

# A Technique for the Analysis of Trace Amounts of Volatile Products from Polymer Degradations

W. J. MCGILL, L. PAYNE, and J. FOURIE, *Department of Materials Science, University of Port Elizabeth, Port Elizabeth, South Africa*

## Synopsis

A technique for the qualitative and quantitative analysis of trace amounts (0, 1 mg) of liquid nitrogen-condensable volatiles produced during polymer degradation is described. Products trapped at liquid nitrogen temperature at  $10^{-5}$  torr are slowly distilled into a second trap as a result of the gradual warm-up of the first trap. Pressure changes accompanying distillation are detected by a Pirani gauge and are used to characterize individual degradation products following calibration of the system using reference liquids. Quantitative analysis is achieved by fractionation of the products and measurement of the total pressure exerted by each component on complete vaporization in a closed system. Variables influencing the sensitivity of the technique are examined.

## INTRODUCTION

The evolution of volatile products during the degradation of a polymer is accompanied by changes in the polymer residue which may lead to the production of new volatile species as the reaction progresses. Thermal volatilization analysis<sup>1</sup> curves of polymeric systems illustrates these changes most pertinently. After a certain amount of degradation has taken place, the degrading material is no longer identical to the original polymer. For studies of the initial stages of degradation, and in particular in photolysis studies where the volume of products may be very small, a sensitive analysis technique for volatiles is required. In an earlier paper<sup>2</sup> we briefly described a distillation technique for the qualitative and quantitative analysis of trace amounts of liquid nitrogen-condensable products on polymer degradation. This technique has been used in various degradation studies in our laboratories, and we here report a more detailed study of the technique itself and various factors which influence the sensitivity of the analysis.

## EXPERIMENTAL

The experimental system used was modified a number of times during the study to allow the effects of various parameters to be examined but the essential elements of the all-glass system are shown in Figure 1. For vacuum photolysis or thermolysis a suitable degradation cell would be connected to the left of stopcock S1 and the whole system evacuated. In this study a small droplet (0.3  $\mu$ l) of the test component or a mixture of components was placed in a 20-ml bulb attached to the left-hand side of S1. The system to the right of S1 was evacuated to a pressure of  $10^{-5}$  torr, trap T2 was cooled to liquid nitrogen temperature, and S1 slowly opened. Once the test droplet had been transferred to T2, trap T1 was cooled to liquid nitrogen temperature. The inner glass tube around this trap

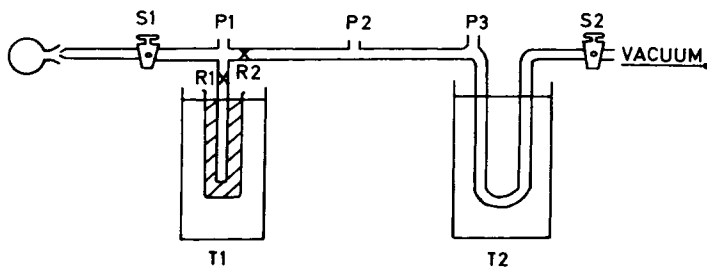


Fig. 1. Sketch of apparatus used.

contained benzene and the outer Dewar, liquid nitrogen. (Pentane, petroleum ether, or any other suitable liquid may be used provided its time-temperature curve on warm-up is smooth in the regions where the different products are detected.) Stopcocks S1 and S2 were closed and the liquid nitrogen Dewar around T2 removed, allowing the volatiles to distil rapidly into T1. Once the pressure had returned to  $10^{-5}$  torr, indicating that all of the volatiles had been transferred to T1, T2 was recooled to liquid nitrogen temperature. The components were now distilled slowly from T1 to T2 by removing the liquid nitrogen Dewar from T1 and allowing to benzene trap to warm up gradually. A Pirani gauge at position P1, P2, or P3 was used to monitor pressure changes in the system during distillation while the temperature in T1 was recorded from thermocouple readings. Since the system warmed up at a reproducible rate, pressure curves obtained during distillation could be plotted against temperature or time.

## RESULTS AND DISCUSSION

The solid line in Figure 2 depicts a typical pressure-time curve for Pirani P1 obtained during the distillation of  $0.3 \mu\text{l}$  acetone. The first small peak was due to  $\text{CO}_2$  and the last, to  $\text{H}_2\text{O}$  present in the air in the sample bulb. The middle peak corresponds to the distillation of acetone between the two cold traps.

Distillations using Pirani gauges in positions P1, P2, and P3 simultaneously showed that the best resolution of peaks was achieved with the Pirani gauge

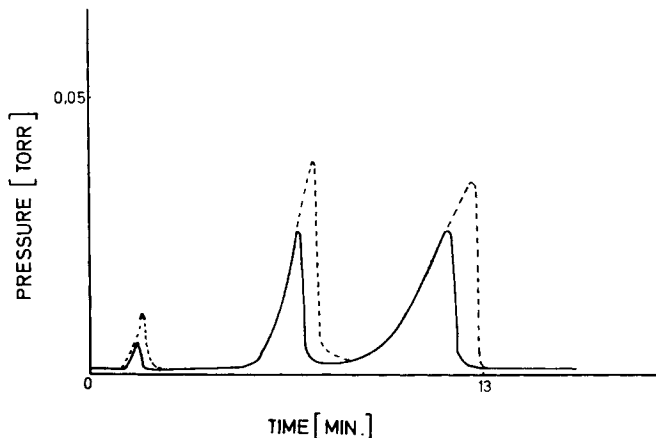


Fig. 2. Pressure-time distillation curve for a  $\text{CH}_3\text{COCH}_3$  sample showing  $\text{CO}_2$  and  $\text{H}_2\text{O}$  peaks. Dotted line shows shift in peaks for larger amounts of components.

positioned as close to trap T1 as possible. The closer the gauge is placed to the condensing trap T2, the smaller and more rounded were the different pressure peaks. This was not unexpected since there must be a pressure gradient between T1 and T2 for volatiles to diffuse across, and maximum pressures would therefore be recorded at T1. It was found that opening the system to the vacuum pumps during distillation facilitated transfer from T1 to T2, thus sharpening pressure peaks, enabling better separation to be achieved between components with closely similar boiling points, and improving the low-pressure baseline between peaks. When two components distilled at closely similar temperatures, the pressure did not return to  $10^{-5}$  torr between peak maxima; and when such closely boiling liquids were present in greatly differing proportions, one component appeared as a shoulder to the greater product peak. Poor baselines were also found when the volume of volatiles in the system was large ( $>10^{-5}$  mole).

The effect of restrictions at positions R1 and R2 before and after Pirani P1 in Figure 1 were studied. A restriction after the Pirani would impede diffusion to T2 and increase the pressure recorded. This slightly increased pressure, it was hoped, would retard evaporation of the next lowest boiling component, but it did not enable better peak separation to be obtained, and instead the peaks of two closely boiling components were merged rather than resolved. A restriction at R1 ahead of the Pirani likewise retarded diffusion and lead to smaller and less symmetrical peaks (Fig. 3). Similarly, when the diameter of trap T1 was smaller than that of the interconnecting tubing, diffusion from this narrow zone was impeded and some resolution of smaller peaks was lost. A 5-mm diameter trap connected to a 10-mm diameter system gave very poor results. Within limits the diameter of the tubing used to construct the system was not found to be important, provided it was of uniform diameter throughout. Systems using 5 and 10-mm internal diameter tubing gave equally good results when

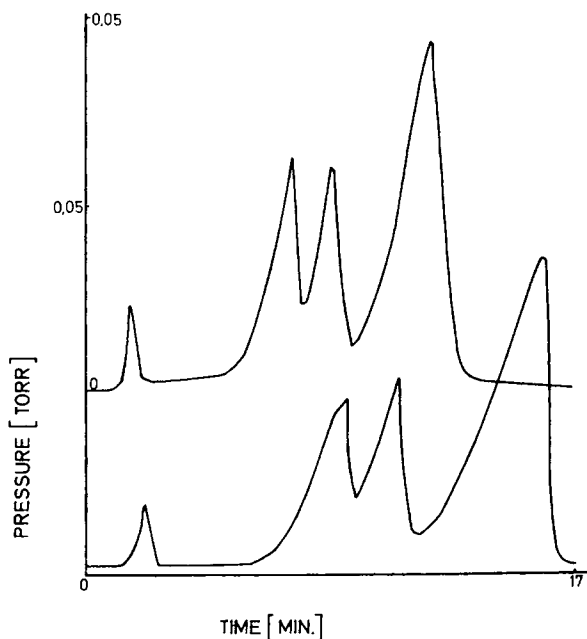


Fig. 3. Pressure-time distillation curve for  $\text{CO}_2$ ,  $\text{CH}_3\text{COCH}_3$ ,  $\text{C}_6\text{H}_6$ , and  $\text{H}_2\text{O}$  with (lower) and without (upper) a restriction at position R1.

vapors were allowed easy access to the Pirani gauge. It was found best to connect the Pirani to the system with slightly wider bore tubing than used for the rest of the system.

For a given amount of vapor, the height of the distillation peaks and their separation were determined by the rate at which the cold trap T1 warmed up. This rate can be varied by changing the diameter of the tube containing frozen benzene. Very slow warm-up resulted in well-separated peaks with small peak heights, while fast distillation gave poor resolution. This can be seen from the curves in Figure 4, which were obtained by distilling a particular sample repeatedly using different heating rates. A benzene tube of diameter 30 mm around a 10-mm external diameter trap was found to yield a satisfactory compromise between these two extremes. These measurements should be regarded as a guide only since the absolute as well as the relative amounts of products and the differences in their boiling points are important in obtaining a satisfactory distillation curve. Minor components may remain undetected or appear as small bumps only in a very slow distillation.

The resolution of distillation peaks was better when products were transferred from T2 to T1 before distillation than when they were collected directly into T1 as they were formed. (The procedure of first trapping in a U-tube also allowed the pumps to be operated during degradation studies which assisted both in drawing products from the degradation zone before they could undergo secondary reactions and helped maintain a good vacuum in the degradation chamber.) T1 need not be a cold finger but could be a U-tube if desired; but when a U-tube is used, it is important that the products, on distillation, move out of the trap in the reverse direction to which they entered, i.e., products must not be required to move through the U. Volatiles condense near the top of the cold trap, and a ring of condensed products can clearly be seen when a liquid nitrogen Dewar is rapidly removed from a trap. If the system is so designed that volatiles are required to move through the U-tube during distillation, some vapor would move

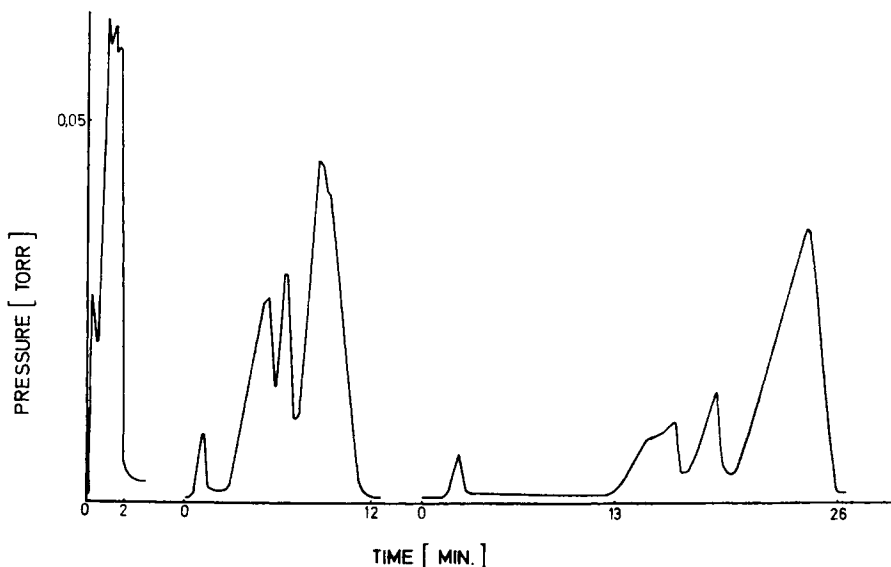


Fig. 4. Pressure-time distillation curves for  $\text{CO}_2$ ,  $\text{CH}_3\text{COCH}_3$ ,  $\text{C}_6\text{H}_6$ , and  $\text{H}_2\text{O}$  at different heating rates.

into the space directly above the trap while the remainder would diffuse through the trap. Only when the pressure started to drop would the vapor above the U-tube be drawn through the trap. Rather broad distillation peaks were obtained with such a system (Fig. 5).

### Qualitative Analysis

By counting the peaks on the distillation curve, one can very rapidly establish the minimum number of liquid nitrogen-condensable volatile products produced in a degradation. In a previous paper<sup>2</sup> we indicated how a qualitative identification of products corresponding to the different peaks could readily be achieved and have more recently improved on the technique. Since the rate at which the cold trap warmed up was reproducible, peak positions were reproducible and constituted a basis for product identification. The times and temperatures at which pressure peaks occurred for different components, expected as degradation products, were obtained when small amounts of such compounds were distilled individually and as mixtures. Mixtures were retained in the cold trap for slightly longer times (30–60 sec) than pure components, and the times before the peak maximum was reached showed a slight increase when larger amounts of test compounds were used (Fig. 2). When two product peaks appear very close together, positive identification using the above procedure may at times be difficult due to these slight shifts in the position of the peak maxima. This problem has recently been overcome by introducing a very small amount of the particular pure standard compound into the system containing the degradation products and comparing the distillation curves before and after the addition. If the peak in question showed a slight increase identification was correct while the development of a shoulder to the peak indicated incorrect identification. This is clearly illustrated in Figure 6, which shows changes in a  $\text{H}_2\text{O}$  peak on addition of  $\text{H}_2\text{O}$  and  $\text{HCOOH}$  (bp  $100.8^\circ\text{C}$ ), respectively. The peak shifted slightly on addition

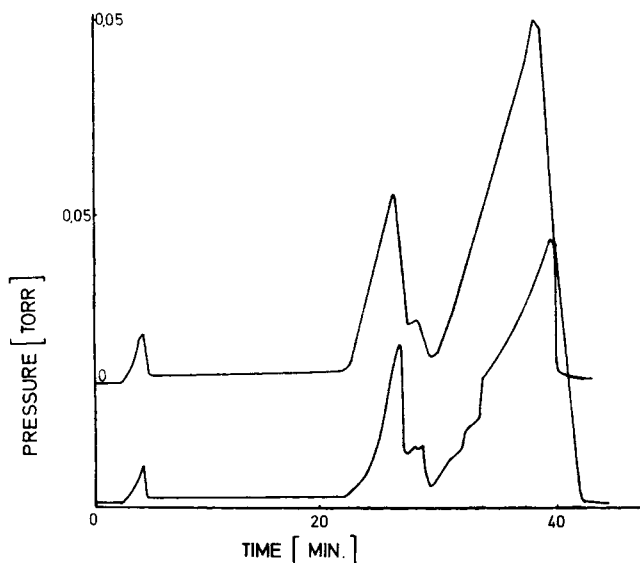


Fig. 5. Pressure-time distillation curves for  $\text{CO}_2$ ,  $\text{CH}_3\text{COCH}_3$ , and  $\text{H}_2\text{O}$  from finger trap (upper) and through U-tube (lower).

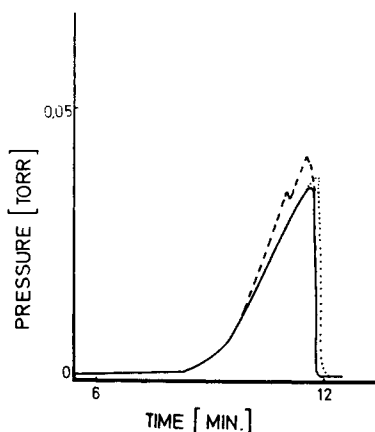


Fig. 6. Identification of components with closely similar boiling points; (—)  $\text{H}_2\text{O}$  "unknown"; (···) shift on addition of more  $\text{H}_2\text{O}$ ; (---) shoulder developed on addition of  $\text{HCOOH}$ .

of  $\text{H}_2\text{O}$ , while the addition of  $\text{HCOOH}$  lead to the development of a shoulder to the peak.

The introduction of trace amounts of standard compounds into the system already containing degradation products was done using a small (5 ml) bulb attached to the position occupied by Pirani P2 in Figure 1. Approximately  $0.1 \mu\text{l}$  of the component was first placed in the bulb using a microsyringe which was touched to the walls to dislodge the droplet. Degradation products were held in the cold trap and the bulb was opened to the system to allow the component to be vaporized and to be drawn into the system. (The  $\text{CO}_2$  and  $\text{H}_2\text{O}$  peaks also grow due to the air in the bulb and can be reduced with a smaller bulb.)

### Quantitative Analysis

Provided the different pressure peaks are sufficiently well resolved, a quantitative estimate of the amount of each component can be made. A wide-bore stopcock is required at position R1 in Figure 1. This stopcock was closed after distillation of each component, and trap T1 was immediately recooled with liquid nitrogen. Stopcock S2 was closed and the component, trapped in T2, allowed to evaporate by removal of the liquid nitrogen Dewar. Once the system had attained room temperature, the pressure of the component was measured on the Pirani gauge. The component was then pumped out and the next component was fractionated and its pressure measured.

Instant recooling of trap T1 after distillation of each component was found to be essential to prevent partial evaporation of the next-higher boiling component. Delayed recooling presumably caused an evaporated component to condense at a different position in the trap since the shape of the subsequent distillation curve was altered and made it difficult to know where to cut the next peak.

Qualitative analyses were most sensitive when the volume of the system was small, while quantitative analyses required a larger volume if the Pirani gauge was to be used in its most sensitive pressure region. This was achieved by attaching a 1-liter flask to the system via a stopcock at position P3 in Figure 1.

The pressure as indicated by a Pirani gauge should be calibrated for each gas

used. However, the condensible hydrocarbons produced on polymer degradation have approximately similar thermal conductivities, and tests, using a variety of mixtures of known composition, showed that qualitative analyses conducted as described here were accurate to within 8% in all cases.

### Sensitivity

The technique is best suited to the detection and analysis of  $10^{-6}$  mole (0.1 mg) of product vapors in a qualitative system of volume 50 ml and a quantitative system of volume 1000 ml. This corresponds to 0.05% degradation when using 200-mg polymer films.

In view of the high sensitivity of the technique which is designed to analyse for trace amounts of degradation products, the use of absolutely dry films is essential. Residual solvent in solution-cast films will yield solvent peaks which may obscure peaks due to products having closely similar boiling points.

### Degradation in Oxygen Atmospheres

This technique can also be applied to the analysis of volatile products formed during degradation studies in oxygen atmospheres, provided oxygen pressures are a few centimeters below atmospheric pressure when oxygen will not condense in the liquid nitrogen traps. Degradation is done in a closed system, the volatiles are trapped, and the oxygen is pumped out before analysis.

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### References

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