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Combined pyrolysis and radiochemical gas chromatography
for studying the thermal degradation of polymers

- by -

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Synopsis

Pyrolysis gas chromatography and radioactive tracer techniques have been used independently to study the thermal degradation of polymers. In these laboratories the two techniques have been combined to elucidate some of the mechanisms of the thermal degradation of epoxy resins and polyimides. This paper describes the apparatus developed for this work.



Introduction

Pyrolysis gas chromatography has become one of the most extensively used techniques for investigating the thermal breakdown of organic compounds. It has proved particularly useful for studying the mechanisms of polymer degradation, especially in those cases where the pyrolysis products are simply related to the original structure of the polymer.

When complex polymers, such as cured phenolic or epoxy resins, are pyrolysed large numbers of degradation products are formed which are not simply related to the original structure (1)(2)(3). Chromatographic separation of these products gives a characteristic pyrogram for each polymer. These 'finger print' pyrograms may be used for polymer identification, but they are of limited value in determining the mechanisms of thermal breakdown because although the components of each pyrogram can be identified, it is not often possible to say how they were formed.

Radioactive tracer techniques have a unique advantage in that specific atoms or groups in complex molecules can be labelled, and hence their fate through any number of operations can be followed. This facility is obviously useful for following degradation processes and has been exploited in a number of polymer degradation (4)-(7) and stabilisation (8)(9) studies.

In these laboratories the thermal degradation of cured epoxy resins (2)(10)(11)(12) and polyimides has been studied. The use

of pyrolysis gas chromatography alone made it possible to postulate degradation mechanisms for these polymers, and it was considered that isotopic techniques would provide conclusive evidence for some of the mechanisms. Consequently an attempt has been made to combine the two techniques to form a continuous and quantitative pyrolysis gas chromatography and radiochemical analysis system. This system is described below; details of the polymer degradation work will appear in future publications.

The pyrolysis gas chromatography unit

Pyrolysis gas chromatography techniques have been comprehensively reviewed by Levy (13)(14) and need no further discussion here. The pyrolysis unit used for the present work consisted of an electrically heated nichrome filament housed in a pyrex glass tube (2)(10). This tube was built into a Perkin Elmer 452 gas chromatograph so that degradation products that were volatile at the chromatograph oven temperature were swept into the column and separated.

Pyrolysis temperatures were obtained using a chromel/alumel thermocouple attached to the mid point of the filament. The filament temperature was correlated with the supply voltage for various carrier gas flow rates and oven temperatures.

The gas chromatograph was fitted with a thermal conductivity detector, and since nitrogen was used as the carrier gas throughout this work positive and negative peaks appear on the pyrograms. (Figs. 4 and 5).

Detection of radioactive compounds in the gas chromatograph effluent

(a) Discussion of methods

In order to determine the fate of labelled atoms when a sample of labelled polymer is pyrolysed it is necessary to monitor the various breakdown products for radioactivity. The 'char' and tar like products which remain in the pyrolysis tube may be analysed by conventional liquid scintillation counting techniques, but the volatile products which emerge from the gas chromatograph are more difficult to analyse.

The methods available for detecting and measuring radioactivity in the effluent of a gas chromatograph have been reviewed by Karmen (15). They may be divided into two main types; continuous methods in which radioactivity is detected and measured in the gas stream, and discontinuous or two stage methods in which the labelled compounds are condensed in a scintillator solution (or on scintillator crystals) and counted by conventional counting techniques.

The continuous methods have the advantages of speed and convenience, but the time taken for an active compound to pass through the detector must be limited in order to preserve the resolution of the various compounds. It is therefore impossible to count low levels of activity with accuracy when using continuous techniques.

The tendency for high boiling compounds to condense in the

detector may be overcome by either using a heated detector cell, or, if only ^{14}C and ^3H are to be detected, by burning all organic compounds to CO_2 and H_2 (and $^{14}\text{CO}_2$ and $^3\text{H}_2$).

Heated proportional counters have been designed to operate at temperatures up to 200°C but the problem of adsorption of polar compounds onto the detector walls has not been satisfactorily overcome. Crystal scintillation detectors may be used at reasonably high temperatures. Anthracene for example melts at 216°C and presumably may be used at temperatures up to about 200°C , but the heated cell must be separated from the photomultiplier tube with a cooled light pipe in order to keep the thermionic noise from the tube at a low level.

Combustion of organic compounds to CO_2 and H_2 is easily achieved by passing them first over copper oxide heated to 700°C and then over iron filings or steel wool also at 700°C . The reaction with copper oxide gives CO_2 and H_2O , and the reaction with iron converts H_2O to H_2 . The ferric oxide formed in the latter reaction strongly absorbs water and it is necessary to keep the iron reduced by introducing hydrogen into the gas stream, (16). Combustion is not suitable when isotopes other than ^{14}C and ^3H are to be detected; halogen acids for example are retained by copper oxide and labelled halogens would therefore be undetected.

In polymer degradation work it is desirable to collect the volatile breakdown products for characterisation. If radioactivity is measured using a two stage method the breakdown products are retained in solution or adsorbed on crystals and can not be

characterised easily. If a continuous technique with combustion is used the products are destroyed.

This difficulty may be overcome by using a stream splitter, but when a stream splitter is used only a small percentage of the effluent may be taken for fractionation because otherwise the level of activity reaching the detector becomes too low for accurate measurement. This may mean that insufficient material is available for identification of minor degradation products and the alternatives of increasing sample size or increasing the specific activity of the sample must be considered. This problem is less acute if a two stage method is used because here the counting time is unlimited and low activity samples can be counted with accuracy. A larger proportion of the gas stream may therefore be split off for characterisation. The main disadvantage of a two stage method is that every product must be collected and counted separately; a tedious and time consuming operation unless an automatic fraction collector and a scintillation counter with an automatic sample changer is available.

(b) Description of the scintillation detector

The apparatus developed for the present work was intended to be used as a flow through scintillation counter with or without a combustion train. It was constructed so that the flow cell could be removed easily and the unit used as a conventional scintillation counter. The following description refers to FIG. 1.

The detector unit was a modified Nuclear Enterprises NE5504

shielded scintillation head unit. A water cooled quartz light pipe (A) was fitted between the flow cell (B) and the face of the photomultiplier tube (C) so that the photomultiplier remained at constant room temperature while the flow cell was heated to prevent the condensation of organic compounds.

The flow cell consisted of a pyrex glass spiral (30 cm. of 0.3 cm. I.D. tubing) loosely packed with scintillation grade anthracene crystals (m.p. 216°C). A plane mirror (D) was mounted above the spiral to reflect scintillations occurring near the top surface of the spiral into the light pipe and thence to the photomultiplier tube. A highly polished brass collar (E) surrounded the spiral and mirror, and the enclosure thus formed was filled with an optically clear grade of silicone oil (F). The function of the oil was to make optical contact between the glass spiral and the light pipe, and also to make thermal contact between the brass collar and the spiral. The brass collar was heated by the heating coil (G). The temperature of the flow cell was recorded using a chromel/alumel thermocouple (H) dipping into the silicone oil.

This system detected ^{14}C labelled compounds with about 20% efficiency and there was no tendency for active material to be retained in the flow cell. When the cell was operated at temperatures above about 80°C however the cooling system was inadequate and the photomultiplier gave excessive noise as it became warm. Consequently when high boiling compounds were being separated a combustion train was placed between the gas chromatograph and the scintillation detector.

In order to use the detector as a conventional liquid scintillation counter the flow cell, mirror, and thermocouple were lifted out and replaced by a 12 ml. glass counting bottle containing the sample to be counted. Counting was found to be about 65% efficient using 0.5% butyl P.B.D. in redistilled A.R. toluene as the liquid scintillator. Efficiencies approaching 100% may normally be expected with this scintillator and the low efficiency of the present system may be attributed to light loss in the quartz light pipe.

The integrator unit

The integrator unit was designed to drive a chart recorder with the events per second data obtained from the photomultiplier tube, and to integrate each radioactive peak and display the total count digitally. The following description of the system refers to FIG. 2.

Pulses from the photomultiplier tube (caused by scintillations in the flow cell) are amplified and fed via the 'UP' gate into the REVERSIBLE BINARY COUNTER. At the end of each 1 sec. period the count is transferred to STORE I which drives the CHART RECORDER via the DIGITAL TO ANALOGUE CONVERTER, producing a deflection proportional to the number of events in that 1 sec. period. This reading is held until STORE I is set to the count for the next 1 sec. period, thus a histogram type record is produced on the chart.

At the same time as STORE I is loaded (i.e. at the end of a 1 sec. period) the UP/DOWN STORE is set to 'down'. This isolates

the counter from the data source and connects it to CLOCK I, which causes the counter to count down towards zero at 10^6 pulses per second. When zero is detected the UP/DOWN STORE is set to 'up' and the next counting period begins. The capacity of the counter is 255 so the maximum time for reset is 0.25 millisecon., giving a negligible error in the 1 sec. gating periods.

Since the number of pulses required to bring the counter back to zero equals the number reached when counting data pulses, there is at the output of the DOWN GATE, during the resetting phase, a train of that number of pulses. This is used to drive the DECIMAL COUNTER via the INTEGRATE GATE which is controlled by the THRESHOLD DETECTOR. If the preset threshold (background count) is reached or passed by the data count the reset pulse train is fed into the DECIMAL COUNTER and added to the number already there, but if the threshold is not reached the reset pulse train does not enter the DECIMAL COUNTER.

During a radioactive chromatogram peak the threshold is reached during every data count and the count total accumulates in the decimal counter. When at the end of the peak the threshold is not reached the DISPLAY CONTROL is armed and the INTEGRATE GATE is closed. The DISPLAY CONTROL causes STORE 2 to hold the number reached by the decimal counter, and the counter is reset to zero ready for the next peak. The DIGITAL DISPLAY shows the number held in STORE 2. In this way the total count for each peak is displayed until the next total has been accumulated, and may be noted on the recorder chart or otherwise.

The effects of overflow in the two counters were considered and measures were taken to prevent the generation of wrong data. A signal is produced if the REVERSIBLE COUNTER reaches full scale which isolates the counter input thus storing full scale in the counter. At the end of the 1 sec. period this count is transferred in the normal way to STORE I producing full scale deflection on the chart recorder. In addition a warning light shows that an overflow has occurred.

An overflow in the DECIMAL COUNTER produces a carry signal which sets a store so connected that when the count next reaches 8000 the input is isolated locking the counter at that number. When the display is set a warning light is also set if an overflow has occurred. The display was therefore interpreted as follows:

<u>Display</u>	<u>Overflow</u>	<u>True Count</u>
< 9999	No	As display
< 8000	Yes	As display + 10,000
8000	Yes	≥ 18,000

By interposing a suitable voltage to frequency converter between the input of this instrument and a chromatograph detector having a voltage output, the peak integration facility would be available for conventional gas chromatography. The complete pyrolysis radio gas chromatograph is shown in FIG. 3

Results

The apparatus has been used in a study of the pyrolytic

degradation of epoxy resins and polyimides. Details of this work will appear in separate publications but FIGS. 4 and 5 show some 'pyrograms' and 'radiopyrograms' obtained on pyrolysis of the diglycidyl ether of bisphenol A (DGEBA) cured with phthalic anhydride (PA). The resin was ^{14}C labelled at the 1,3 atoms of the glycidyl groups (FIG. 6).

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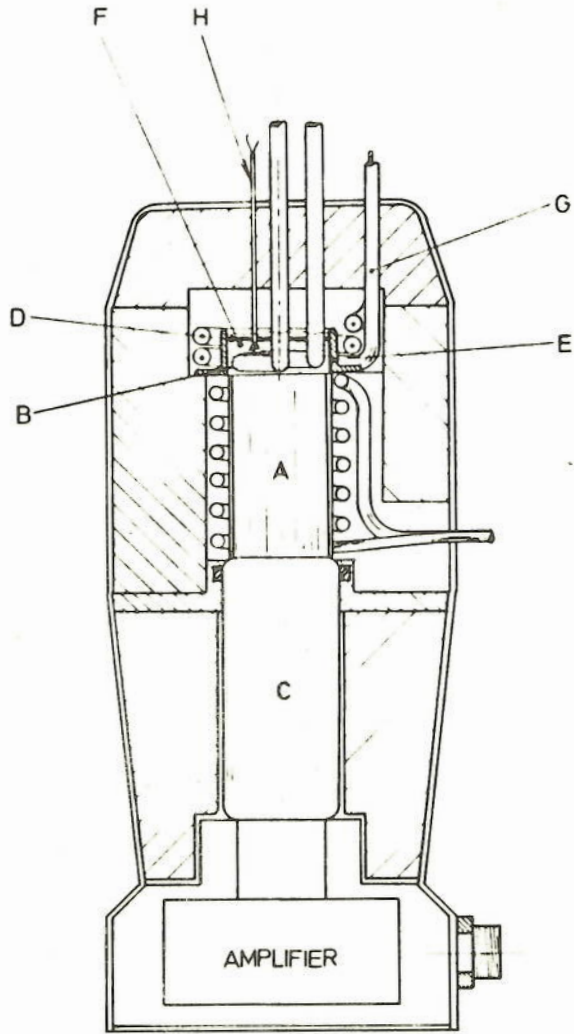


FIG. 1 The scintillation detector unit

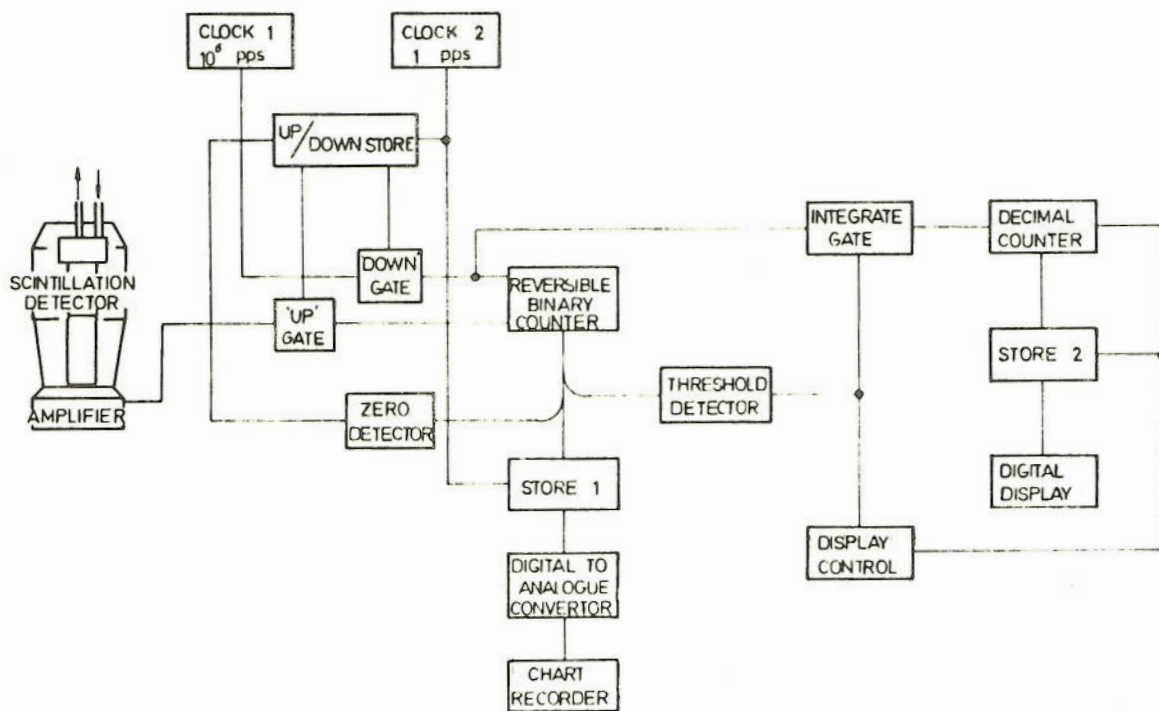


FIG. 2 Block diagram of the integrator and display unit

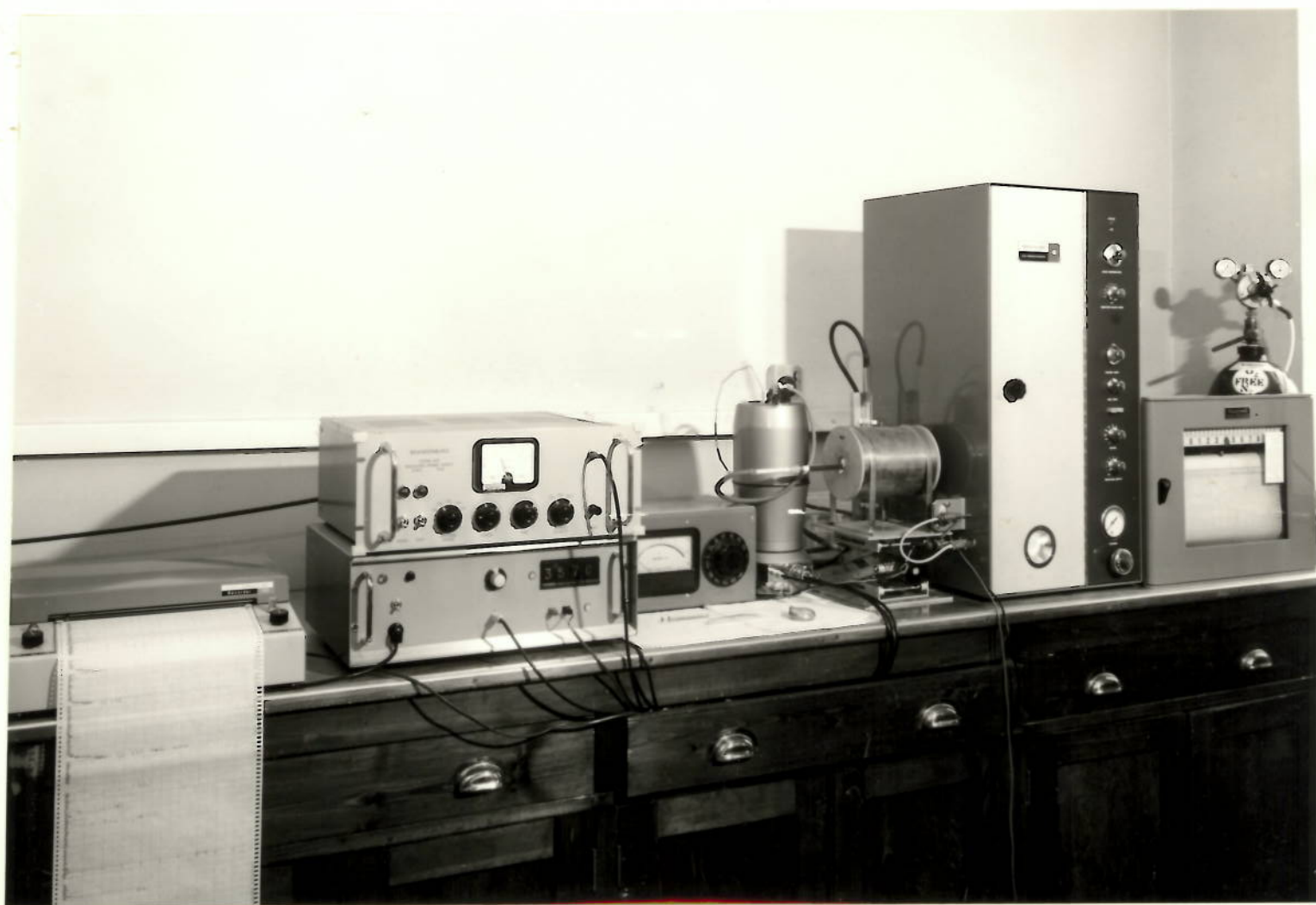


FIGURE 3 The combined pyrolysis gas chromatography and radiochemical analysis apparatus (with combustion train).

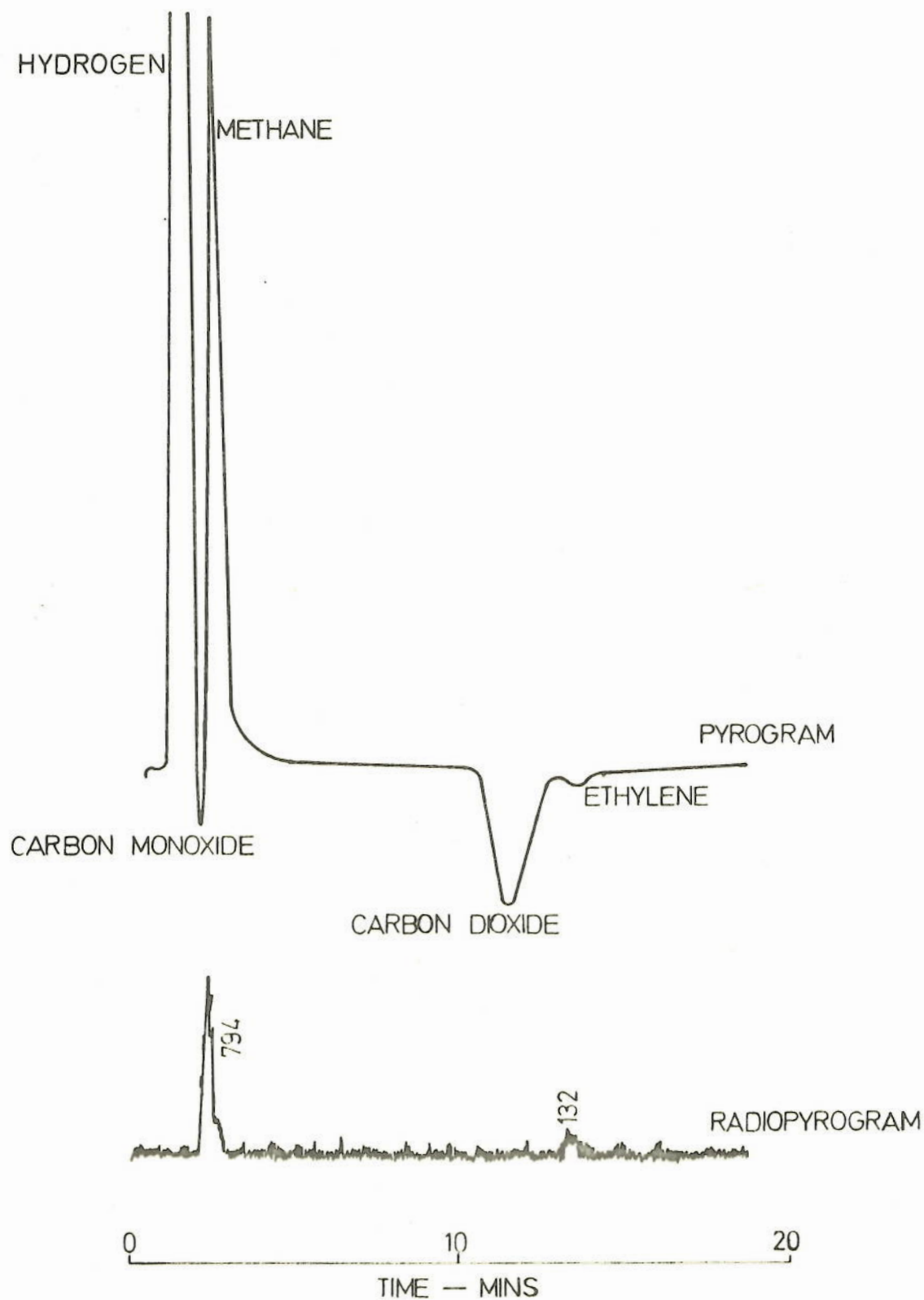


FIG. 4 Separation of gaseous degradation products from DGEBCPA (^{14}C 1,3-glycidyl)/PA (20 mg). Pyrolysis temp.: 700°C . Column: 30-60 mesh silica gel. Oven temp.: 50°C . Carrier gas: Nitrogen, 20 ml./min.

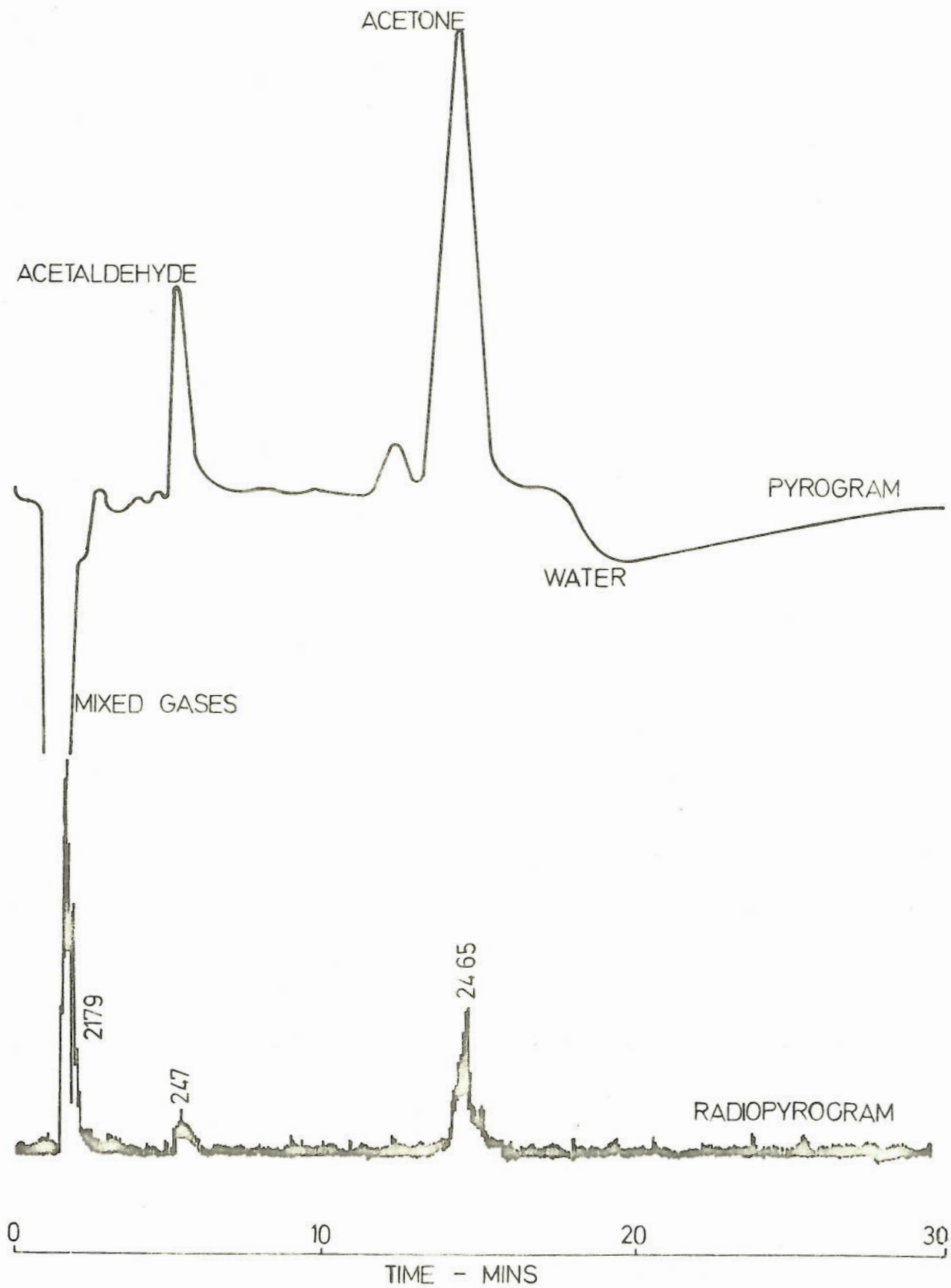


FIG. 5 Separation of low boiling degradation products from DGEBA (^{14}C 1,3-glycidyl)/PA. (50 mg.) Pyrolysis temp. : 700°C .
 Column: 7,8 benzoquinoline/60-80 mesh Chromosorb P, 15/85.
 Oven temp. : 50°C . Carrier gas: Nitrogen, 20 ml./min.

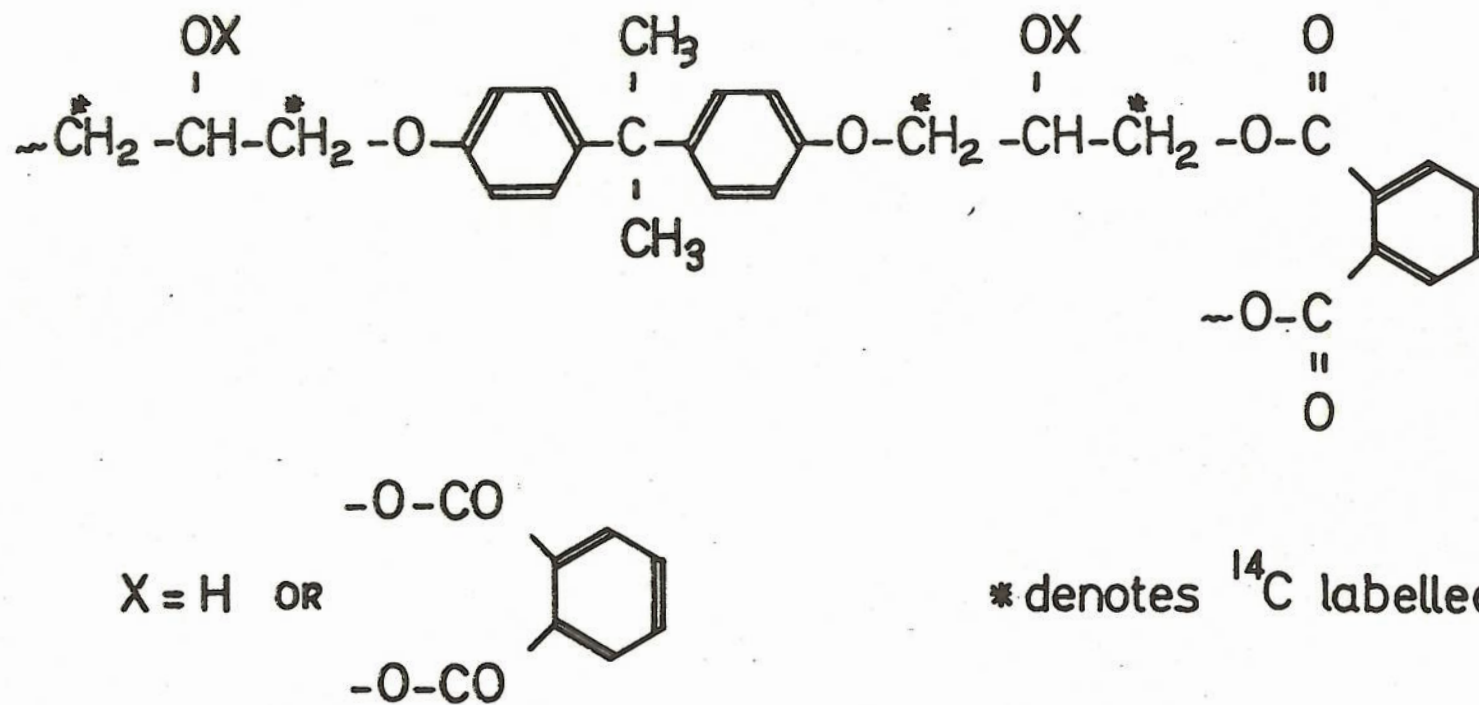


FIG. 6 Structure of DGEBA (^{14}C 1,3-glycidyl)/PA.