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PYROLYSIS-GAS CHROMATOGRAPHY OF SEPARATED ZONES ON THIN-LAYER CHROMATOGRAMS

I. APPARATUS AND METHOD

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SUMMARY

An apparatus is described for the pyrolysis-gas chromatographic determination of amounts of substances in the approximate range 0.1–10 μg . It consists of a tubular, externally wound, electric furnace attached to the column of a gas chromatograph at one end and fitted with a sampling port and carrier gas entry tube at the other. Although primarily intended for the determination of substances separated by thin-layer chromatography without removal from the substrate, with minor changes to the entry port and furnace hot-zone, samples in liquid form can also be accommodated. The apparatus was tested using poly(vinyl chloride) and partially hydrolysed poly(vinyl acetate).

INTRODUCTION

Among the separation techniques available to the chemist, thin-layer chromatography (TLC) is one of the most versatile and inexpensive in terms of financial outlay on equipment. The versatility is reflected in the range of sample size accommodated, for example, relative to paper chromatography, linear (one- or two-dimensional) and radial development of chromatograms, ease of location of separated zones and wide ranges of stationary and mobile phases available. However, quantitative determination of a component separated by TLC is less convenient than in gas-liquid or liquid-liquid chromatography. Existing measurement techniques applied to thin-layer chromatograms are generally less sensitive and frequently less accurate than those available in gas-liquid or liquid-liquid chromatography¹.

Pyrolysis-gas chromatography (Py-GC), initially applied largely to the study of the thermal degradation of polymers, has, more recently, been extended to the determination of a variety of substances. Where applicable, it offers a rapid and sensitive route to an analytical determination². In an attempt to extend the range of techniques available for quantitative measurement of separated zones on thin-layer chromatograms, work has been carried out on the application of Py-GC to such determinations. The separated zone, after location, is cut, along with its portion of

backing plate, from the dried, developed chromatogram and transferred to the pyrolysis chamber. Pyrolysis products are swept by the carrier gas into the gas chromatograph for separation and to complete the determination. A furnace, meeting specifications determined by the properties of the samples to be pyrolysed and convenience of operation, was designed and tested; it is described here along with ancillary equipment and validation experiments using poly(vinyl chloride) (PVC) and partly hydrolysed poly(vinyl acetate) (PVA) as test substances.

EXPERIMENTAL

The apparatus, as developed, consists of a tubular electric furnace attached at one end to a gas chromatograph. The other end has facilities for sample introduction and entry of the carrier gas.

Furnace

A scale diagram of the furnace is presented in Fig. 1. It consists of a quartz tube, 15 cm \times 0.95 cm O.D. \times 0.70 cm I.D. At one end it is fused to a small bore (0.15 cm I.D.) thick-walled quartz tube for connection to the GC column. The other end of the furnace tube is closed by a sampling port and carrier gas entry unit (Fig. 2a). The furnace and tube connecting it to the top of the GC column are heated by an externally wound heating filament consisting of a 2-m length of Vacrom ribbon (0.15-cm wide) having an electrical resistance of $10 \Omega \text{ m}^{-1}$ at ambient temperature. The number of turnings, per unit length of tube, is arranged so that the furnace hot-zone with 3.5 turns cm^{-1} is located between 10.5 and 12.5 cm from the entrance end of the quartz tube. The heating element, which is heavily lagged on the outside with asbestos cord, is energised by a variable-voltage (0 to 260 V, 5 A rating) a.c. Variac unit

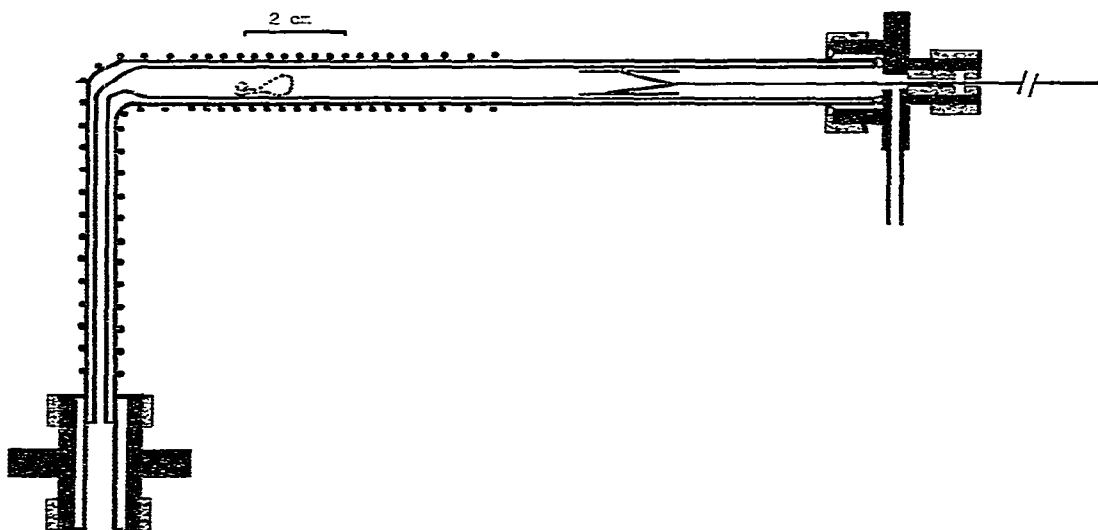


Fig. 1. Scale drawing of the furnace with push-rod arrangement for introduction of solid samples, sample entry and gas exit ports. The heat-insulating layer over the hot furnace winding has been omitted. The scale (2 cm) marking is positioned over the furnace hot-zone and the quartz obstructor (broken line) for injection of liquid samples.

supplied by the Zenith Electric Co. (London, Great Britain). Within the hot-zone the heating coil is capable of giving temperatures up to 1100°C . The temperature drop 1 cm distance along the tube to either side of the centre of this zone is 7°C at 530°C . The heating time for a sample to reach 530°C is *ca.* 0.5 sec.

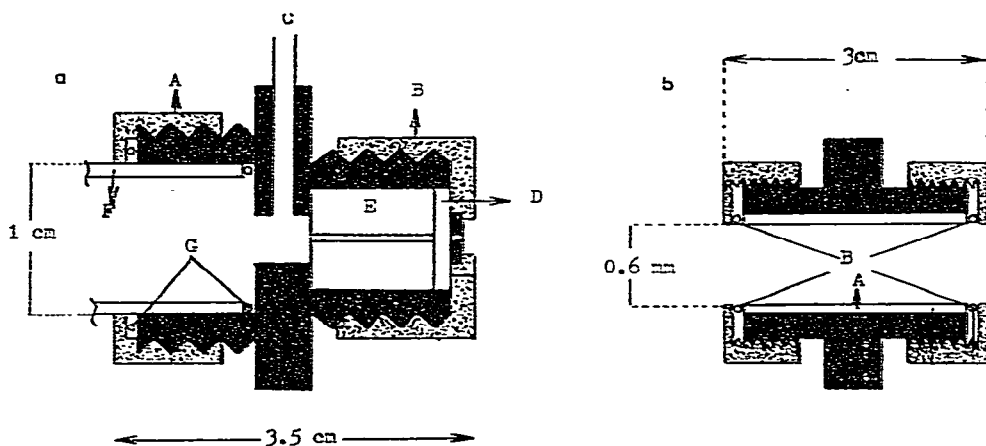


Fig. 2. (a) Entry port showing demountable nuts A and B, carrier gas inlet (2 mm I.D.) C, septum D, metal needle and push-rod guide E, furnace tube F and O-rings G. (b) Furnace coupling to GC column showing the teflon coupling A and positions of O-ring seals B. In (a) and (b) the nuts (speckled cross-section) and main bodies (mat black) of the couplings are all made from brass.

Sample introduction

Sample adsorbed on the detached portion of the thin-layer chromatogram or dried on small pieces of quartz plate are introduced into the furnace through a demountable entry port (Fig. 2a) and moved to the hot-zone by a push-rod. The push-rod is constructed from stainless-steel rod (20 cm \times 0.20 cm) to which is attached a piece of quartz tube (2 \times 0.60 cm O.D.). The attachment is made by means of a steel syringe needle bent to a V-shape and silver-soldered at its apex to the end of the rod. The end of one limb of the V is bent and passed into a small hole drilled in the inner quartz tube as shown in Fig. 1. The push-rod passes through a cylindrical metal guide and a septum at the entrance to the furnace. The entry port is shown in greater detail in Fig. 2a. It is constructed of brass with O-rings, and the septum is placed as shown to give gas-tight seals. The stainless-steel tube admitting the carrier gas is silver-soldered to the brass coupling. In order to introduce a solid sample, the entry port is detached and removed with the push-rod by undoing the nut at A, and the sample is placed inside the furnace tube in the cool zone. After replacement of the port and push-rod and waiting for 2.5 min for restoration of the baseline of the GC output signal, the sample is pushed to the centre of the furnace by the push-rod which is then immediately withdrawn to the cool zone. Liquid samples are introduced into the furnace using a Hamilton syringe. To facilitate the handling of such samples, the push-rod is removed and a new silicone rubber septum and a brass-cylinder having a narrower guide channel is inserted by uncoupling at B (Fig. 2a). The syringe needle is inserted through the septum and the contents are discharged 1 cm from the furnace centre. To prevent the discharged liquid from being propelled too rapidly through the

hot-zone to cooler regions down-stream before efficient pyrolysis can occur, a pear-shaped piece of quartz (broken line, Fig. 1) is inserted as an obstruction at the centre of the furnace. (This is not required when dealing with solid samples).

Gas chromatograph

The coupling between the pyrolyser unit and the top of the gas chromatographic column is shown in Figs. 1 and 2b. A Pye series 104 chromatograph fitted with a flame ionisation detector maintained at the column oven temperature and a glass column (160 × 0.35 cm I.D.) packed with Porapak Q (50–80 mesh), was used in the work described here. The carrier gas through the furnace and chromatograph was nitrogen at 50 ml/min controlled by a needle valve, flow restrictor and damping coil.

Standard solutions

PVC was dissolved in cyclohexanone to give solutions containing 875 ng/ μ l and 87.5 ng/ μ l. PVA was dissolved in water to give solutions containing 1.00 μ g/ μ l and 100 ng/ μ l.

Pyrolysis and measurement

A known volume of polymer solution was transferred on to the surface of a small square (0.5 × 0.5 cm) of quartz 0.1 cm in thickness and the solvent carefully removed by evaporation. The piece of quartz carrying the polymer sample was then introduced into the furnace, following the procedure for solid samples described above. The optimum temperature for pyrolysis of either polymer was 440°C in this furnace. The oven temperature for gas chromatography was set at 180°C.

RESULTS AND DISCUSSION

Considerable attention was given to the type of furnace to be used, particularly with regard to Py-GC of substances *in situ* on portions of thin-layer chromatograms. A Curie-point pyrolyser of conventional design was considered unsuitable because of the limitation on sample sizes. Various hot-filament devices were constructed and tested but their use revealed major problems. These related to support of the sample on the filament, large temperature gradients due to the nature of the heat source and expansion of the carrier gas during the heat-up period. The last-mentioned phenomenon was particularly serious because of its effect on the GC detector output signal. Other problems, related to the size and geometry of the pyrolysis chamber, gas leakage and deposition of sample debris in the chamber and connecting tubes, were also experienced. On the other hand, the externally heated tubular furnace resulted in relatively fast heat-up times for samples, particularly those on thin-layer substrate or other solid support. Problems relating to disruption of the carrier gas temperature and flow were overcome and good temperature control during pyrolysis was made possible. Furnaces of various dimensions were tested before selection of the version described here.

Typical pyrograms for PVC and PVA pyrolysed at 440°C in the hot-zone of the furnace under the conditions described are presented in Figs. 3 and 4, respectively. Pyrolysis products are known^{2,3} for these substances, and hence to relate peaks in the pyrogram to particular products it is only necessary to check retention times for GC.

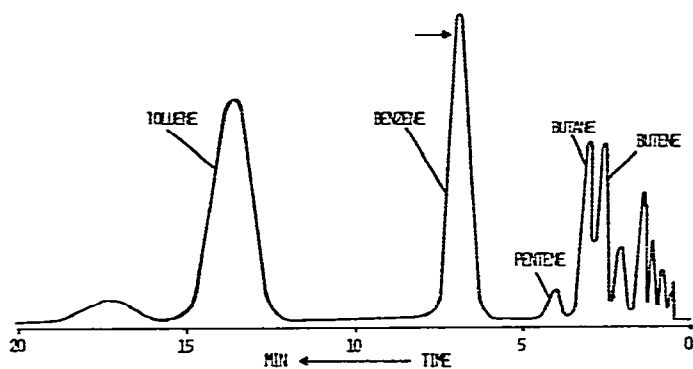


Fig. 3. Pyrogram for PVC showing the peak (marked by the arrow) on which the measurement was based.

In this way, the peaks attributed to particular substances have been identified (Figs. 3 and 4). Thus one or more well-resolved peaks in the pyrogram can be selected for use in quantitative analysis. When the peak(s) have been selected, the yield can be optimised by varying the temperature of pyrolysis. The amount of polymer pyrolysed is compared with peak height or area; in the present work the former was found to be adequate. The benzene and crotonaldehyde peaks were selected for the measurements on PVC and PVA, respectively, and relevant data are presented in Tables I and II. From the standard deviations obtained for replicate determinations, it is seen that reproducibility of results is good. This can be attributed in part to the small amounts of polymer pyrolysed in each experiment. The concentrations of reactive pyrolysis products are kept low as they enter the carrier gas stream. Towards the upper end of the sample ranges investigated (Tables I and II) there is some indication that the standard deviations increase somewhat with sample weight, and this is attributable,

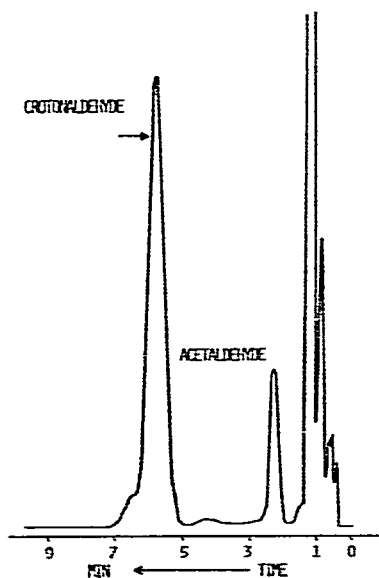


Fig. 4. Pyrogram for PVA showing the peak (marked by the arrow) on which the measurement was based.

TABLE I
PYROLYSIS OF PVC ON QUARTZ AT 440°C

Sample weight (ng)	Peak height (mm)	Standard deviation (mm)	Number of measurements
350	10.0	0.0	3
525	14.5	1.3	3
875	25.0	0.0	3
1750	47.0	0.0	3
2625	70.0	2.8	3
3500	89.0	0.7	5
4375	114.0	1.4	5
5250	135.0	0.6	3
6125	163.0	2.0	3
7000	180.0	2.1	3
7875	206.0	4.7	3

at least in part, to secondary reactions before stabilisation in the carrier gas stream². When peak height is plotted against sample weight, good rectilinear relations are obtained for each polymer over the weight ranges investigated and, as noted, the reproducibility is such that a single measurement can be expected to give a reliable result.

TABLE II
PYROLYSIS OF PVA ON QUARTZ AT 440°C

Sample weight (μg)	Peak height (mm)	Standard deviation (mm)	Number of measurements
0.10	4.0	0.0	3
0.30	9.5	0.0	3
0.50	17.0	0.0	3
0.70	26.0	0.5	3
0.90	28.5	0.5	3
1.00	33.0	0.6	3
2.00	64.0	1.0	4
3.00	101.0	2.4	10
4.00	133.0	2.8	3
5.00	163.0	2.1	5
6.00	204.0	1.4	5
7.00	238.0	1.0	3
8.00	264.0	1.6	3

Experiments in which substances adsorbed on thin-layer substrate are pyrolysed and determined using this apparatus are described in Part II⁴.

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