEDGEMENT

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