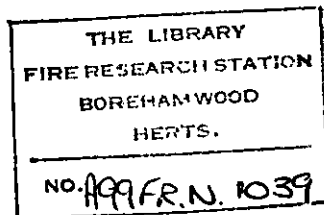




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THE THERMAL DECOMPOSITION PRODUCTS OF
RIGID POLYURETHANE FOAMS UNDER LABORATORY
CONDITIONS

by

W D Woolley, P J Fardell and I G Buckland

August 1975

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SUMMARY

The thermal decomposition of four commercial rigid polyurethane foams (two of which contain organophosphorus flame retardants) has been studied over the temperature range 200 to 1000°C using elemental analysis and gas chromatography.

The general decomposition mechanisms of the foams appear to be similar and involve a preferential release of some of the polyol content followed by a uniform fragmentation of the residue to release particulate material. This particulate material (smoke) appears to volatilise from the furnace zone at temperatures up to 600°C but decomposes above 700°C to give the typical family of nitrogen containing products of low molecular weight (hydrogen cyanide, acetonitrile, acrylonitrile, pyridine and benzonitrile) as observed with flexible polyurethane foams. The main nitrogen containing product of low molecular weight observed in this work is hydrogen cyanide which increases markedly in yield from 700°C to the maximum temperature studied (1000°C). At 1000°C the yields of hydrogen cyanide from the foams range between 3.8 to 7.3 weight per cent conversion which represents 28 to 42 per cent of the theoretically available nitrogen.

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Joint Fire Research Organization

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1. INTRODUCTION

For a number of years there has been concern that the flexible polyurethane foams which are used widely in furniture and bedding may release substantial amounts of other toxic gases in addition to carbon monoxide when involved in fires.

Recent work at the Fire Research Station has established that the thermal degradation of these flexible materials proceeds via the low temperature loss (200 to 300°C) of a nitrogen rich material¹ which has been termed 'yellow smoke' and which appears to be a polymerised or condensed form of the tolylene diisocyanate (TDI) part of the foams. This yellow smoke is known to decompose at temperatures in excess of 800°C and produces hydrogen cyanide together with other organic nitriles such as acetonitrile, acrylonitrile and benzonitrile. The production of the yellow smoke at 300°C is accompanied by the release of a little free TDI².

This information, obtained from pyrolysis experiments carried out under carefully controlled laboratory conditions, is vital for the effective design of full scale fire tests. These fire tests have shown that the hazard from hydrogen cyanide in the fire gases can be significant in the very high temperatures encountered during the burning of industrial loads of polyurethane foams³. The cyanide risk seems to be relatively low, in comparison with the risk from carbon monoxide, during fires involving domestic loads of these foams⁴. The hazard of isocyanate production during both industrial and domestic situations seems to be very much lower than might be expected from estimations from the thermal decomposition (laboratory) experiments.

More recently, a considerable amount of concern has been voiced about the possible release of toxic products from the rigid polyurethane and polyisocyanurate foams which are now used within buildings in 'structural' applications. Typical examples are the use of rigid foams in ceiling and wall boards and hot water tank insulation. Many other areas of application exist where thermal or acoustic insulation is required such as in cold storage areas and various transport media such as ships, aircraft and cars.

Current knowledge about the thermal decomposition mechanism and production of toxic materials from rigid polyurethane foams is rather limited and has generally been obtained during studies at relatively low temperatures^{5,6,7}, and usually not in excess of about 600°C.

Some preliminary work carried out at the Fire Research Station in 1971 on the thermal degradation of a rigid polyurethane foam⁸ using elemental ultramicro-analysis of residues, showed that there were some marked differences between the thermal decomposition behaviour of the flexible (TDI) and rigid (MDI) foams. In the case of the flexible foams there was a rapid and almost complete loss of the nitrogen content of the foam at about 300°C (15 min decomposition period) whereas the rigid material tended to fragment uniformly with little or no preferential loss of nitrogen rich species. No products were monitored in this study.

The work outlined in this report was therefore undertaken to provide some additional basic information about the decomposition mechanism and generation of decomposition products from some selected rigid polyurethane foams (based on diphenylmethane diisocyanate - MDI) both with and without organophosphorus flame retardants. In the study small samples of the foams were decomposed under carefully controlled laboratory conditions in an inert atmosphere with the decomposition products analysed by gas chromatography and the residues examined using elemental analysis. In this way some important features about the decomposition mechanism have been observed and the yields of the cyanides at various decomposition temperatures have been recorded.

It must be emphasised that the work outlined in this report does not represent an exhaustive study of the thermal degradation of polyurethane foams. The work was carried out to provide some basic background information and to highlight important areas of research for the more detailed study of the thermal degradation of rigid polyurethane and isocyanurate foams which is currently active in these laboratories.

2. EXPERIMENTAL

2.1 Low temperature decompositions and elemental analyses of residues

In the low temperature studies, weighed samples of the foams (approximately 100 mg) were decomposed in a small ceramic boat inside a silica furnace tube (18 mm internal diameter) for 15-minute periods in a flow of oxygen-free nitrogen at 100 ml/min. The tube furnace was 320 mm long and was controlled to better than $\pm 2^\circ\text{C}$ at 500°C with a proportional electronic controller.

At the end of the decomposition period the residues were removed and reweighed to find the weight loss and the residues then analysed for elemental composition (carbon, hydrogen, nitrogen and phosphorus) by a commercial consultancy laboratory.

2.2 Chromatographic analyses of products

The main decomposition and product collection system which has been used in these laboratories for chromatographic studies of the thermal decomposition products of plastics has been outlined in detail in a number of reports^{1,9}. Basically the system consists of a silica tube heated with a furnace (as in 2.1) with a maximum temperature of 1000°C ($\pm 5^\circ\text{C}$). Samples of foam (usually 10 mg) or polyol are introduced into the furnace in a small ceramic boat in a flow of oxygen-free nitrogen, again at 100 ml/min. The decomposition products are carried by the nitrogen gas from the furnace zone into the refrigerated 'loop' of a heated stainless steel gas sampling valve fixed in the usual way to the inlet of a gas chromatograph. The sampling 'loop' of the valve consists of a 350-mm length of stainless steel tubing (3.2 mm outside diameter) immersed in liquid nitrogen (-196°C).

After the collection period the valve is turned to the 'inject' position, the refrigerant removed and the stainless steel 'loop' heated quickly to 200°C to flash-vaporise the products into the gas chromatograph.

Chromatographic analyses of the decomposition products were carried out using both thermal conductivity and flame ionisation detectors with a Porapak Q column (2 m x 3.2 mm) temperature programmed from 30 to 280°C at 4 degC/min with a helium flow rate of 40 ml/min. Hydrogen cyanide was determined using the thermal conductivity detector; all other measurements were made with the flame ionisation detector. All chromatograms shown in this report are flame ionisation traces and were recorded at the same chromatographic attenuation and range.

2.3 Materials

Four foams were chosen for the study:

- (i) Foam A is a commercial polyester foam based on MDI containing approximately 4 per cent by weight of tris (chloroethyl) phosphate (TCEP). The density is 29 kg/m³. This foam is no longer available commercially. The experimental composition (elemental) is 65.80 per cent C, 5.95 per cent H, 7.02 per cent N and 0.44 per cent P; the remainder is mainly oxygen.
- (ii) Foam B is a commercial polyether foam based on MDI of density 36 kg/m³. No flame retardant is present. The experimental composition (elemental) is 65.00 per cent C, 6.20 per cent H and 9.41 per cent N; the remainder is mainly oxygen.

- (iii) Foam C is a commercially made polyurethane foam based on a polyether polyol (OP glycerol of hydroxyl number 540) and MDI. The density is 35.9 kg/m^3 . The experimental composition (elemental) is 64.12 per cent C, 6.57 per cent H and 7.08 per cent N; the remainder is mainly oxygen.
- (iv) Foam D is similar to foam C but contains 12 per cent by weight of tris (chloropropyl) phosphate (TCPP) flame retardant. The density is 37.5 kg/m^3 . The experimental composition (elemental) is 61.38 per cent C, 6.23 per cent H, 6.14 per cent N and 1.32 per cent P; the remainder is mainly oxygen.

Samples of the polyols used to prepare each foam were available and were used in the chromatographic studies. The polyol of foam A contained the added flame retardant (TCEP). With foam D, the polyol was available separately.

The diphenylmethane diisocyanate (MDI) used in decomposition experiments together with the various nitrogen containing materials and hydrocarbons used for direct seeding experiments were obtained commercially.

3. RESULTS

3.1 Low temperature decompositions and elemental analyses of residues

Samples of the four foams were decomposed, in turn, in the decomposition system as outlined in Section 2.1 at temperatures between 200 and 700°C . The results showing the weight, nitrogen and phosphorus (where appropriate) losses as percentage of the theoretical for foams A, B, C and D are given in Figs 1, 2, 3 and 4 respectively. The percentage loss of weight was obtained directly from the initial and final weights of the samples. The nitrogen and phosphorus losses were obtained from the weight losses and the initial and final elemental compositions. From Figs 1 to 4 inclusive a number of points are apparent:

- (i) With the polyester foam A (Fig. 1) a significant weight loss occurs particularly at low temperatures with a relatively low loss of nitrogen. For example, at 300°C there is a weight loss of about 25 per cent with a nitrogen loss of only 10 per cent. At temperatures above about 200°C there is a substantial loss of phosphorus, and although there is a rather large scattering of points for phosphorus loss in Fig. 1, it appears that about 50 per cent of available phosphorus is lost very rapidly but the remainder stays in the residue. The loss of phosphorus, probably as volatilised flame retardant, would contribute to only a few per cent loss in weight and the general weight and nitrogen loss curves of Fig. 1 suggest that the decomposition may proceed via the initial loss of some polyol (by some form of volatilisation) followed by a general fragmentation of the residue involving loss of both polyol and isocyanate fractions; the latter being the 'nitrogen'-containing part of the molecular structure.

At high temperatures (around 700°C) the weight and nitrogen losses appear to be equivalent with approximately 77 per cent of the theoretical weight and nitrogen content being lost.

- (ii) With the commercial polyether foam B (Fig. 2), the weight loss at low temperature (200°C) is markedly greater than the nitrogen loss which again suggests that polyol is being volatilised from the foam in some way. At higher temperatures (300-600°C) the weight loss tends to be greater than the nitrogen loss and at 700°C the two losses are equivalent.

Again, the overall pattern of weight and nitrogen losses of Fig. 2 indicates that there is a preferential release of some polyol followed by a general fragmentation of residue which eliminates both polyol and isocyanate part of the molecular structure in approximately equal amounts.

- (iii) With the commercial 'pedigree' foam C (Fig. 3) the decomposition curves are somewhat similar to those recorded with foams A and B. At low temperatures there is a significant weight loss with a limited nitrogen loss and again suggests that polyol is eliminated in some way from the foams followed by a uniform fragmentation of residue. At high temperatures (about 700°C) the nitrogen and weight losses are similar and of the order of 85 to 95 per cent.

- (iv) With the commercially made pedigree foam D (as for foam C but with TCPP flame retardant) the general decomposition curves of weight and nitrogen losses (Fig. 4) are similar to those observed with foam C, and again show the preferential loss of polyol, particularly at the low temperatures. Again, the general parallel nature of the two curves shows the general uniform fragmentation of the residue. As observed with the phosphorus containing foam A, the phosphorus from foam D is lost very readily at low temperatures but some phosphorus is retained to very high temperatures.

3.2 Chromatographic experiments (300-600°C)

Initial chromatographic experiments were carried out at decomposition temperatures between 300 and 600°C to represent broadly the temperature range used in the decomposition experiments of Section 3.1. In these experiments 10 mg samples of each foam were decomposed in turn in the furnace system and the products injected into a gas chromatograph for analysis as outlined in the Experimental Section. Comparative chromatograms were obtained by decomposing 5 mg samples of the respective polyols in each case. A sample weight of 5 mg was chosen for the polyol experiments as being approximately equivalent to the polyol content of each foam. The polyol of foam A contained the TCEP flame retardant, whereas the polyol of foam D was decomposed without the retardant.

At 300°C, only very small amounts of products were detected by gas chromatography using the Porapak Q column (which elutes materials up to a molecular weight of about 120) from any of the foams. The chromatographic pattern of decomposition products became much more intense and clearly defined as the decomposition temperature was increased. At all temperatures the chromatographic pattern of products showed a very strong resemblance to that of the respective polyol for each foam and there was little or no evidence to suggest that any significant products were derived from the isocyanate part of the foams.

Chromatograms at 600°C, recorded with flame ionisation detection, for foam A and polyol, foam B and polyol, and foams C and D with the joint polyol (without flame retardant) are recorded in Figs 5, 6 and 7 respectively.

In Fig. 5, the chromatographic pattern of products from foam A (commercial polyester) is clear but the main 'structure' of the chromatogram is also present in the chromatogram of the polyol. There are only a few small peaks, at large retention times which appear to be produced from the foam and which are absent with the polyol but, at the chromatographic sensitivity used in this work, these peaks would need to be large to be important.

In Figure 6, foam B (commercial polyether) produces a distinct pattern of products but the main structure is again present in the chromatogram of the polyol. Again, as in the case of foam A, some small peaks are present at large retention times which do not appear to be present from the polyol. The chromatogram of the polyether foam B is different from that of the polyester foam A (Fig. 5) as might be expected.

In Figure 7, foam C (glycerol polyether) produces a distinct chromatogram which is similar in some respects to that of the polyether foam B (Fig. 6). Again, the chromatogram of foam C is very similar to that of the polyol. The presence of the flame retardant in foam D appears to modify the relative intensities of certain peaks in the chromatograms but the main 'structure' of the chromatogram is retained.

The earlier work (Section 3.1) has established that the decomposition proceeds via the initial release of polyol and at 600°C approximately 75 to 90 per cent of both the weight and nitrogen content of all foams is lost. In spite of this, the chromatographic experiments at 600°C do not indicate the presence of any significant amounts of decomposition products which can be attributed to the isocyanate (ie. the nitrogen containing) part of the foams. It is therefore concluded that the main nitrogen containing products released at temperatures up to 600°C are not amenable to analysis in this way. Further, since the observed decomposition products of the foams are derived from the polyol content, it follows that the nitrogen

containing products must be more enriched in nitrogen than the original foams.

3.3 Chromatographic experiments (700 to 1000°C)

Chromatographic experiments were carried out at temperatures between 700 and 1000°C at 100 degC intervals with all the foams and the respective polyols. In these experiments two main points emerged:

- (a) At these temperatures the chromatographic pattern of products of the polyols were simplified and the regular spacing of the peaks indicated that they were essentially hydrocarbons. This is similar to observation of the high temperature degradation of the polyols from the flexible foams.
- (b) A new 'set' of products were distinct in the chromatograms of the products of the foams when compared with the polyols. This 'set' of products was similar for each foam and was soon recognised as the same pattern observed during the high temperature decomposition (800 to 1000°C) of flexible polyester and polyether foams.

Chromatograms recorded at 900°C using flame ionisation detection of foam A and polyol, foam B and polyol, and foams C and D and polyol are given in Figs 8, 9 and 10.

In Figure 8, the simplified pattern of the decomposition products of the polyol and the additional products in the chromatogram of the foam are clear. There is a strong resemblance between these chromatograms and those observed for the flexible foams. Because of this, it was relatively easy to confirm the nature of the important products by direct seeding experiments (ie. where a small amount of pedigree product is added to the decomposition products before analysis to give an increase in peak height without any doublet formation). In this way, the following identifications were made and where possible confirmed by mass spectrometry. Products evolved during the first 5 minutes of the chromatograms (largely C₁ and C₂ hydrocarbons) were not monitored.

Peak nomenclature	Direct seeding
f	Propane
g	Hydrogen cyanide*
i	C ₄ hydrocarbon
j	Acetonitrile*
k	Acrylonitrile*
n	Benzene*
r	Pyridine
s	Toluene*
x	Benzonitrile*
E	Naphthalene*

* confirmed by mass spectrometry

For convenience this peak nomenclature is identical to that adopted during the earlier work involving flexible foams. Traces of the nitrogen containing products are observed in the chromatogram of the polyol because the polyol alone contains a few tenths of one per cent of nitrogen by elemental analysis.

With the commercial polyether foam B and polyol (Fig. 9), the nitrogen containing products are again clear and are superimposed on a hydrocarbon background. Elemental analysis of the polyol showed that the nitrogen content was large (4 to 5 per cent) which explains the relatively large amounts of nitrogen containing products during the decomposition of polyol alone. These nitrogen containing products, particularly hydrogen cyanide (g) are even greater with the foam.

In Figure 10 (glycerol polyether), the regular hydrocarbon pattern from the polyol alone is very clear. The additional products (containing nitrogen) are distinct in both the ordinary (C) and flame retarded (D) foam. The presence of the flame retardant does not appear to alter significantly the general structure of the chromatograms but peak (g), hydrogen cyanide, is somewhat reduced with the flame retarded foam (D), at this temperature.

The low temperature experiments of Sections 3.1 and 3.2 show that a nitrogen containing material is released during degradation at temperatures up to 600°C which is not detected by chromatography, possibly because the product has a relatively large molecular weight

At temperatures in excess of about 700°C, this nitrogen containing product is thermally decomposed into a range of nitrogen containing products of low molecular weight and which appear to be the same series of products as observed during the high temperature decomposition of flexible foams (which is known to proceed via an intermediate yellow smoke).

3.4 Quantitative chromatographic experiments (700 to 1000°C)

The chromatographic experiments between 700 and 1000°C described in Section 3.3 were repeated with integration of the main peaks (hydrogen cyanide, acetonitrile, acrylonitrile, benzene, pyridine, toluene, benzonitrile and naphthalene) using either the thermal conductivity or flame ionisation detectors. The experimental sensitivities of the detectors to these products are given in the Appendix. Hydrogen cyanide was analysed with the thermal conductivity detector; all other materials were analysed with the flame ionisation detector. The C₁ and C₂ hydrocarbons are not included because the collection technique tends to be unreliable with low boiling point materials.

The yields of the main products for foams A and B and foams C and D are given in

Tables 1 and 2 respectively. These tables show the predominance of hydrogen cyanide as the main nitrogen containing product at high temperatures, with 3.8 to 7.3 per cent of the weight of the foams being converted to hydrogen cyanide at 1000°C.

Table 1. Yields of the main products during the thermal decomposition of Foams A and B between 700 and 1000°C

Product	Yields of products (μ g)							
	Foam A (10 mg)				Foam B (10 mg)			
	700°C	800°C	900°C	1000°C	700°C	800°C	900°C	1000°C
Hydrogen cyanide (g)	5.14	85.9	315	509	50.0	63.5	471	732
Acetonitrile (j)	12.3	27.8	33.1	17.8	*	12.1	48.4	33.4
Acrylonitrile (k)	7.9	32.5	26.8	2.8	*	4.3	25.3	5.3
Benzene (n)	64.3	162	478	418	24.0	47.5	405	438
Pyridine (r)	1.4	3.5	11.0	0.3	3.8	4.0	14.6	1.5
Toluene (s)	101	100	41.8	3.7	27.9	298	33.5	4.1
Benzonitrile (x)	52.5	114	90.7	45.2	39.3	54.3	126	61.4
Naphthalene (E)	19.7	51.9	151	80.1	27.6	*	78.2	104

Table 2. Yields of the main products during the thermal decomposition of Foams C and D between 700 and 1000°C

Product	Yields of products (μ g)							
	Foam C (10 mg)				Foam D (10 mg)			
	700°C	800°C	900°C	1000°C	700°C	800°C	900°C	1000°C
Hydrogen cyanide (g)	15.1	65.1	186	381	15.2	31.2	76.2	508
Acetonitrile (j)	13.9	37.8	36.3	21.4	*	12.8	29.6	18.5
Acrylonitrile (k)	11.5	44.6	30.2	2.6	*	14.3	36.2	1.3
Benzene (n)	35.4	156	313	339	39.6	70.6	194	378
Pyridine (r)	1.9	3.8	6.9	0.2	2.2	0.9	3.5	0.2
Toluene (s)	28.4	47.2	34.0	4.6	31.0	28.1	29.4	4.7
Benzonitrile (x)	70.9	105	149	21.0	7.2	19.1	93.4	26.1
Naphthalene (E)	8.0	52.9	141	50.3	12.7	55.3	57.2	64.9

*not recorded

Table 3. Nitrogen recoveries during the thermal degradation of Foams A, B, C and D at 1000°C

Product	Nitrogen recovery (per cent of theoretical)			
	Foam A (7.02% N)	Foam B (9.41% N)	Foam C (7.08% N)	Foam D (6.14% N)
Hydrogen cyanide (g)	37.6	40.3	27.8	42.8
Acetonitrile (j)	0.9	1.2	1.0	1.0
Acrylonitrile (k)	0.1	0.1	0.1	0.1
Pyridine (r)	*	*	*	*
Benzonitrile (x)	0.9	0.9	0.4	0.6
TOTAL	39.5	42.5	29.3	44.5

*very small; less than 0.03 per cent and not included.

For mass balance studies of the nitrogen containing products, the nitrogen recoveries for foams A, B, C and D at 1000°C are given in Table 3. At this temperature the degradation of the volatile nitrogen containing intermediates produces hydrogen cyanide equivalent to 28 to 43 per cent of the theoretically available nitrogen in the foams. Temperatures in excess of 1000°C may give higher degrees of conversion to hydrogen cyanide. These conversions (28 to 43 per cent) are somewhat lower than the values of 66 to 75 per cent recorded for the flexible foams, possibly because of the greater thermal stability of intermediates based on MDI rather than TDI.

3.5 Studies of decomposition smokes and residues

Earlier work described in this report has established that a large part of the nitrogen content of each foam is released at temperatures of around 600°C but the nitrogen containing products are not amenable to normal chromatographic analysis. Formation of these nitrogen containing products is preceded by the elimination of some polyol degradation products.

Some experiments were therefore carried out to examine the solid (and liquid) condensates volatilised from the furnace zone and likely to be of too large a molecular weight for analysis with Porapak Q.

Considerable difficulties were encountered in trapping particulate matter effectively and several different methods of collection were investigated before a technique using a long aluminium tube was finally adopted. For this study, decomposition experiments were carried out using the decomposition system described in Section 2.1 but modified with a long tube (18 mm outside diameter and about 450 mm long), rolled out of aluminium foil (domestic) and inserted into the exit end of the silica furnace tube. This aluminium tube provided a relatively cool surface for deposition of particulate matter and was easily unrolled to give access to condensed materials. The smokes formed in this way from repetitive decompositions of the various foams were then subjected to high temperature degradation with chromatography of the products as a means of interpreting the nature of the smokes.

In this way, smokes were prepared from the commercial 'pedigree' foam C at 400°C. Samples of the smokes (5 mg) were then decomposed at 600 and 900°C and the chromatograms are recorded in Fig. 11. At 600°C the chromatogram is very similar to that observed during the direct decomposition of foam or polyol at 600°C (see Fig. 7). At 900°C, the chromatogram shows the typical family of nitrogen containing products superimposed on a hydrocarbon background as observed during the direct decomposition of foam at 900°C. However, although the chromatogram of the smoke shows distinct similarities to that of the foam (based on purely visual comparisons), any enrichment in the MDI content caused by polyol release would be difficult to detect in this way.

In the second set of experiments, smokes were prepared from the polyester foam A, which proved to be better foam for smoke generation and collection experiments, at 600°C. About 50 mg of smoke was collected from the aluminium foil and refluxed for 2 hours with diethylether to extract any free polyol.

The chromatogram of the ether extracted material (10 mg) decomposed at 900°C is given in Fig. 12 and suggests that this material is essentially polyol but small amounts of nitrogen containing products are also present. The chromatogram of the ether 'residue' (10 mg) is also given in Fig. 12 and shows that the material is essentially a rigid polyurethane when compared with the chromatograms of Figs 8, 9 and 10. The ratio of polyol to MDI is not clear but the experimental nitrogen content (9.59 per cent) of this residue suggests that enrichment of MDI has taken place. An interesting point to note in Fig. 12 (ether residue) is that a new and distinct peak (labelled L) is present in addition to the normal family of nitrogen containing products (g, j, k, r and x). This peak is also present with smoke decomposed at 900°C from foam C (Fig. 11) but does not appear significantly in the chromatograms obtained during the direct decomposition of the foams. Attempts to analyse the component by mass spectrometry have not, as

yet, been successful. Small components near to peak L give good spectral data but peak L itself gives little or no total ion current and does not provide a mass spectrum. Peak X, which follows peak L, gives a very large and distinct spectrum of benzonitrile. It is assumed that peak L is being removed in some way in the interface equipment between the chromatograph and mass spectrometer.

3.6 Additional chromatographic studies of residues

Because of difficulties in collecting samples of smoke, some additional attention was directed towards a study of decomposition residues of polyester foam A.

In this work, 10 mg samples of the foam were decomposed at temperatures between 300 and 600°C (at 100 degC intervals) and the residues then decomposed further at 900°C with quantitative analysis of the decomposition products. The hydrogen cyanide yields recorded during this study together with the weight (in mg) after the initial heating period and the nitrogen content (as per cent, based on the nitrogen content of the foam as 100 per cent) are recorded in Table 4 as runs R300 to R600 inclusive.

Table 4. Yields of hydrogen cyanide from the thermal decomposition of polyester foam A, residues, smoke and pure MDI at 900°C

Run	Initial weight (mg)	Temperature (°C)	Final weight ϕ (mg)	Nitrogen content * (per cent)	Yield of hydrogen cyanide (mg)
R300	10.0	300	7.6	90	0.31
R400	10.0	400	3.8	52	0.17
R500	10.0	500	2.6	29	0.076
R600	10.0	600	2.3	25	0.067
Foam	10.0	-	10.0	100	0.32
Smoke	10.0	600 *	10.0	136	0.39
MDI	10.0	-	10.0	160	0.52

* Prepared at 600°C

ϕ Based on smooth curve data of Fig. 1

* Based on 100 per cent equivalent to nitrogen content of foam (7.02 per cent); values for residues recorded from smooth curve data of Fig. 1; experimental nitrogen content of smoke 9.59 per cent; MDI based on theoretical nitrogen content of 11.2 per cent.

Also shown in Table 4 are the hydrogen cyanide yields from 10 mg of foam, smoke (ether residue material) and MDI. The nitrogen content values of 136 and 160 per cent for the smoke and MDI* are calculated on the basis of the nitrogen content of the foam being 100 per cent.

The data of Table 4 becomes more meaningful when the hydrogen cyanide yields are plotted against the weight and nitrogen content as in Figs 13(a) and (b).

In Fig. 13(a), the points for runs R300, 400, 500 and 600 and smoke form an approximately linear relationship of hydrogen cyanide yield versus the weight. The hydrogen cyanide yield for foam is well below the general linearity line and the MDI is above.

During the heating of this foam at 300°C, a weight loss of about 25 per cent takes place with a small nitrogen loss of about 10 per cent. This overall loss seems to be mainly polyol based but subsequent loss of weight (Fig. 13(a)) involves the fragmentation of the polyurethane (now enriched in MDI) with constant MDI/polyol fragmentation. This 'constant' fragmentation seems to be broadly independent of the extent of decomposition and the volatilised fragments (collected as smoke) have a similar MDI/polyol content to the residues.

The data of Fig. 13(a) when plotted as a function of the nitrogen content (rather than weight) are shown in Fig. 13(b). In this case there is a general linearity of all residues, foam, smoke and MDI. This confirms the general similarities between the residues, smoke, foam and MDI with respect to release of hydrogen cyanide. Further, the overall linearity in the experiments with the residues and foam shows that hydrogen cyanide can be released over the whole band of nitrogen content without any apparent threshold limitations.

The chromatogram of the decomposition products of MDI (10 mg) decomposed at 900°C for the above studies is shown in Fig. 14. The chromatogram clearly shows the main series of nitrogen containing products (g, j, k, r, x) as observed during the work with the polyurethane foams but with the virtual absence of the 'background' normally associated with the degradation of the polyol.

4. DISCUSSION AND CONCLUSIONS

The decomposition experiments (weight and elemental loss) show that the general decomposition mechanisms of all four foams (A, B, C and D) are similar but quite different to that observed with flexible polyester and polyether foams. With the rigid foams there appears to be a preferential loss of some polyol followed by a general fragmentation of the residue involving loss of polyol and MDI content in broadly equal proportions.

* Decomposed simply by adding 10 mg into the furnace in the ceramic boat.

Phosphorus appears to be lost very readily from the flame retarded foams (A and D), possibly by volatilisation of the organophosphorus additive. At low temperatures (200°C) there is a substantial loss of phosphorus (50 and 70 per cent for foams A and D respectively) with little overall degradation. A proportion of the phosphorus remains in the residue up to the maximum temperature of this study (700°C).

Chromatographic experiments (300 to 600°C) show that the products amenable to analysis are derived mainly from the polyol and little or no nitrogen containing products are observed. At high temperatures (700 to 1000°C) all the foams studied showed the familiar pattern of nitrogen containing products (hydrogen cyanide, acetonitrile, acrylonitrile, pyridine and benzonitrile), as observed with the flexible foams, superimposed on a polyol of 'background'.

Studies of the decomposition smokes (ie. particulate matter) and additional chromatographic experiments of residues indicate that the smokes released at low temperatures (up to 600°C) and which volatilise from the furnace zone are probably fragmented polyurethanes. These smokes are slightly enriched in nitrogen (above that of the foam) because of the preferential release of some polyol.

The decomposition of pure MDI at high temperatures shows the same pattern of nitrogen containing products of low molecular weight as observed during the high temperature degradation of rigid (and flexible) polyurethane foams.

Studies of hydrogen cyanide production at 900°C from the foams, partly decomposed foams, smokes and MDI show that the yields of hydrogen cyanide are directly proportional to the nitrogen content. This observation adds additional weight to the nitrogen enrichment and uniform fragmentation theory of degradation.

The main nitrogen containing product of low molecular weight observed in this work from all foams is hydrogen cyanide which becomes important at temperatures above 700°C and increases markedly with temperature to the maximum temperature studied of 1000°C. At 1000°C the foams release a range of between 3.8 and 7.3 weight per cent as hydrogen cyanide. This represents a range of 28 to 42 per cent of the theoretically available nitrogen.

There is little information from this work to indicate that the presence of the organophosphorus additive substantially alters the general decomposition mechanism.

It should be emphasised that the thermal degradation studies outlined in this report were carried out under carefully controlled laboratory conditions. The results of this work are required to establish the general decomposition mechanisms and decomposition temperatures for the effective design of an immediately forthcoming series of full scale fire tests which are to be carried out at the

Fire Research Station to study the release of toxic products when rigid polyurethane foams are involved in real fire situations.

5. ACKNOWLEDGMENT

The authors wish to thank Mr J V Murrell for his help with certain parts of the experimental work of this report.

6. REFERENCES

1. WOOLLEY, W D. Nitrogen containing products from the thermal decomposition of flexible polyurethane foams. Br. Polym. J. 1972 4(1) 27-43.
2. WOOLLEY, W D. The production of free toluene diisocyanate from the thermal decomposition of flexible polyurethane foams. J. Fire flammability, Comb. Toxicology Supp. Nov. 1974 259-267.
3. WOOLLEY, W D. Toxic products from plastics materials in fires. Plastics and Polymers 1973 41 (156) 280-6.
4. STARK, G W V, FIELD, P and PITT, A I. The hazard from fires of small loads of flexible polyurethane foam. Joint Fire Research Organisation Fire Research Note 1017, 1974.
5. ASHIDA, K, YAMAUCHI, F, KATOM, M and HARADA, T. HCN generation from urethane and isocyanurate foams. J. Cell. Plast. July/Aug. 1974 181-185.
6. NAPIER, D H and WONG, T W. Toxic products from the combustion and pyrolysis of polyurethane foams. Br. Polym. J. 1972 4, 45-52.
7. BOTT, B, FIRTH, J G and JONES, T A. Evolution of toxic gases from heated plastics. Br. Polym. J. 1969 1 203-204.
8. WOOLLEY, W D and FIELD, P. A preliminary study of the thermal decomposition of polyurethane foams by elemental ultramicroanalysis. Joint Fire Research Organisation Fire Research Note 880, 1971.
9. WOOLLEY, W D. The decomposition products of PVC from studies of fires. Br. Polym. J. 1971 3(4) 186-93.

APPENDIX

Chromatographic sensitivities for the main decomposition products:

	<u>Integrator counts* per mg</u>	<u>Detector*</u>
Hydrogen cyanide	1023 (3)	TCD
Acetonitrile	1024 (4)	FID
Acrylonitrile	1504 (4)	FID
Benzene	3363 (4)	FID
Pyridine	2056 (4)	FID
Toluene	3213 (4) ϕ	FID
Benzonitrile	2315 (4)	FID
Naphthalene	3213 (4) ϕ	FID

* The integrator counts are in arbitrary units; the figure in brackets denotes the power of ten, ie. 1504 (4) \equiv 1504 x 10⁴.

ϕ From data by Dietz using benzene as a reference material.
Value for naphthalene assumed to be the same as for toluene.

* TCD = Thermal conductivity detector

FID = Flame ionisation detector.

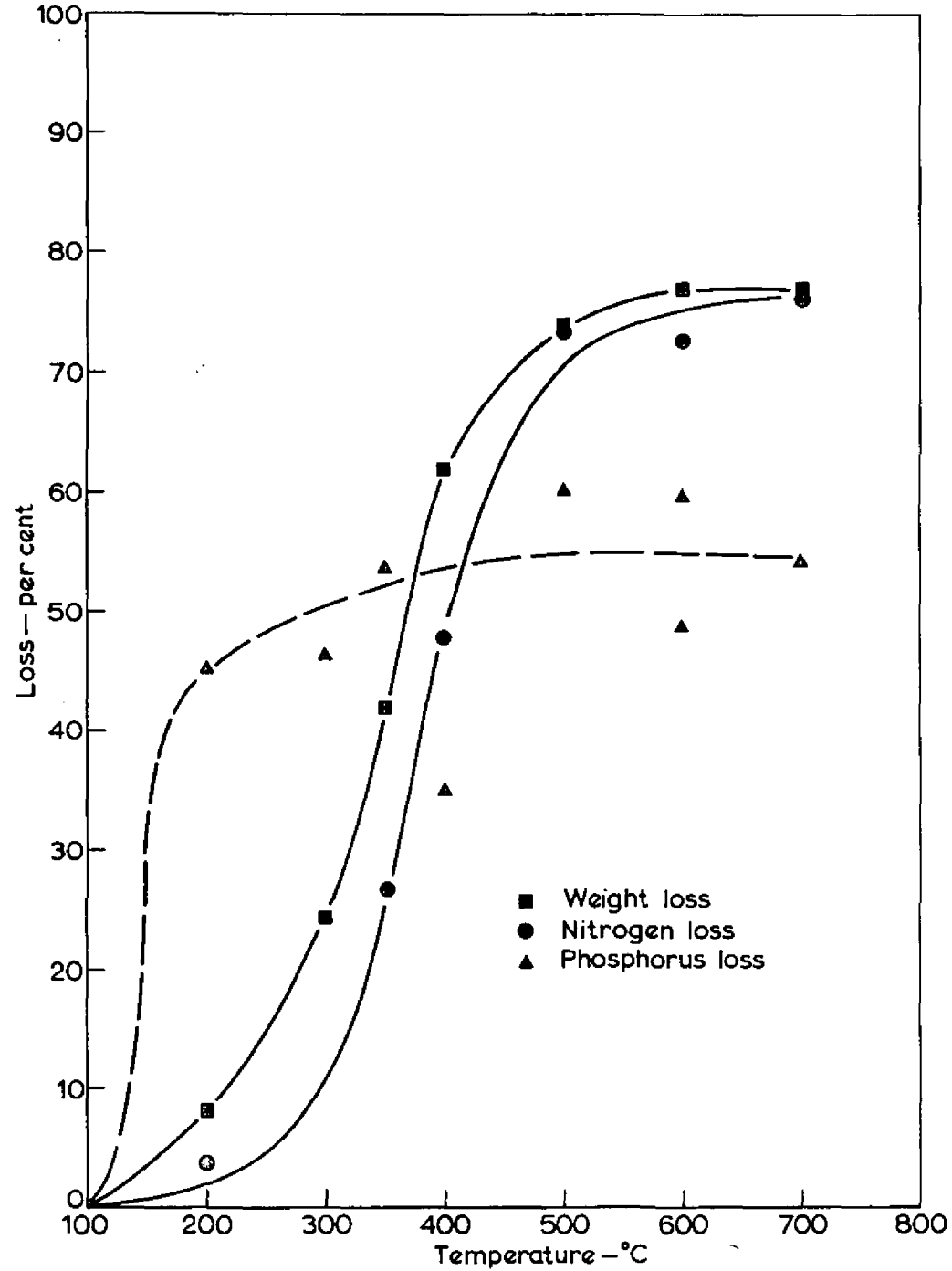


Figure 1 Decomposition data for foam-A

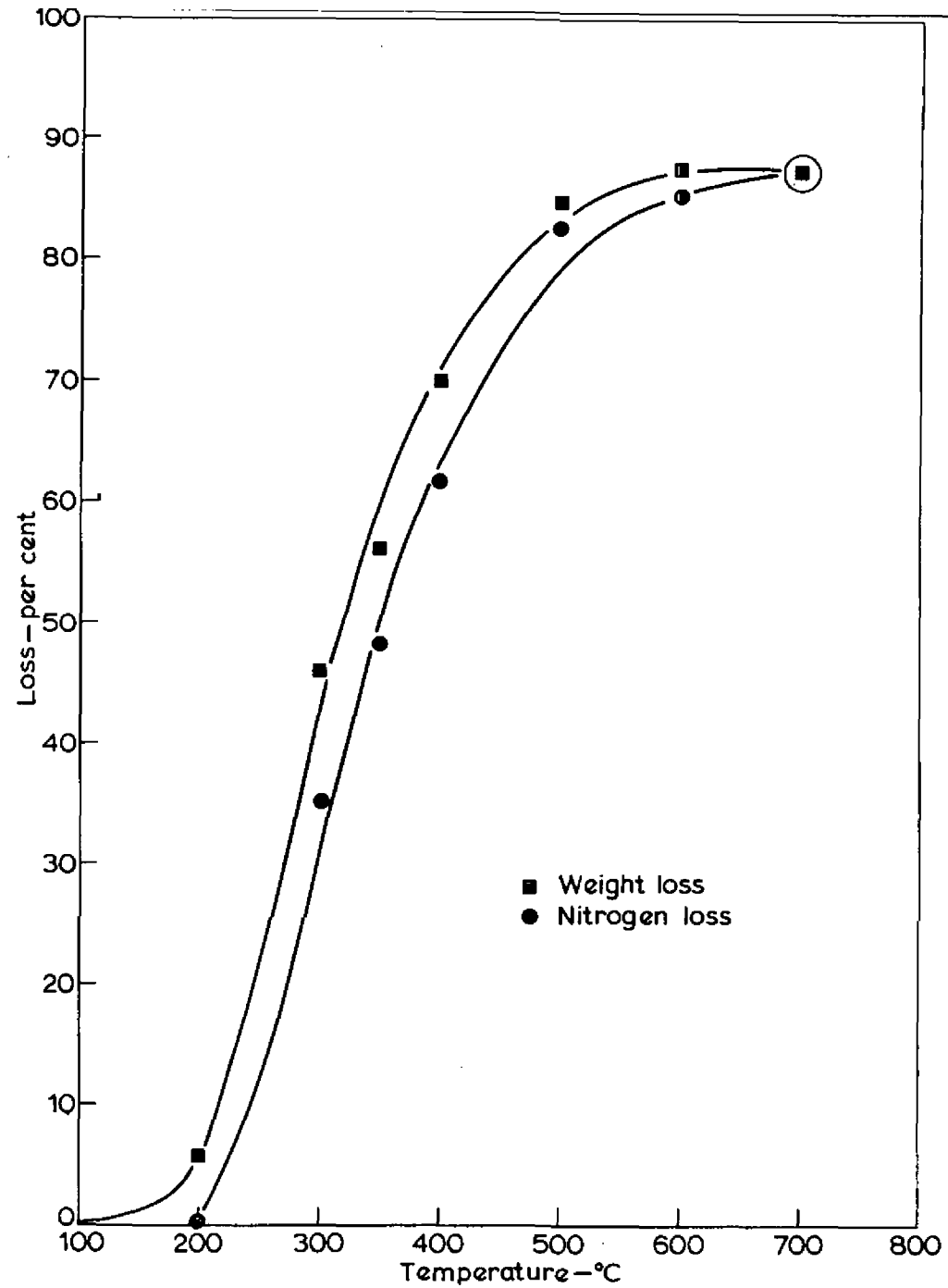


Figure 2 Decomposition data for foam-B

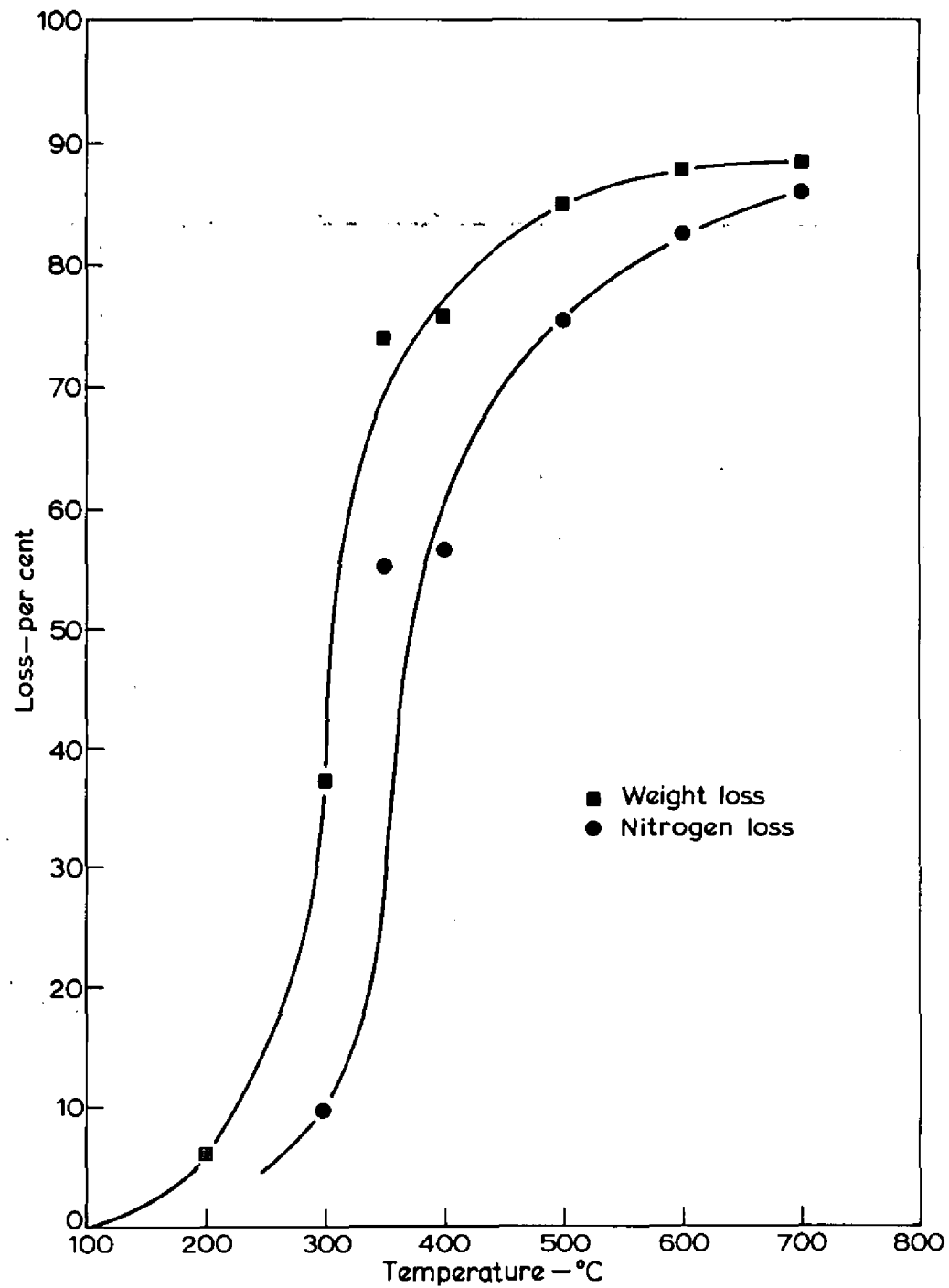


Figure 3 Decomposition data for foam C

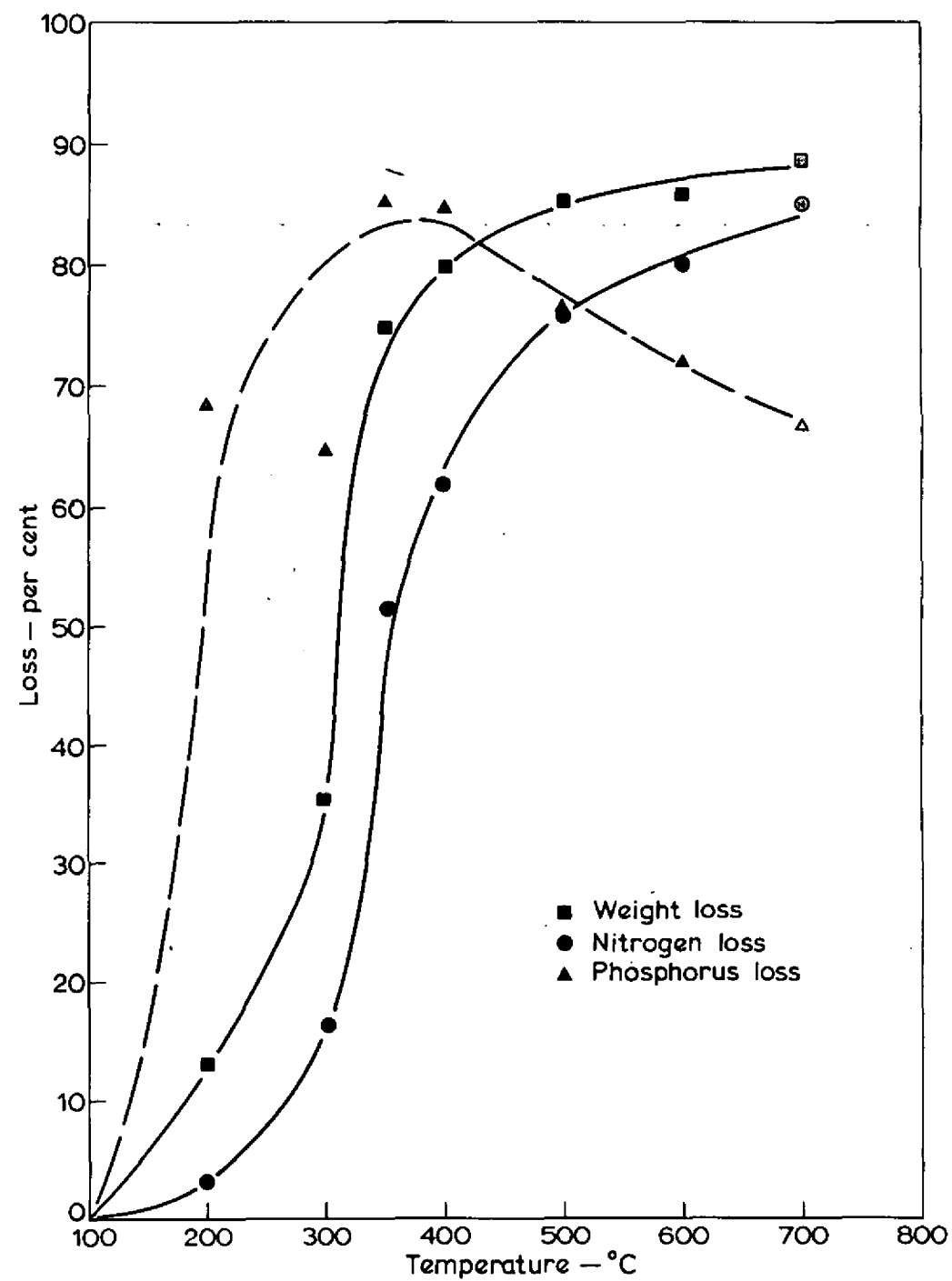
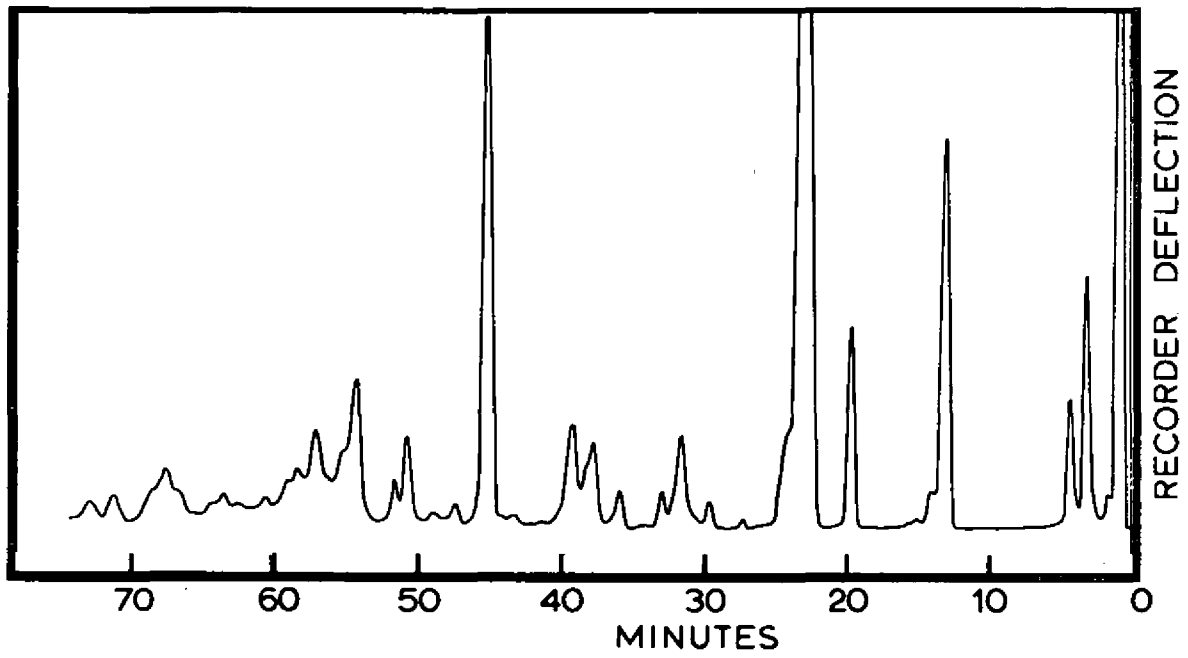


Figure 4 Decomposition data for foam D

FOAM A



POLYOL

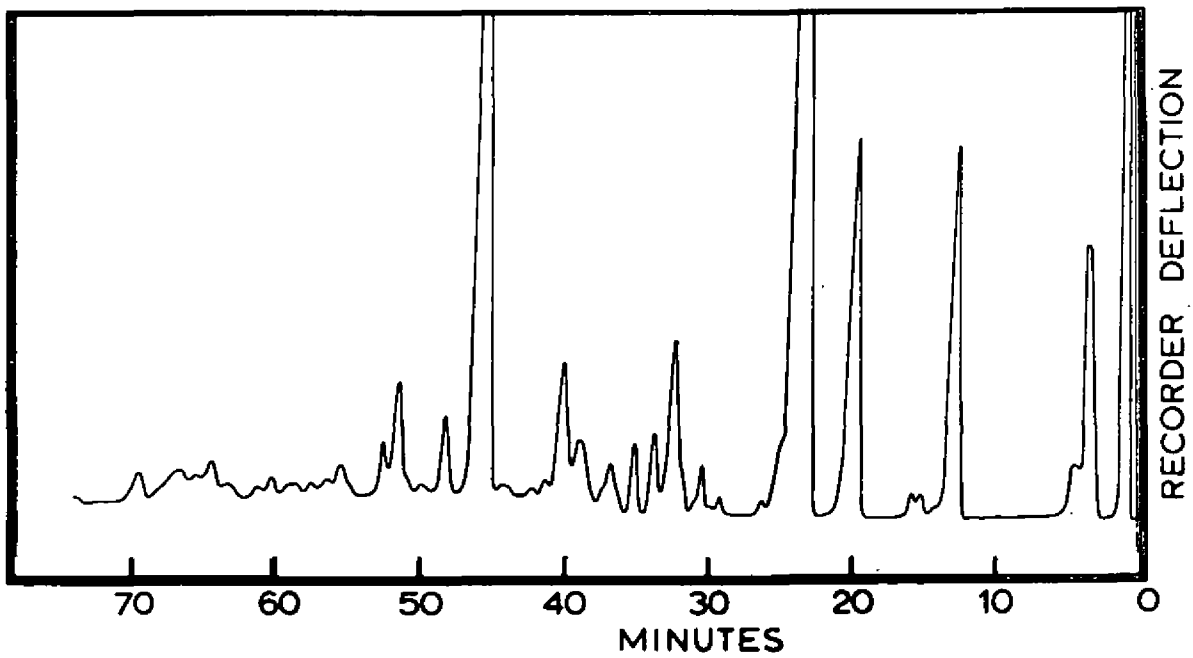
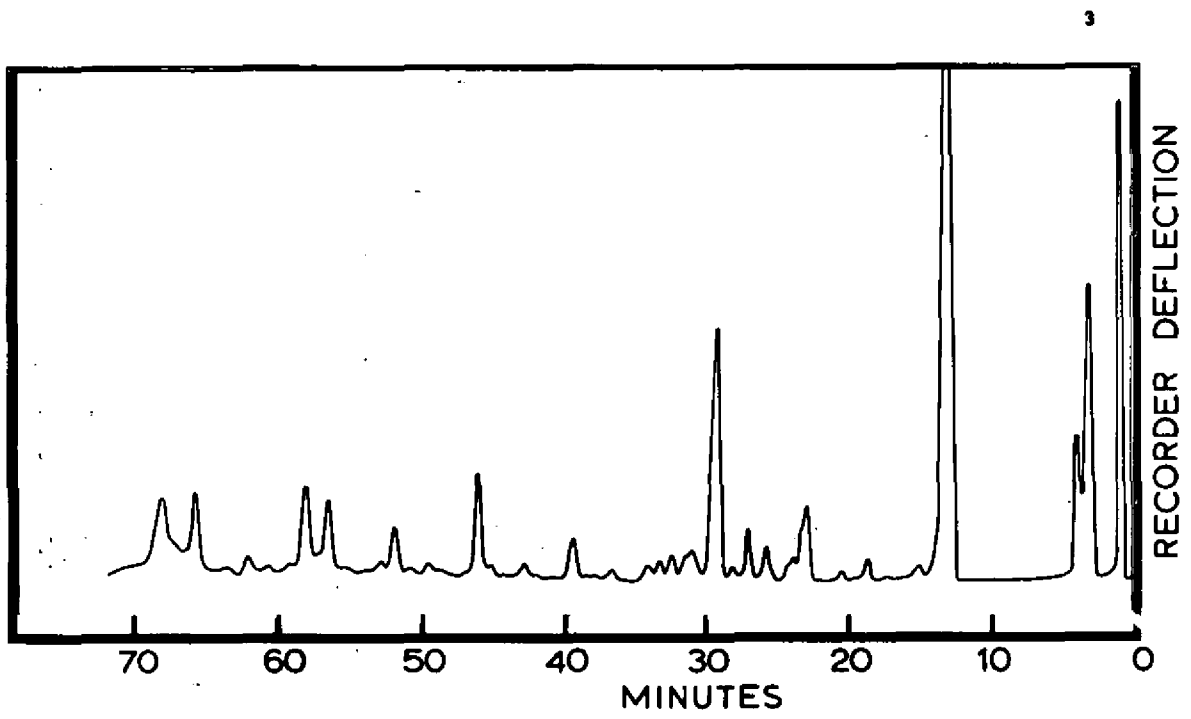


FIG. 5. DECOMPOSITION PRODUCTS OF
FOAM A AND POLYOL AT 600°C

FOAM B



POLYOL

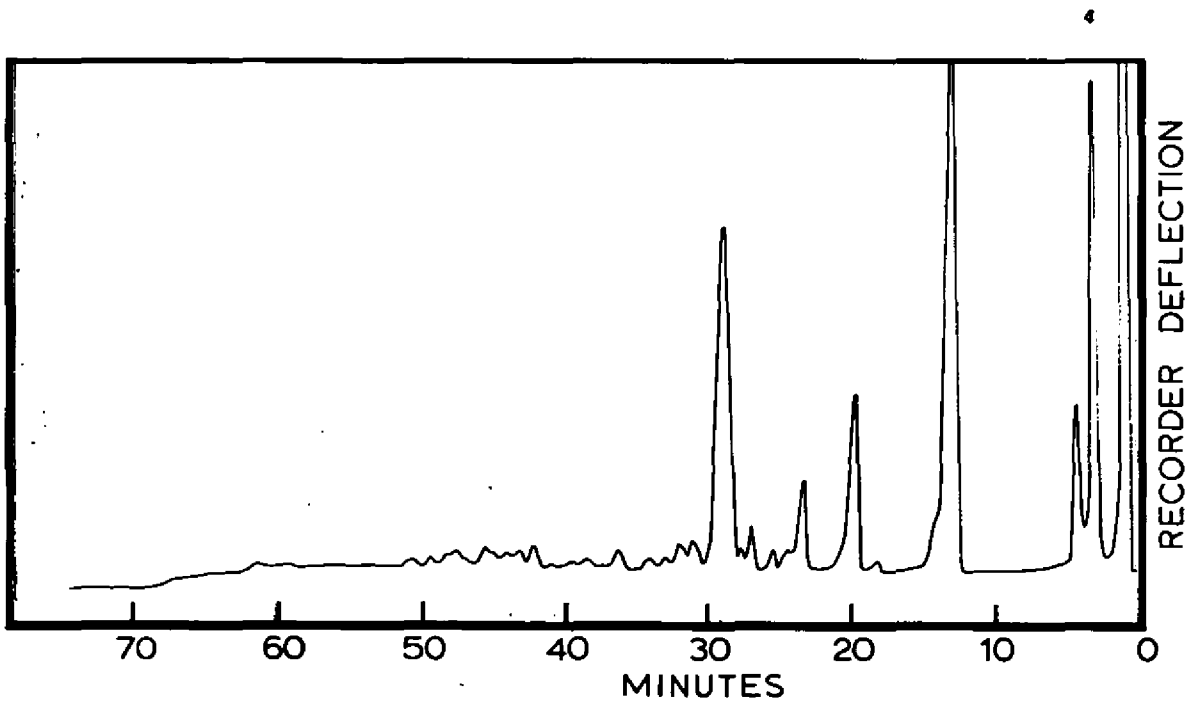


FIG. 6. DECOMPOSITION PRODUCTS OF
FOAM B AND POLYOL AT 600°C

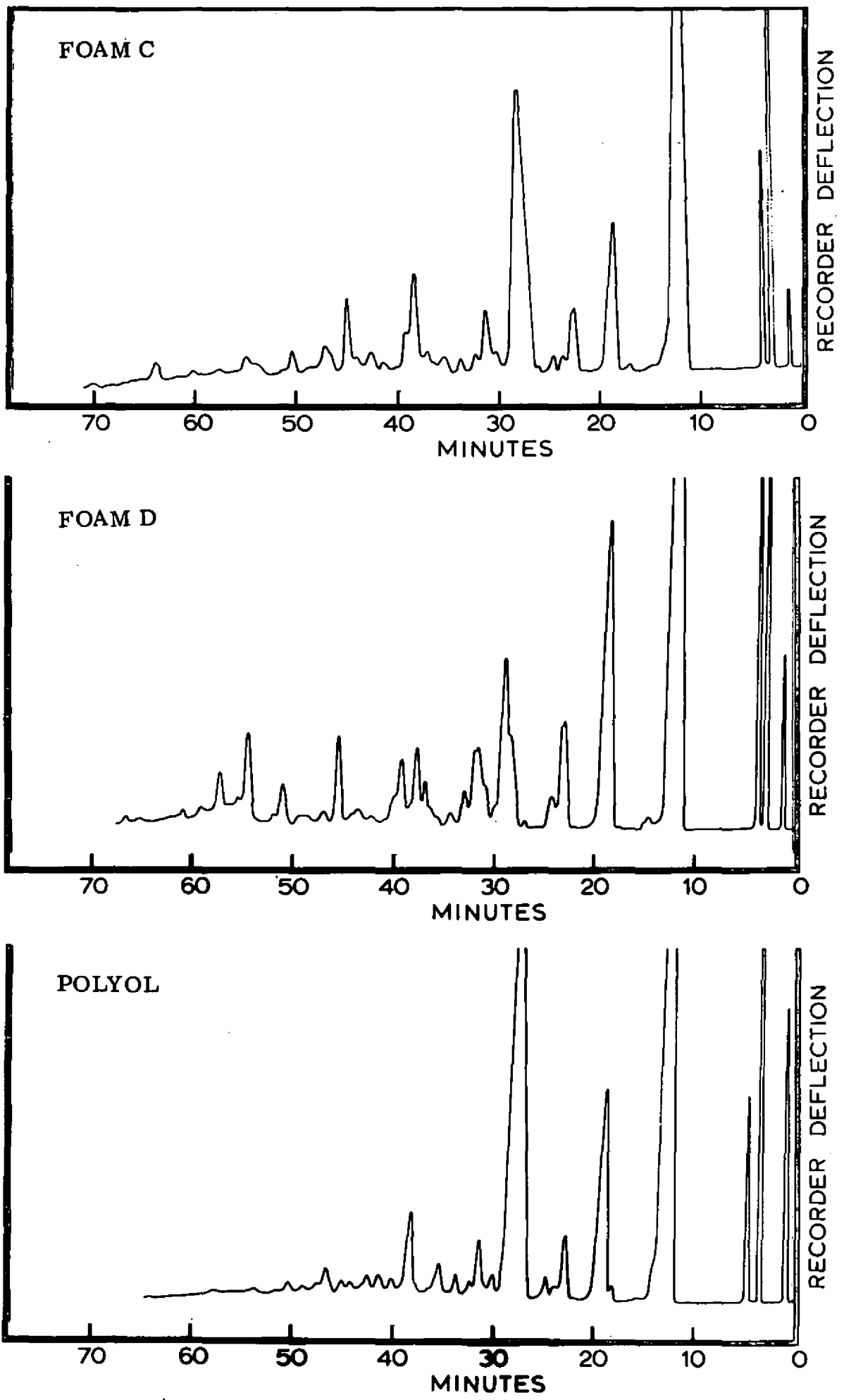
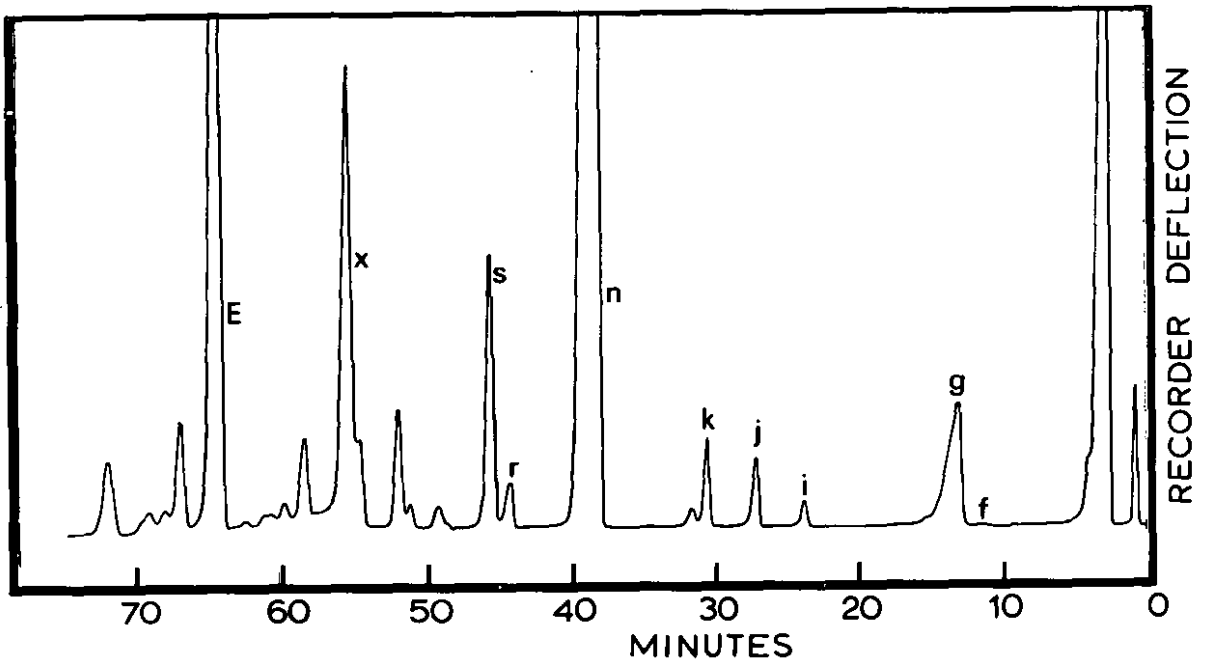


FIG. 7. DECOMPOSITION PRODUCTS OF FOAMS C AND D AND POLYOL AT 600°C

FOAM A



POLYOL

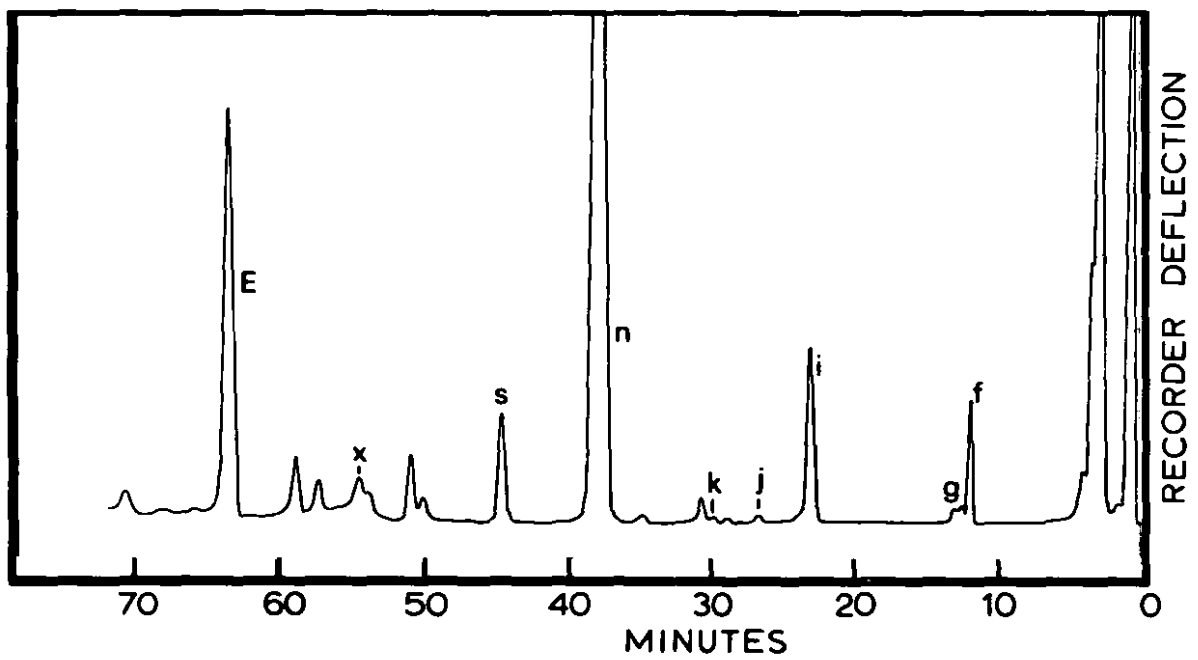
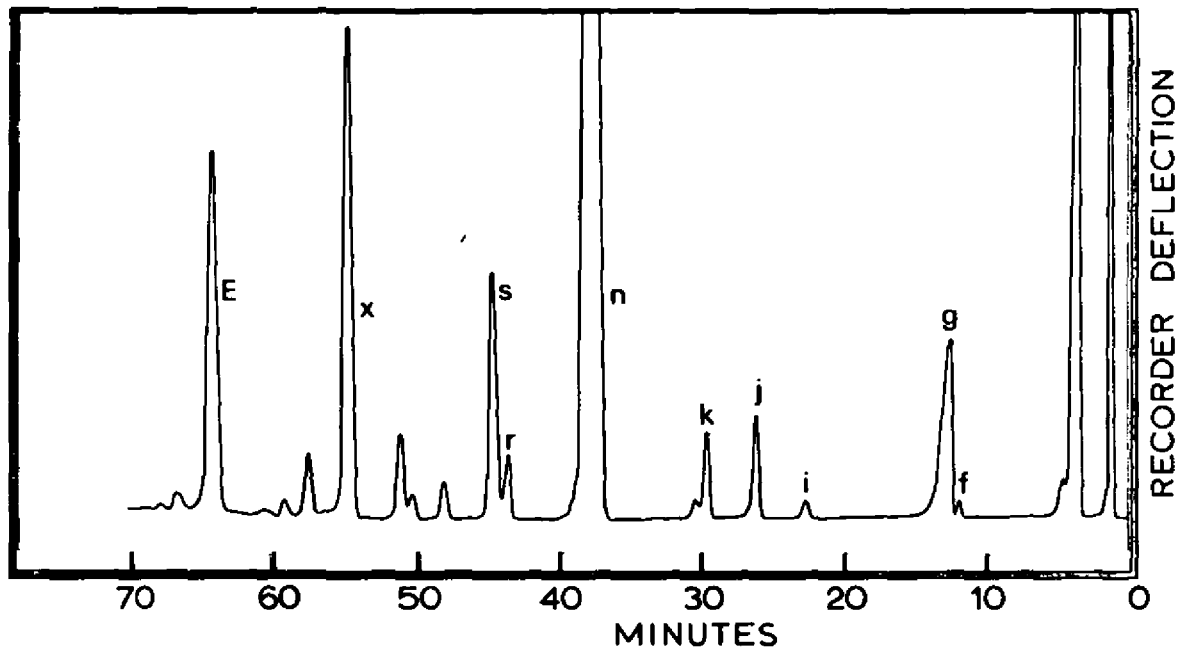


FIG. 8. DECOMPOSITION PRODUCTS OF
FOAM A AND POLYOL AT 900°C

FOAM B

10



POLYOL

11

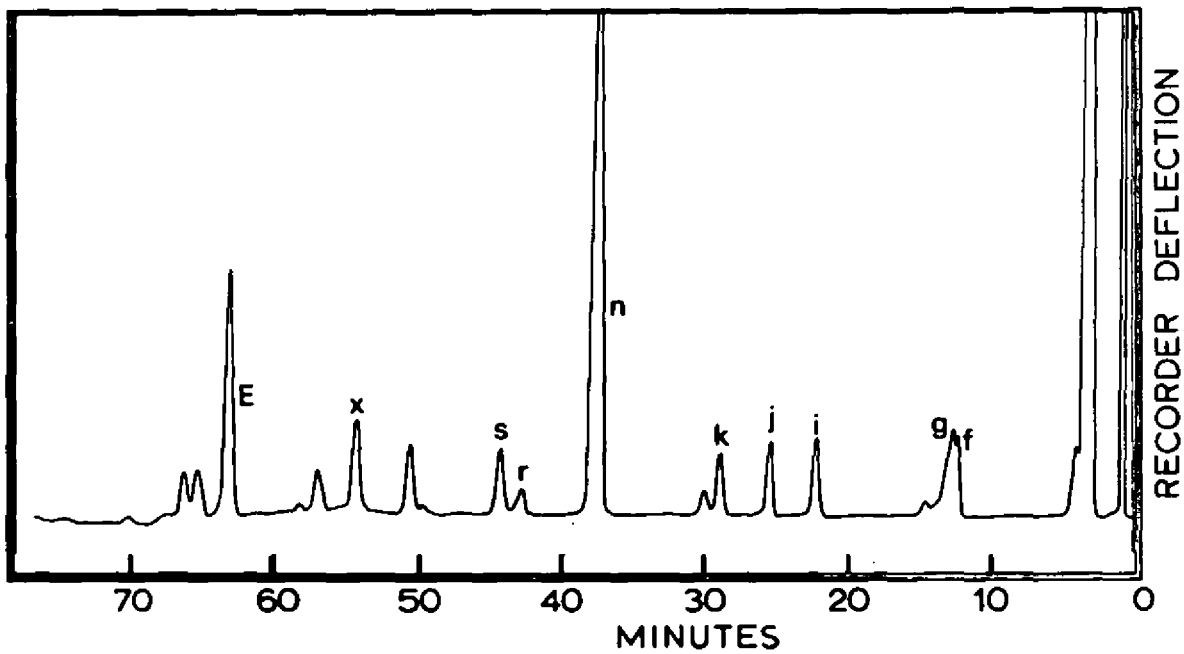


FIG. 9. DECOMPOSITION PRODUCTS OF
FOAM B AND POLYOL AT 900°C

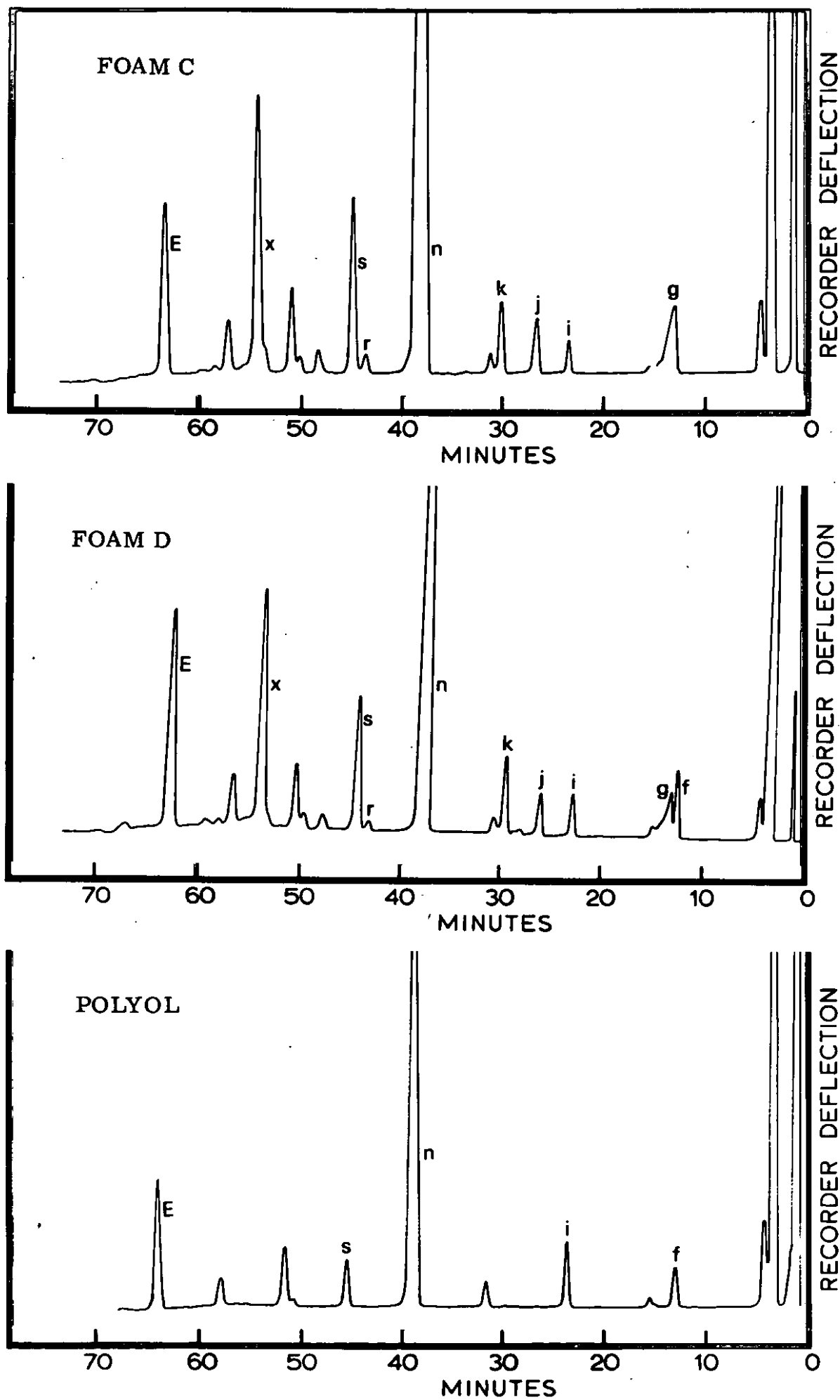
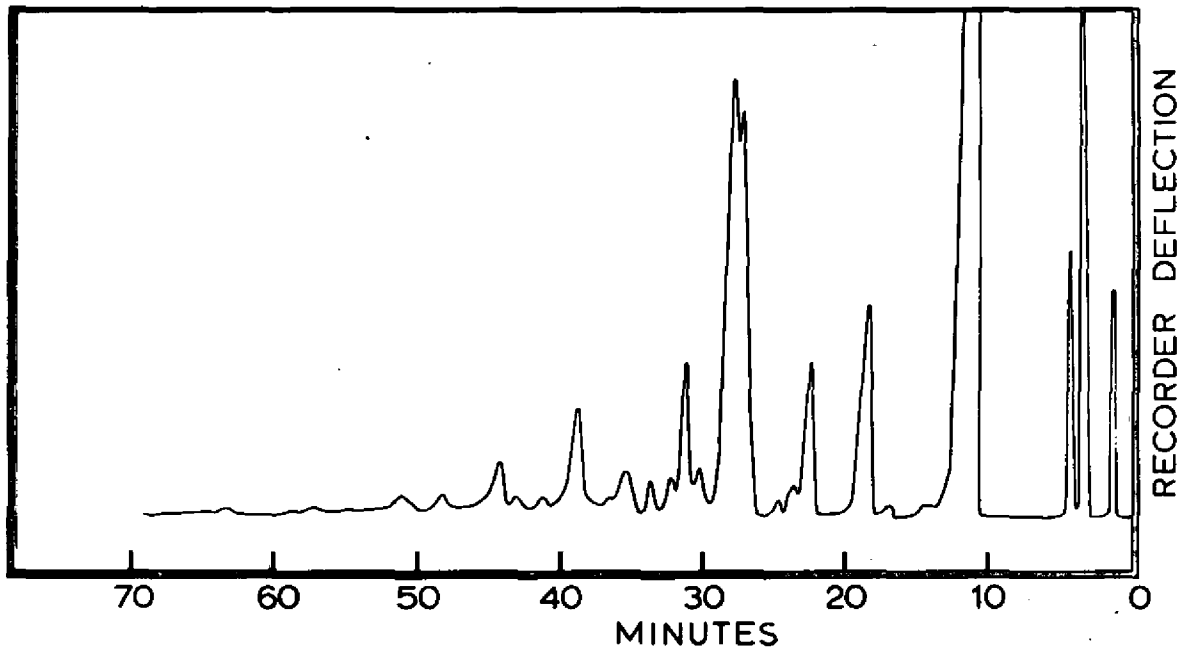


FIG. 10. DECOMPOSITION PRODUCTS OF FOAMS C AND D AND POLYOL AT 900°C

600°C

15



900°C

16

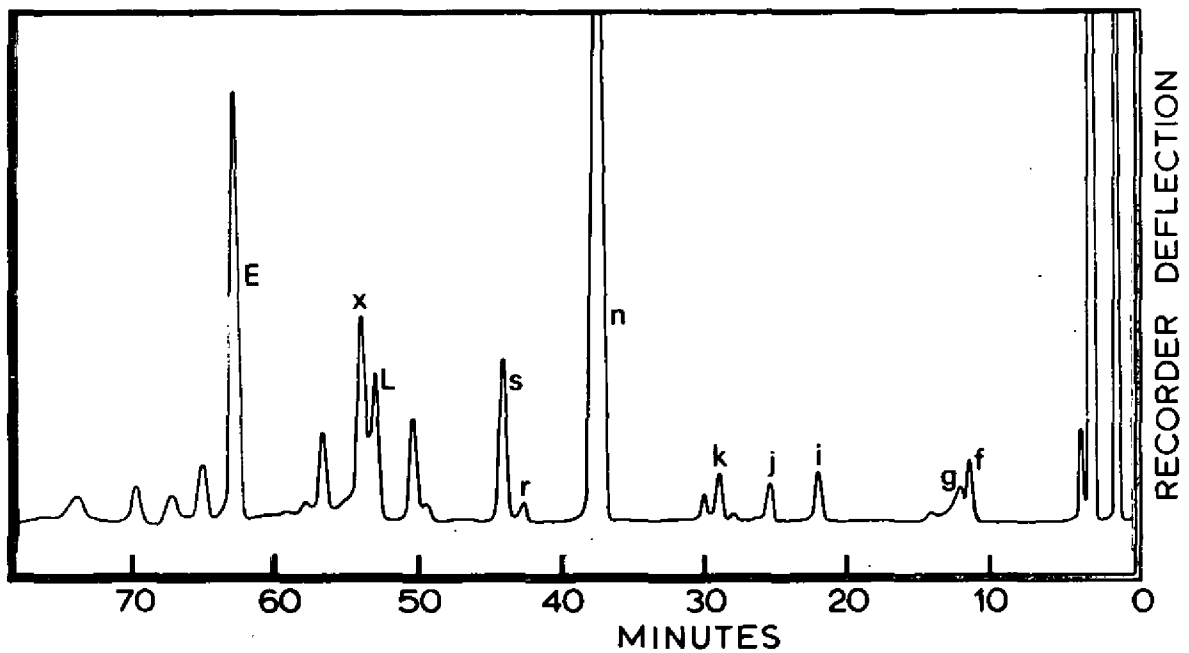
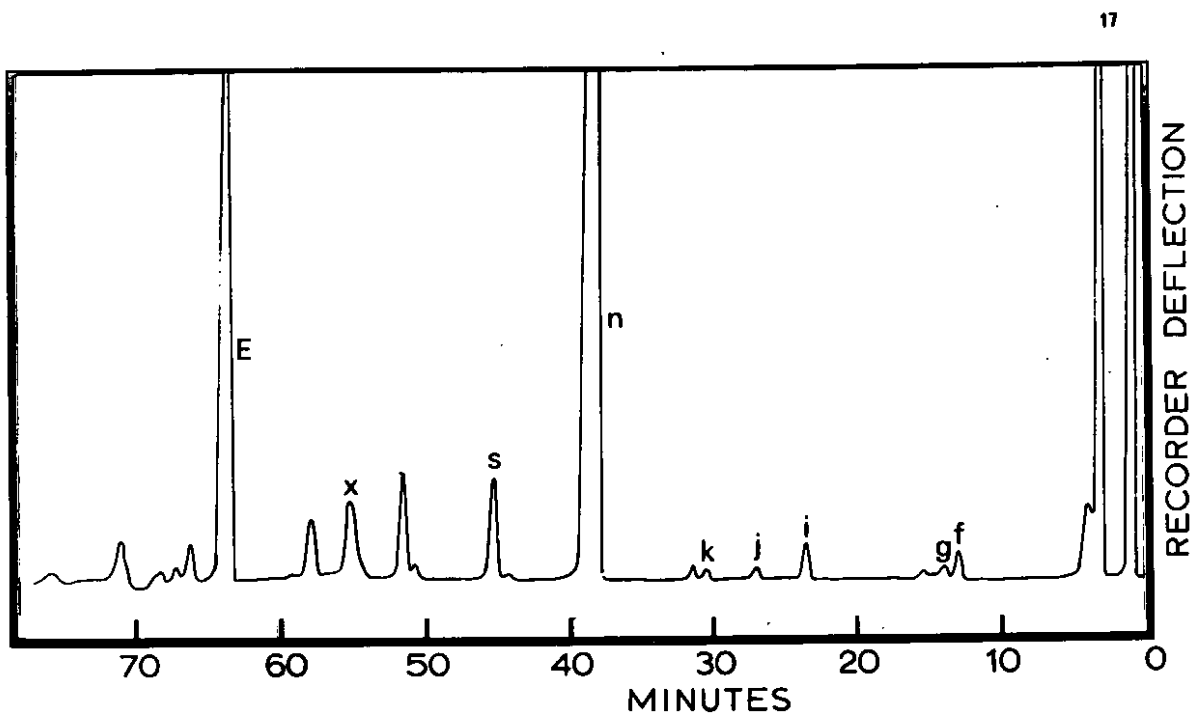


FIG. 11. DECOMPOSITION PRODUCTS OF SMOKES FROM FOAM C PREPARED AT 400°C THEN DECOMPOSED AT 600°C AND 900°C

a) ETHER EXTRACT MATERIAL



b) ETHER RESIDUE

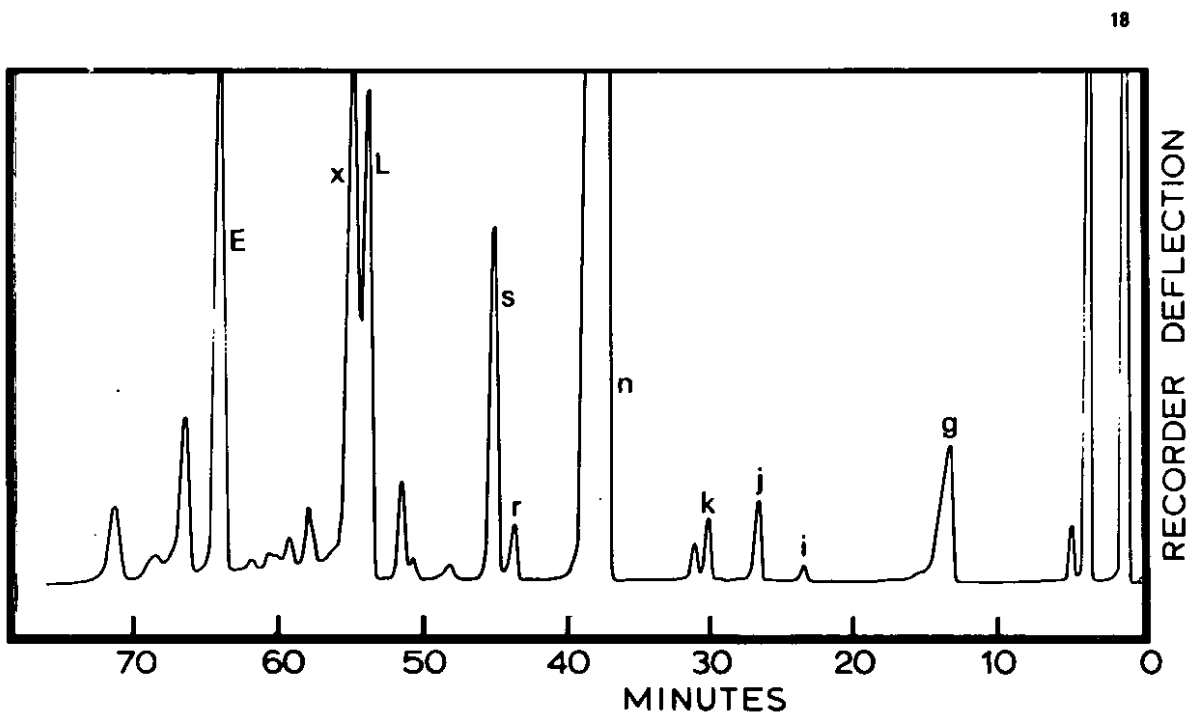
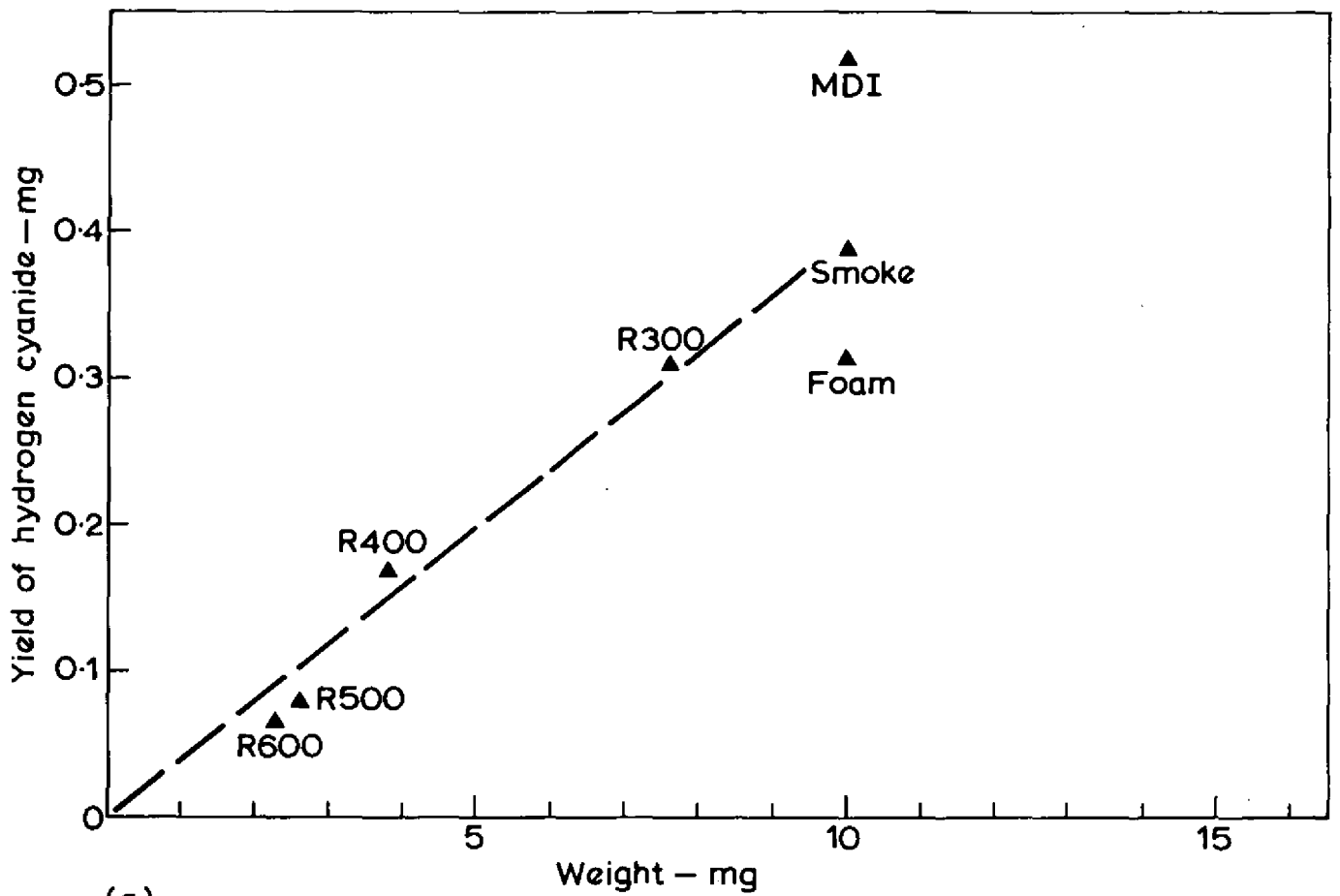
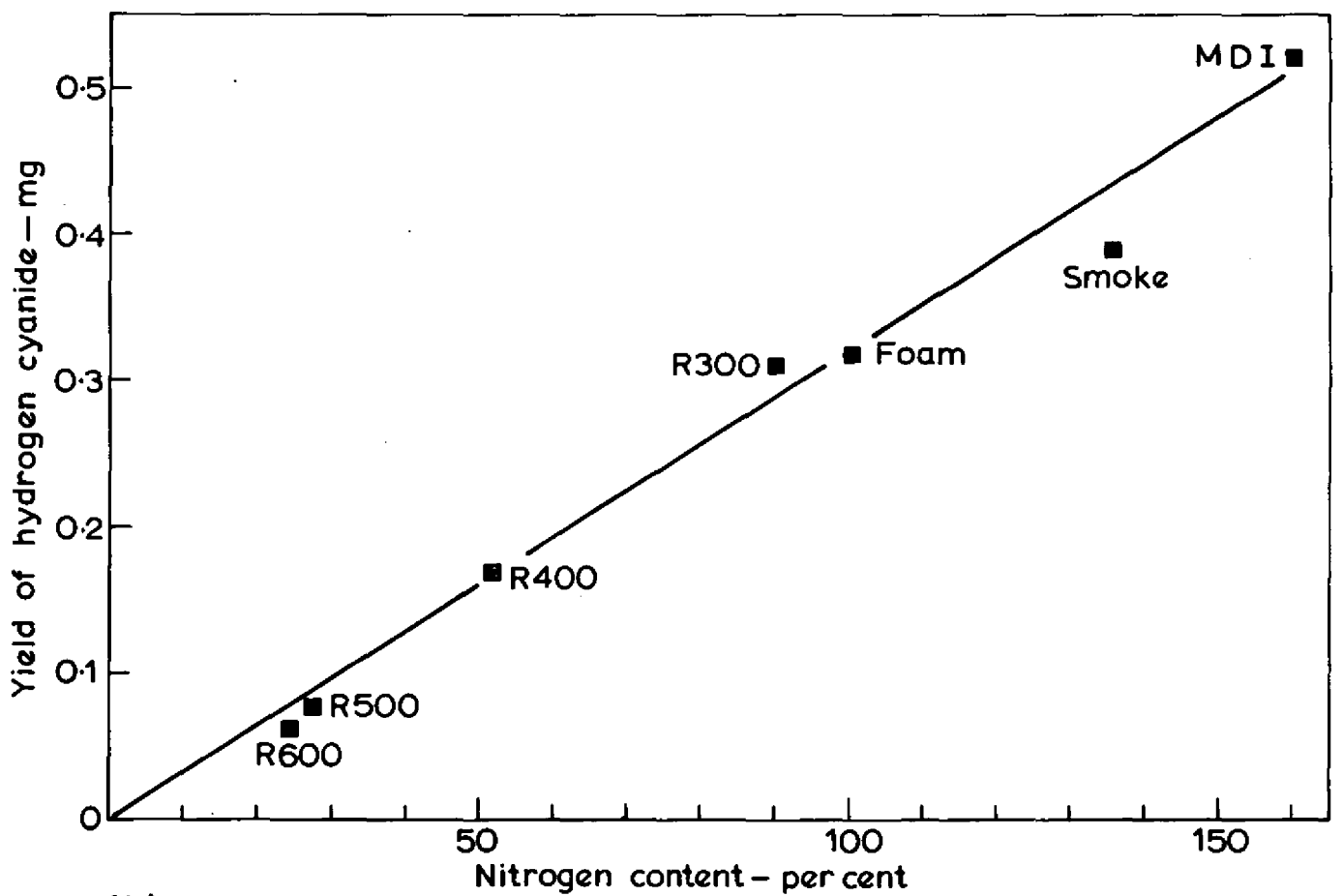


FIG. 12. DECOMPOSITION PRODUCTS OF SMOKES
FROM FOAM A PREPARED AT 600°C
THEN DECOMPOSED AT 900°C



(a)



(b)

Figure 13 Yields of hydrogen cyanide from pyrolysis residues, foam, smoke and MDI at 900 °C

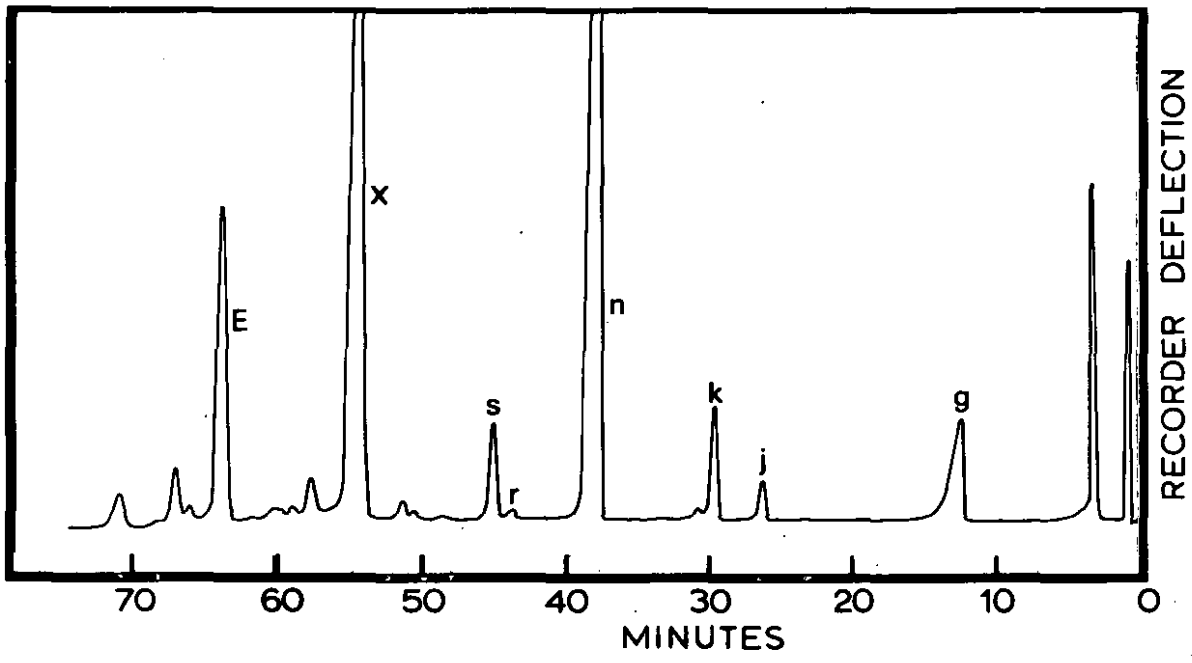


FIG. 14. DECOMPOSITION PRODUCTS OF MDI AT 900°C