Fire Research Note No 881

THE FORMATION OF NITROGEN-CONTAINING PRODUCTS FROM THE THERMAL DECOMPOSITION OF FLEXIBLE POLYURETHANE FOAMS

by

W. D. WOOLLEY, ANN I. WADLEY AND P. FIELD

August 1971

FIRE
RESEARCH
STATION

F.R.Note No. 881
August 1971

THE FORMATION OF NITROGEN-CONTAINING PRODUCTS FROM THE THERMAL DECOMPOSITION OF FLEXIBLE POLYURETHANE FOAMS

by

W. D. Woolley, Ann I. Wadley and P. Field

SUMMARY

The thermal decomposition of a polyester and a polyether flexible foam in a nitrogen atmosphere has been studied by gas chromatography, mass spectrometry and elemental ultramicroanalysis. It is shown that the decomposition behaviours of the two foams are similar. At low temperatures (200 to 300°C) there is a rapid and complete loss of the tolylene diisocyanate unit of each foam as a volatile smoke leaving a polyol residue. This smoke, which has been isolated as a yellow solid (common to both foams) is shown to contain all the nitrogen of the original foams. Under the conditions of this report the smoke is stable at temperatures up to 750°C. The nitrogen-containing products of low molecular weight (mainly hydrogen cyanide, acetonitrile, acrylonitrile, pyridine and benzonitrile) observed during the high temperature decompositions of the foams are shown to be derived from the decomposition of the yellow smokes. At 800°C, the 5 products listed above are present. At 900°C, hydrogen cyanide and benzonitrile are predominant and at 1000°C, hydrogen cyanide is virtually the only product. At 1000°C, approximately 70 per cent of the available nitrogen of the foams has been recovered as hydrogen cyanide.

KEY WORDS: gas chromatography, mass spectrometer, polyurethane foam, pyrolysis, toxic gas.

DEPARTMENT OF THE ENVIRONMENT AND FIRE OFFICES' COMMITTEE
JOINT FIRE RESEARCH ORGANIZATION

CONTENTS

CONTENTS

F.R.Note No. 881
August 1971

THE FORMATION OF NITROGEN-CONTAINING PRODUCTS FROM THE THERMAL DECOMPOSITION OF FLEXIBLE POLYURETHANE FOAMS

by

W. D. Woolley, Ann I. Wadley and P. Field

1. INTRODUCTION

a) General introduction

Polyurethane foams are becoming an important nitrogen-containing material present in buildings. The foams are mainly used in flexible form within the furnishings but some rigid foams are now used within the building structures.

When involved in fires there is concern that polyurethane foams may release toxic pyrolysis products containing nitrogen such as hydrogen cyanide, organic cyanides and ammonia. Nitrogenous products of this kind can be expected to be present in unburnt fire gases and could, in principle, seriously contribute to the toxicity of the fire gases.

Published studies of the thermal decomposition of polyurethane foams have hitherto been restricted to selected products[1], such as hydrogen cyanide. These studies have accounted for only a small fraction of the theoretically available nitrogen and yield little or no information on the main routes for the formation of nitrogenous products.

A preliminary study[2] of the decomposition of flexible and rigid polyurethane foams has shown that with the flexible foams, and contrary to the behaviour of the rigid foams, almost all of the available nitrogen can appear in the products of decomposition (15-minute periods) at temperatures as low as 300°C. For this reason the present study deals with two common flexible foams namely a polyester and a polyether type.

As far as possible all the nitrogenous products formed under specific conditions are identified and the way in which the proportions of these products vary with decomposition temperature is determined. It is shown that the initial and major decomposition product is a volatile yellow solid, appearing as a smoke, and that this smoke is the precursor of all the simpler nitrogenous products.

The study has been effected principally with the aid of coupled gas chromatograph - mass spectrometry for the separation and identification of the decomposition products. In this work comparisons have been made between the

chromatograms of the decomposition products of the foams and parent polyols in order to isolate products which are derived from the nitrogen part (i.e. the tolylene diisocyanate) of the foams.

Details are recorded of various techniques developed for the collection of the smoke for volatity tests and studies by elemental ultramicroanalysis.

A brief outline of the chemistry of polyurethane foams is presented since knowledge of this kind is of help for understanding the general principles of the decomposition processes.

b) Chemistry of polyurethane foams

The detailed chemistry of both rigid and flexible polyurethane foams can be found in a number of excellent texts[3-6] and only the general details will be recorded here with an emphasis on flexible foams.

The fundamental reaction in polyurethane chemistry is the interaction between an isocyanate (R.NCO) and alcohol ($R^1.OH$) as in reaction (1); other important

$$R.NCO + R^1.OH \longrightarrow R.NH.CO.OR^1 \quad \text{.....reaction (1)}$$

reactions occur between isocyanate units and groups such as COOH and NH_2. The general name of 'polyurethane' refers to a series of polymers where the urethane type of link (i.e. as in $R.NH.CO.OR^1$) is repeated. For example if a diisocyanate $R(NCO)_2$ is linked to a dihydric alcohol $R^1(OH)_2$, a linear polyurethane can be prepared with the general type of formula:

$$- O.R^1 .O.CO. NH. R. NH. CO -$$

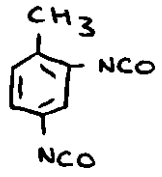
The cellular structure of the foam is generated in a number of ways normally by the addition of water which reacts with the isocyanate giving carbon dioxide as the blowing agent by reaction (2), with the

$$R.NCO + H_2O \longrightarrow R.NH_2 + CO_2 \quad \text{.....reaction (2)}$$

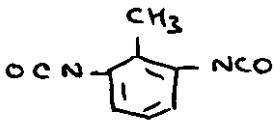
amine further reacting with additional isocyanate.

In present day foams two diisocyanates are commonly used, namely tolylene diisocyanate (known as T.D.I. and used predominantly in flexible foams) and diphenylmethane diisocyanate (known as M.D.I. and used mainly in rigid foams). The chemical structures of the two materials are given below:

(i) Tolylene diisocyanate (2:4 and 2:6 isomers)

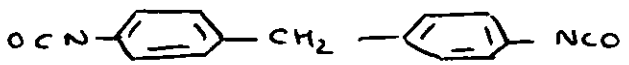


2:4 isomer



2:6 isomer

(ii) Diphenyl methane 4,4' diisocyanate



It should be noted that both isocyanates are toxic. The T.L.V.[7] of the 2:4 isomer of T.D.I. is quoted as 0.02 p.p.m; it is irritating to the nose and throat at 0.5 p.p.m.

The alcohols commonly used with T.D.I. and M.D.I. in the manufacture of foams are not simple alcohols but are themselves polymers. These polymers, often termed parent polyols or simply polyols, are based on either polyester or polyether units (i.e. with repetitive ester or ether links throughout the polymer chain). The rigid or flexible structure of the foams is determined by a number of features but mainly by the degree of cross linking of the polyols.

With flexible foams, typical polyester polyols are prepared from adipic acid ($HOOC(CH_2)_4$ COOH) and diethylene glycol to give hydroxyl terminated polyesters. Typical polyether polyols are prepared from the polymerization of propylene oxide and glycerol. Foams, based on similar compositions to the typical polyols given above, have been used in the decomposition experiments of this report.

There are two main processes used in the manufacture of flexible foams, firstly a prepolymer and secondly a one-shot process. In the prepolymer method the polyol is reacted with an excess of diisocyanate to give an isocyanate terminated prepolymer. The prepolymer has a useful shelf life and is foamed by the addition of water. Semi-polymers are sometimes used where the diisocyanate is reacted with a portion of the polyol giving a low molecular weight polymer dissolved in an excess of diisocyanate. Foaming is achieved by adding the remainder of the polyol and water.

In the one-shot process the reactants (including water) are reacted simultaneously to produce the foam.

2. EXPERIMENTAL

a) The main decomposition system.

The decomposition system used in this report is essentially the same as outlined in a number of recent reports involving the thermal decomposition of PVC[8] and phenol-formaldehyde resins[9]. For convenience the main details of the system are shown diagrammatically in Fig 1 and described briefly below.

Weighed samples of the material under study are placed into a small ceramic boat which is introduced into the furnace (temperature stability $\pm$ 1°C at 500°C)

by the influence of an external magnet on the steel plug P. During the decomposition a flow of dry nitrogen (B.O.C. white spot grade) is maintained through the silica furnace tube at 100 ml/min to carry the volatile decomposition products along the heated outlet tube and into a heated stainless steel gas sampling valve coupled in the usual way to a research gas chromatograph. During a collection period (15 min) the nitrogen from the furnace is directed through the collecting loop (stainless steel tubing, 3.2 mm o.d.) and condensable materials are trapped from the gas stream by surrounding the loop with a refrigerant (liquid nitrogen at -196°C). During this collection period an internal bypass in the valve maintains the supply of helium to the chromatograph.

After collection, the products are transferred to the chromatograph by turning the valve to the inject position, removing the refrigerant and heating the collecting loop quickly to 200°C by direct electrical heating supplied with a variable 10 volt-50 amp transformer.

The stainless steel valve and flow lines coupling the valve to the furnace tube and chromatograph respectively are controlled at approximately 150°C in order to avoid problems from the absorption and condensation of analysable products prior to chromatography.

b) Furnace systems for smoke collection and volatility tests.

The thermal decomposition of the foams was accompanied by the formation of smokes which condensed as yellow solids on the cooler walls of the furnace tube and also tended to block the valve and heated lines (150°C) of the main decomposition system.

Separate furnace systems were devised for studies of the smoke (later termed yellow smokes) firstly to collect small quantities of smoke for volatility tests and secondly to collect substantial quantities for further experimental studies. The two furnace systems are outlined below.

The furnace system for the smoke collection and volatility tests is shown diagrammatically in Fig 2 and consists of a sliding tube furnace fitted around a borosilicate furnace tube (10 mm o.d.). A weighed piece of glass wool (A) is inserted into the furnace tube as shown for smoke collection. In Fig.2(a), a weighed sample of polyurethane foam (100 mg) is decomposed in a ceramic boat in a stream of oxygen-free nitrogen at 50 ml/min. The smoke is collected in the plug A which can be removed for weighing (the furnace slightly overlaps plug A in order to prevent any condensation of smokes on the side of the furnace tube prior to reaching the plug. After the decomposition period, the ceramic boat and residual polyurethane are removed and the furnace cooled and moved to the position shown in Fig.2(b). The volatility of the smoke can be tested by monitoring the amount of smoke which is lost from Plug A at various furnace temperatures.

A number of different furnace and collection systems were examined for collecting substantial quantities of yellow smokes for analytical studies. The final method adopted is shown in Fig.3. It consists of a 380-mm tube furnace (controlled at 300°C) fitted with a glass furnace tube (18 mm o.d.) as shown. Samples of polyurethane foam (100 to 500 mg) are introduced into the furnace in a ceramic boat by the influence of a magnet on the steel plug. A flow of nitrogen (B.O.C. white spot grade) at 100 ml/min carried the yellow smokes to a short length of glass tubing (6 mm o.d.) fitted into the exit end of the furnace tube with a rubber bung as shown. After a number of repetitive decompositions (10 to 15 minute periods each) the glass collection tube is removed and the yellow needle like crystals on the tip of the tube are removed with a spatula.

c) Chromatography

A Hewlett Packard 5750 Research Chromatograph fitted with simultaneous dual flame ionization and thermal conductivity detectors was used. The products were separated using Porapak Q columns (2 m x 3.2 mm in stainless steel) temperature programmed from 30°C to 265°C at 4°C/min with a helium flow rate of 40 ml/min.

For quantitative analysis of the decomposition products, peak areas were determined using a Hewlett Packard 3370 A automatic electronic integrator with printout facilities.

d) Mass spectrometry

For the identification of materials separated by the gas chromatograph, mass spectra were obtained using a fast scanning version (termed 'Rapide') of the organic A.E.I. MS 20 coupled directly to the chromatograph. Essentially the instrument is a magnetic scanning unit with a resolution of 1 in 475 at 10 per cent valley. Additional details and a general evaluation of the coupled GC-MS system have been recorded in an earlier publication[10]. All spectra were recorded at 70 eV and were interpreted using the spectral data compiled by Cornu and Massot[11].

e) Elemental analysis studies

All elemental analyses were undertaken using a commercial elemental ultramicroanalyser using samples weighing approximately 500 μg. Details of the application of elemental analysis to studies of the thermal decomposition of polyurethane foams has been presented[2]. The quoted accuracy of the analyser is %C ± 0.25 per cent, %H ± 0.10 per cent and %N ± 0.30 per cent. Oxygen is obtained by difference from 100 per cent.

f) Materials

Samples of polyester and polyether foams (flexible) together with samples of the respective parent polyols were obtained commercially. Both foams were prepared from tolylene diisocyanate. The polyester foam is based on a lightly branched polyester of adipic acid and diethylene glycol and the polyether foam prepared from a polyether (mean molecular weight of 3500) produced from glycerol, propylene oxide and ethylene oxide. A very small addition of green pigment is present with the polyether foam.

The samples of organic nitriles and pyridine used in calibration and direct seeding experiments were obtained commercially. Hydrogen cyanide was prepared by the action of dilute sulphuric acid on an excess of potassium cyanide.

3. RESULTS

a) Weight-loss and elemental analysis studies.

Table 1 shows the experimental elemental analyses of the polyester and polyether foams (from an earlier report)[2] and the respective parent polyols. Each recorded value represents a mean experimental figure. Also shown in Table 1 are the percentages of tolylene diisocyanate (T.D.I.) and polyol in each foam, calculated from the experimental compositions of each foam and the theoretical composition of T.D.I. (62.1 per cent C, 3.45 per cent H, 16.1 per cent N).

TABLE 1. Elemental analyses (C, H and N)[ø] of polyurethane foams and parent polyols and the calculated compositions of the foams

	Polyurethane			Polyol			Foam composition*	
	C%	H%	N%	C%	H%	N%	T.D.I(%)	Polyol (%)
Polyester	59.2	6.9	4.3	54.0	7.4	0	26.7	73.3
Polyether	61.3	9.0	4.1	60.3	10.1	0	25.4	74.6

*by weight ø oxygen by difference from 100%

When decomposed for 15-minute periods in an inert atmosphere at low temperatures, it has been shown[2] (by elemental analyses of the residues) that the two foams preferentially release the nitrogen contents. Fig.4 shows the weight-losses and the nitrogen-losses (as percentages of the theoretical losses) at temperatures between 200 and 300°C re-recorded from the earlier report. From this figure it is clear that the decomposition behaviours of the two foams are similar and at 300°C there is a virtually complete loss of nitrogen with a weight-loss of only about 35 per cent in each case.

b) Preliminary Chromatographic experiments

Because of the virtually quantitative loss of nitrogen during the thermal decompositions of the two foams at 300°C, chromatographic analyses of the decomposition products were first undertaken at this temperature. In these experiments 10-mg samples of each foam were decomposed in turn in the furnace at 300°C for 15-minute periods in a flow of oxygen-free nitrogen at 100 ml/min. The products were collected using liquid nitrogen (-196°C) as the refrigerant and injected into the chromagraph as outlined in the experimental section.

Comparitive chromatograms were then obtained by decomposing the parent polyol of each foam under identical conditions as used for the foams. The weight of each polyol was chosen to represent the weight present in the 10 mg of each foam as recorded (by per cent composition) in Table 1. For 10 mg of each foam, this represents 7.3 mg of polyester polyol and 7.5 mg of polyether polyol. These comparative tests involving the polyols were undertaken in order to provide reference chromatograms such that by superimposing the respective chromatograms of the foam and respective polyol, the chromatographic peaks associated with the T.D.I. (i.e. the nitrogen-containing part of the foam) would be distinct.

Fig.5 shows the chromatograms of the decomposition products of the polyester foam (10 mg) and polyol (7.3 mg) recorded by the flame ionization detector (F.I.D.) at an attenuation of 10^2 x 8. The equivalent data for the polyether foam (10 mg) and polyol (7.5 mg) are given in Fig.6.

From previous experience of the sensitivity of the chromatograph it is clear that the total quantities of products detected by chromatography at 300°C from both the polyester and polyether foams are very small*. Further, although some fine detail may be lost during the duplication processes, there are distinct similarities between the chromatograms of each foam and the respective polyol. In the polyester case (Fig.5), although there are differences between the intensities of the peaks from the foam and polyol, it is evident that these peaks in the chromatogram of the foam are derived from the polyol content. With the polyether (Fig.6) there is a larger number of products than in the polyester case but once again all products appear to be derived from the polyol. Also, the polyether polyol appears to be more thermally stable when present in the foam than alone.

---

*The F.I.D. chromatograms indicate quantities of the order of a few microgrammes.

From earlier experiments, it has been established that both foams show a weight loss of approximately 35 per cent (i.e. approximately 3.5 mg for 10 mg of foam) during decomposition at 300°C. From the chromatographic experiments outlined above it is clear that the main products are not amenable to analysis in this way being either unstable under the conditions of analysis or, more likely, of too large a molecular weight for analysis by Porapak Q. Further, the small quantities of products detected at 300°C are derived from the polyol content of each foam. There is no evidence of products which can be attributed to the decomposition of the T.D.I. part of the foams.

In addition to the experiments at 300°C, product analyses by chromatography were also undertaken at 400 and 600°C. Fig 7 and 8 show the chromatograms of the decomposition products of the polyester foam (10 mg) with polyol (7.3 mg) and the polyether foam (10 mg) with polyol (7.5 mg) respectively at 400°C. The equivalent data for 600°C is shown in Fig.9 and 10. All chromatograms were recorded with flame ionization detection using the same attenuation (10^2 x 8) as used in the experiments at 300°C.

From Fig 7 to 10 inclusive it is clear that both foams produce a complex range of decomposition products; as expected the number and intensities of the products increase with increasing temperatures. Further, the chromatograms of the two foams (i.e. polyester and polyether) are quite different and this phenomena is very useful in 'finger printing' unknown types of foam. However, the most important features of Fig.5 to 8 inclusive are the similarities between the decomposition products of each foam and respective polyol. There is no evidence in the chromatograms of the foams of material generated in any way other than by the decomposition of the polyol. It therefore seems likely that the material 'lost' at 300°C with a weight loss of approximately 35 per cent for each foam is the tolylene diisocyanate* (T.D.I.) unit. This T.D.I. unit is common to both foams (26.7 and 25.5 per cent by weight for the polyester and polyether foams respectively as given in Table 1) and loss of this unit could explain the similarities between the weight-losses of the two foams between 200 and 300°C and the rapid loss of nitrogen at these temperatures. The additional weight-losses at 300°C between the observed values (39 and 34 per cent for the polyester and polyether foams respectively) and the weight-losses due to T.D.I. may be

---

*but not necessarily as free T.D.I.

associated with the loss of relatively low molecular weight polyol, carbon dioxide or water from the polyol in the foam.

c) Preliminary smoke investigations

During the decomposition experiments recorded earlier in this report, it was evident that the decomposition of each foam was accompanied by the formation of a smoke which condensed in various parts of the decomposition apparatus as a yellow solid. An experimental furnace system for collecting small quantities of the smoke for volatility tests has been outlined in the experimental section (see section 2(b) and Fig.2).

The results obtained from the smoke generated from the decomposition of 100 mg of polyester and polyether foams at 300°C and the volatilities of the smokes are recorded in Table 2. Volatility tests were undertaken at 100, 200 and 300°C.

Table 2. Smoke collection and volatility tests

a) Smoke collection (300°C)

	Polyester	Polyether
Initial weight of foam - mg	100	100
Weight-loss (15 minutes) - mg	38.2	33.1
Weight-gain of plug A - mg	27.6	26.8

b) Volatility tests (100 - 300°C)

Temperature °C	Total weight-loss of plug A (15 minutes)-mg	
	Polyester	Polyether
100	2.3	2.8
200	7.9	8.3
300	25.4	22.0

In Table 2 it is clear that the main material 'lost' at 300°C in each case is recovered in the glass wool plug. The loss in weight of each foam is in agreement with the weight loss experiments of an earlier report; also, the weights recovered on the plug A are of a similar magnitude to the experimental weight percentages of T.D.I. in the foams. The smoke volatility tests confirm that the smokes can be revolatilised but do not clarify their chemical composition (i.e. whether they are built up of one or many chemical species). It is however, quite evident from the experiments that the smokes are not free T.D.I.

Using the smoke collection system of Fig 2(a), a number of repetitive decompositions (100 mg each) were undertaken at 300°C using firstly the polyester and secondly the polyether foam in order to collect sufficient quantities for elemental ultramicroanalysis. In these decomposition experiments each foam produced a similar yellow solid which formed needle-like crystals on the glass wool. The crystals were insoluble in acetone, benzene, pentane, carbon tetrachloride, trichlorethane, ethanol and water, but sufficient quantities for elemental ultramicroanalysis were removed from the glass wool with a pair of tweezers. The elemental analyses are recorded in Table 3.

Table 3 Elemental analyses (C, H and N)[ø] of the yellow smokes from the polyester and polyether foams by glass wool collection

Origin of yellow smoke	Elemental Analysis		
	C%	H%	N%
Polyester foam	63.5	5.9	17.3
Polyether foam	64.2	5.6	17.0

ø oxygen by difference from 100%

From Table 3 it is evident that both foams produce similar yellow smokes with elemental compositions not unlike that of T.D.I. (62.1% C, 3.45% H, 16.1% N). From the experiments to date it is concluded that the decomposition of both foams proceeds via the quantitative loss of the T.D.I. unit. Volatility tests confirm that the material is not free T.D.I.; it may be a polymer of T.D.I. or a polymer of a material structurally similar to T.D.I.

d) Collection of yellow smokes

A number of different furnace and collection systems were examined for collecting substantial quantities of yellow smokes for analytical studies and the final method adopted has been outlined in the experimental section (see section 2(b) and Fig 3). In this way approximately 200 mg of yellow smoke from each foam was prepared; this process taking approximately 1 day per 100 mg. In some experiments where the needle crystals were very small the smoke tended to be white rather than yellow.

Table 4 shows the elemental analyses of two samples of yellow smoke from firstly the polyester and secondly the polyether foam cut at different places from blocks of each foam. These elemental compositions are in good agreement with the values recorded by glass wool collection (Table 3).

Table 4 Elemental analyses (C, H and N)$^{\phi}$ of yellow smokes from the polyester and polyether foams by direct collection

Yellow smoke	Sample	Elemental analysis		
		C%	H%	N%
Polyester	1	64.2	6.0	17.5
	2	64.3	5.9	17.5
Polyether	1	64.3	5.7	17.1
	2	64.2	5.7	17.0

ϕ oxygen by difference from 100%

The nitrogen contents of the two yellow smokes are both slightly larger than that of T.D.I. (16.1%). This difference in each case may be due to an initial loss of T.D.I. as a polymer during the decomposition of each foam at 300°C and a subsequent loss of water and/or carbon dioxide (which would not be detected in the chromatographic experiments with flame ionization detection in section 3(b)) to give yellow smokes richer in nitrogen than T.D.I. Alternatively the yellow smokes (with the experimental composition of Table 4) may be released directly from the foam. Assuming conservation of nitrogen during the formation of the yellow smokes, the contents of yellow smoke (calculated from Tables 1 and 4, and rounded to the nearest 0.1 mg) are 2.5 and 2.4 mg in 10 mg of polyester and polyether foam respectively. These quantities will be used throughout this report as representing the amounts of yellow smoke available from the 10 mg of each foam.

e) G.C - MS Analysis of the decomposition products of the yellow smoke.

For chromagraphic analysis of the decomposition products of the yellow smoke, samples representing the amounts which would be generated from 10 mg of each foam (i.e. 2.5 and 2.4 mg of yellow smoke for the polyester and polyether foams respectively - see section 3(d)) were pyrolysed in the decomposition furnace and the products (collected at -196°C) introduced into the chromatograph as outlined in the experimental section. In this work no products were detected during a complete temperature programmed chromatographic analysis at decomposition temperatures up to 750°C for either the polyester or polyether yellow smoke. At temperatures between 800 and 1000°C (maximum temperatured used) both yellow smokes produced distinct but similar chromatograms. Fig.11 and 12 show the chromatograms (flame ionization and thermal conductivity detection) of the decomposition products of the polyester and polyether yellow smoke respectively at 850°C. From these figures it is evident that both yellow smokes (i.e. from the polyester and polyether foams) are chemically similar.

The peaks in each chromatogram have been labelled alphabetically for identification purposes.

Using coupled gas chromatography-mass spectrometry, mass spectra were obtained of all chromatographic peaks detected during the decomposition of the polyester yellow smoke at 850°C* (i.e. as shown by the chromatograms of Fig.11). Spectra were interpreted by the data of Cornu and Massot[11] as shown in Table 5; the interpretations of all significant peaks were confirmed by direct seeding experiments as indicated.

---

* GC-MS studies were undertaken at 850°C since this temperature provided the most suitable intensities of all components, separated by gas chromatography, for mass spectrometry.

Table 5 Analyses of the decomposition products of the polyester yellow smoke at 850°C by mass spectrometry and direct seeding experiments

Peak nomenclature	Mass spectrometric interpretation	Direct seeding confirmation
a	Nitrogen[x]	-
b	Carbon dioxide	-
c	Ethylene	Ethylene
d	Ethane	Ethane
e	Water**	Water
f	Propane	-
g	Hydrogen cyanide	Hydrogen cyanide
h	Not identified*	-
i	Butyne or butadiene	-
j	Acetonitrile	Acetonitrile
k	Acrylonitrile	Acrylonitrile
l	Propionitrile	Propionitrile
m	Methyl Acrylonitrile or	-
	Vinyl Acetonitrile	-
n	Benzene	Benzene
o	Methyl acrylonitrile or	-
	Vinyl acetonitrile	-
p	Not identified*	-
q	Pyrrole	-
r	Pyridine	Pyridine
s	Toluene	Toluene
t	Methyl pyridine[ø]	-
u	Methyl pyridine[ø]	-
v	Cyclooctatetrene or	-
	Styrene	-
w	Vinyl pyridine	-
x	Benzonitrile or	Benzonitrile
	benzamide	-
y	Not identified*	-
z	Indene	-
A	Methyl cyanobenzene[#]	-
B	Methyl cyanobenzene[#]	-
C	Not identified*	-
D	Not identified*	-
E	Naphthalene	-
F	Quinoline or	-
	Iso-quinoline	-
G	Not identified	-

x furnace carrier gas
* not identified - mass spectrum very small
ø other possibility - aniline
\# other possibilities - phenyl acetonitrile or indole
** peak e also contained traces of ammonia

Mass spectra were then obtained of the main components during the decomposition of the polyether yellow smoke at 850°C; mass spectral interpretations were again confirmed by direct seeding experiments as shown in Table 6.

Table 6. Identifications of the main decomposition products of the polyether yellow smoke at 850°C by mass spectrometry and direct seeding experiments

Peak nomenclature	Mass spectrometric interpretation	Direct seeding confirmation
c	ethylene	ethylene
d	ethane	ethane
e	water	water
g	hydrogen cyanide	hydrogen cyanide
j	acetonitrile	acetonitrile
k	acrylonitrile	acrylonitrile
n	benzene	benzene
r	pyridine	pyridine
s	toluene	toluene
x	benzonitrile or benzamide	benzonitrile

f) High temperature decomposition experiments with the foams and parent polyols.

Because of the observed decomposition products of the yellow smokes at high temperatures, studies of the decomposition products of the foams and respective polyols were undertaken at 850°C. These experiments were carried out in a similar manner to those of Section 3(b), namely using 10 mg of foam and 7.3 or 7.5 mg of polyester or polyether polyol respectively. The products were monitored using simultaneous flame ionization and thermal conductivity detection. The chromatograms (F.I.D.only) obtained at 850°C for the polyester foam with polyol and the polyether foam with polyol are recorded in Fig 13 and 14 respectively.

The chromatograms of the two parent polyols in Fig 13 and 14 are similar and much simpler than the chromatograms recorded at 600°C (Fig 7 and 8). Further, because of the regular spacing of the peaks in each chromatogram, it is likely that the products consist mainly of hydrocarbons at this temperature.

By comparing the chromatograms of the foams and respective polyols in Fig 13 and 14, it is evident that additional products are generated from the decomposition of the foams. Close examination shows that the additional peaks are the same for each foam (i.e. polyester or polyether) and also the same as in the chromatograms (F.I.D.) of the decomposition products of the yellow smokes at 850°C (Fig 11 and 12). In order to clarify this point, the

alphabetical notation of certain peaks from the decomposition of the yellow smokes (Fig 11 and 12) have been recorded on the foam chromatograms of Fig 13 and 14; it should be noted, of course, that some peaks are common to both the polyols and the yellow smokes.

It is clear that the decomposition of the foams proceeds by the release and decomposition (depending upon the temperature) of yellow smoke and the separate decomposition of the polyol part of the foam. Even at 850°C, there is no evidence of any chemical interactions between the products of the two routes.

g) Chromatographic calibration experiments

Chromatographic calibration experiments were undertaken in order to determine quantitatively the amounts of nitrogen-containing products generated during the thermal decomposition of the yellow smokes and foams. For these calibration experiments, known quantities of hydrogen cyanide, acetonitrile, acrylonitrile, benzene, pyridine and benzonitrile were injected directly into the chromatograph and the peak areas (in arbitrary units) obtained by automatic electronic integration, were plotted as functions of the weight of each material firstly for the flame ionization detector (Fig 15) and secondly for the thermal conductivity detector (Fig 16 and 17). Both detectors were calibrated because of the low sensitivities of certain nitrogen-containing materials to flame ionization detection. For the calibration, all materials excluding hydrogen cyanide were injected into the chromatograph using a 1 - μl syringe. Hydrogen cyahide calibrations were undertaken using gaseous samples because of difficulties of monitoring the hydrogen cyanide peak with the thermal conductivity detector in the presence of large quantities of water when using dilute prussic acid solutions. Benzene was used in calibration experiments firstly to provide a convenient standard, secondly because of its presence in the decomposition products and thirdly in order to extend the calibrations to the C_2 hydrocarbons and toluene by the data* of Dietz[12].

A summary of the chromatographic sensitivities of the various materials recorded from the best straight lines (drawn by eye) through each set of points in Fig 15, 16 and 17 and the data for the C_2 hydrocarbons and toluene (by Dietz) are summarized in Table 7.

---

* On flame ionization detection, hydrocarbons have a relative sensitivity of near unity. Benzene is an exception with a value of 1.12.

Table 7. Chromatographic sensitivities of various nitrogen-containing materials and certain hydrocarbons

Material	Chromatographic sensitivity	
	F.I.D. (arbitrary units x 10^4 per mg)	T.C.D. (arbitrary units x 10^2 per mg)
hydrogen cyanide	38	5240
acetonitrile	640	6660
acrylonitrile	965	5300
benzene	2230	4700
pyridine	1305	4100
benzonitrile	1415	4400
C_2hydrocarbons*	2030	-
toluene*	2130	-

*by Dietz using benzene as reference material

h) Quantitative analyses of the decomposition products of the yellow smokes and foams.

Chromatographic analyses of the decomposition products of each yellow smoke (2.5 and 2.4 mg for the polyester and polyether products respectively) were undertaken at 800, 900 and 1000°C with peak area integration of the main products shown in the calibration data of Table 7. All products with the exception of hydrogen cyanide were monitored with the flame ionization detector; hydrogen cyanide was monitored by thermal conductivity. For comparison purposes certain products (hydrogen cyanide, acetonitrile and benzonitrile) were also measured during the thermal decomposition of each foam (10 mg) again at 800, 900 and 1000°C;it was not possible to measure the other products (derived from the yellow smoke) of the foams due to interference from the decomposition products of the polyols.

The data giving the quantities of these products in microgrammes for the polyester yellow smoke with foam and the polyether yellow smoke with foam are recorded in Tables 8 and 9 respectively.

The relevant integrator counts are recorded in Appendix 1 and 2 respectively.

In Tables 8 and 9, the quantities and temperature dependence of the products from the yellow smoke and from the respective foam (where measured) show a general agreement. Further, the products from each yellow smoke (and also from each foam) are in general agreement.

For the yellow smokes, all materials excluding benzene and hydrogen cyanide show a tendency for a maximum rate of production at 900°C. Benzene and hydrogen cyanide increase markedly with temperature throughout.

It is apparent from Tables 8 and 9 that in studies of the nitrogen-containing products, the decomposition of each foam can be adequately represented by the decomposition of an equivalent weight (on a nitrogen basis) of yellow smokes.

Table 8

THE DECOMPOSITION PRODUCTS OF THE POLYESTER YELLOW SMOKE (2.5 mg) and CERTAIN EQUIVALENT PRODUCTS FROM THE POLYESTER FOAM (10 mg) BETWEEN 800 and 1000°C ø

Product	Peak letter	Yellow Smoke (µg)			Foam (µg)		
		800°C	900°C	1000°C	800°C	900°C	1000°C
C_2 hydrocarbons	c, d	53.2	81.1	19.3	-*	-	-
hydrogen cyanide	g	26.9	162	549	39.8	285	619
acetonitrile	j	21.4	34.8	15.6	42.3	78.8	28.4
acrylonitrile	k	11.0	23.6	3.9	-*	-	-
benzene	n	5.8	71.8	98.8	-*	-	-
pyridine	r	6.4	34.7	2.4	-*	-	-
toluene	s	4.1	5.6	0.2	-*	-	-
benzonitrile	x	28.6	125	42.0	84.7	212	51.4

* not determined due to interference from polyol

ø 2.5 mg of polyester yellow smoke has the same nitrogen content as 10 mg of polyester foam.

Table 9

THE DECOMPOSITION PRODUCTS OF THE POLYETHER YELLOW SMOKE (2.4 mg) AND CERTAIN EQUIVALENT PRODUCTS FROM THE POLYETHER FOAM (10 mg) BETWEEN 800 AND 1000°C ϕ

Product	Peak letter	Yellow Smoke (μg)			Foam (μg)		
		800°C	900°C	1000°C	800°C	900°C	1000°C
C_2 hydrocarbons	c,d	36.8	38.5	26.5	-*	-	-
hydrogen cyanide	g	23.0	142	546	55.1	243	522
acetonitrile	j	26.8	32.0	18.7	45.0	62.7	30.5
acrylonitrile	k	12.7	21.7	4.6	-*	-	-
benzene	n	6.3	37.9	101	-*	-	-
pyridine	r	5.6	19.7	1.2	-*	-	-
toluene	s	4.9	6.5	0.4	-*	-	-
benzonitrile	x	36.1	102	41.6	74.8	230	41.8

* not determine due to polyol interference

ϕ 2.4 mg of polyether yellow smoke has the same nitrogen content as 10 mg polyether foam.

i) Experimental recoveries of nitrogen

The nitrogen recoveries (recorded as percentages of the available nitrogen) for the nitrogen-containing materials of Tables 8 and 9 are given in Tables 10 and 11 respectively. Also recorded are the total nitrogen recoveries for each temperature. From these Tables it is clear that the total nitrogen recoveries increase markedly with temperature. The maximum total recoveries (recorded at 1000°C) for the yellow smokes and foams are of the order of 70 to 80 per cent of the available nitrogen. The temperature dependence between 800°C and 1000°C indicates that the total recoveries would increase further at temperatures above 1000°C.

Table 10

NITROGEN RECOVERIES FROM THE THERMAL DECOMPOSITION OF POLYESTER YELLOW SMOKE (2.5 mg) AND FOAM (10 mg) BETWEEN 800 and 1000°C

Material	Per cent ø nitrogen (%)	Nitrogen recovery (%) Yellow Smoke			Nitrogen recovery (%) Foam		
		800°C	900°C	1000°C	800°C	900°C	1000°C
hydrogen cyanide	51.8	3.2	19.5	66.1	4.8	34.3	74.6
acetonitrile	34.2	1.7	2.8	1.2	3.4	6.3	2.3
acrylonitrile	26.4	0.7	4.4	0.2	-	-	-
pyridine	17.7	0.3	1.4	0.1	-	-	-
benzonitrile	13.6	0.9	4.0	1.3	2.7	6.7	1.6
TOTAL	-	6.8	29.1	68.9	10.9*	47.3*	78.5*

Note: nitrogen content of 2.5 mg of polyester yellow smoke or 10 mg of polyester foam is 430 µg.

* sub-totals for hydrogen cyanide, acetonitrile and benzonitrile only.

ø of product.

Table 11

NITROGEN RECOVERIES FROM THE THERMAL DECOMPOSITION OF POLYETHER YELLOW SMOKE (2.4 mg) AND FOAM (10 mg) BETWEEN 800 AND 1000°C

Material	Per cent ϕ nitrogen (%)	Nitrogen recovery (%) Yellow Smoke			Nitrogen recovery (%) Foam		
		800°C	900°C	1000°C	800°C	900°C	1000°C
Hydrogen cyanide	51.8	2.9	17.9	69.0	7.0	30.7	66.0
Acetonitrile	34.2	2.2	2.7	1.6	3.8	5.2	2.5
Acrylonitrile	26.4	0.8	1.4	0.3	-	-	-
Pyridine	17.7	0.2	0.9	0.05	-	-	-
Benzonitrile	13.6	1.2	3.4	1.4	2.5	7.6	1.4
TOTAL	-	7.3	26.3	72.4	13.3*	43.5*	69.9*

Note: nitrogen content of 2.4 mg of polyether yellow smoke or 10 mg of polyether foam is 410 µg.

* sub-totals for hydrogen cyanide, acetonitrile and benzonitrile only.

ϕ of products.

4. DISCUSSION

This report shows that the decomposition of the polyester and polyether foams are similar and proceed according to the routes shown in Table 12.

At low temperatures (200 to 300°C) the foams decompose to give a volatile yellow smoke leaving a polyol residue. The volatile smoke is common to both foams and appears to contain all the nitrogen from the original foams.

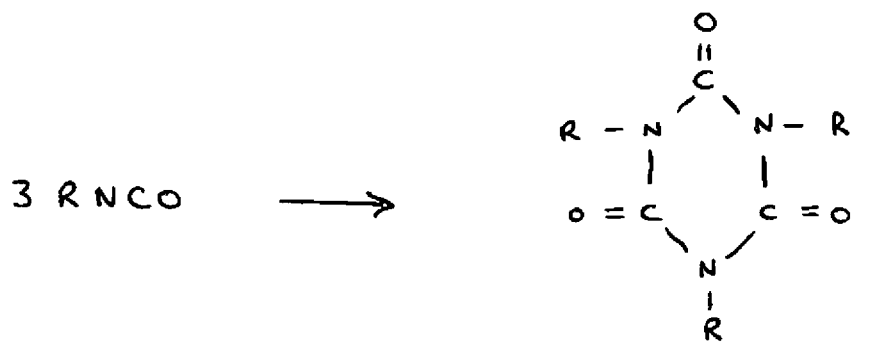
At intermediate decomposition temperatures (300 to 800°C) the yellow smoke is stable at the furnace residence times of this report. The decomposition products of the polyols at these temperatures are complex and probably consist of hydrocarbons and oxygenated species.

At high temperatures (800 to 1000°C) the decomposition products of the polyols are generally simpler than at the intermediate temperatures and may consist only of hydrocarbons. These temperatures are sufficient to decompose the yellow smoke to give a number of nitrogen-containing materials of low molecular weight.

At 800°C the yellow smokes decompose giving hydrogen cyanide, acetonitrile, acrylonitrile, pyridine and benzonitrile as the main nitrogen-containing products with a total nitrogen recovery of the order of 5 to 15 per cent (see Tables 10 and 11); the remaining nitrogen being presumably retained in the yellow product which passes unchanged through the furnace. At 900°C, the total nitrogen recovery is increased (see Tables 10 and 11) and hydrogen cyanide and benzonitrile predominate in approximately equal proportions (Tables 8 and 9) as the main nitrogen-containing products. At 1000°C, the total nitrogen recoveries are of the order of 70 to 80 per cent with the main product being hydrogen cyanide. Only very small quantities of acetonitrile, acrylonitrile, pyridine and benzonitrile are present at this temperature.

Although existing knowledge of the thermal decomposition processes is vague, there have been some reports of the depolymerization[13,14,15], of polyurethane foams at low temperatures to give the isocyanate and alcohol particularly during early studies of the foams. Other important reactions[13,14,15], have been suggested as involving the dissociation of the urethane groups to give a primary amine, olefin and carbon dioxide or a secondary amine and carbon dioxide. In this report the depolymerization of the polyurethane to isocyanate is favoured since amine products are not as readily polymerized as isocyanates and, if polymerized, would yield products with elemental compositions less similar to that of T.D.I.

It has been suggested[15] that the two reactions most likely to occur with the heating of isocyanates at temperatures up to 300°C are carbodiimide formation and trimerization (i.e. isocyanurate formation). Trimerization of T.D.I. involves the coupling of three isocyanurate groups (from separate T.D.I. molecules) to give a ring system of the type:-



isocyanurate (I)

TABLE 12

PRODUCT FORMATION ROUTES DURING THE THERMAL DECOMPOSITION OF POLYURETHANE FOAMS BETWEEN 200 AND 1000°C

		Polyester foam (C, H, N, O)		Polyether foam (C, H, N, O)
(i)	Low temperature (200 - 300°C)	Polyester polyol residue (C, H, O)	Volatile yellow smoke (C, H, N, O)	Polyether polyol residue (C, H, O)
(ii)	Intermediate temperature (300 - 800°C)	Decomposition* products of polyester polyol	Volatile yellow smoke (unchanged)	Decomposition* products of polyester polyol
(iii)	High temperature (over 800°C)	Decomposition** products of polyester polyol	Decomposition products of yellow smoke e.g. hydrogen cyanide acetonitrile etc	Decomposition** products of polyether polyol

*. complex mixture of products (probably hydrocarbons and oxygenated species)

**. probably hydrocarbons - see text.

The overall polymeric isocyanurate of T.D.I. is a complex cross-linked system.

Carbodiimide formation involves the linking of two isocyanate groups with release of carbon dioxide namely:-

$$2\ R.NCO \longrightarrow R - N = C = N - R$$

carbodiimide (II)

Polymeric carbodiimides have been reported[15] in high yields from the decomposition of certain urethanes of diphenylmethane diisocyanate and also from the direct heating of the diisocyanate alone.

In this report the yellow smokes have experimental nitrogen contents between 17 and 17.5 per cent. Trimerization of the T.D.I. to an isocyanurate system (I) would give a polymeric material with a nitrogen content the same as for T.D.I. namely 16.1 per cent. Carbodiimide formation (II) would generate a polymer with a theoretical nitrogen content of 21.5 per cent. The unknown yellow products may exist as polymeric materials (but still volatile at 200 to 300°C) containing both carbodiimide and isocyanurate links, proportioned to give an experimental nitrogen content of around 17 per cent. A material of this kind could well explain the observed stability to temperatures approaching 800°C under the conditions of this report.

When heated to temperatures above 800°C the yellow smoke decomposes to give a number of products with hydrogen cyanide and benzonitrile predominating (Tables 8 and 9). There is evidence that the aromatic ring system is broken in order to provide materials such as the C_2 hydrocarbons and pyridine, but retained in the formation of benzonitrile. Toluene is a minor product and smaller in quantity than benzene suggesting possibly that the observed benzene is reformed in some way, together with pyridine and the C_2 hydrocarbons, following the cleavage of the aromatic ring. The ring breakage and subsequent re-arrangements presumably provide the available hydrogen for the production of hydrogen cyanide.

Finally, although this work shows that the T.D.I. unit is released as a polymeric material, this does not preclude the possibility of the release of some free T.D.I. which is known to be a highly toxic material[7]. This material would not be detected by chromatography under the conditions of this report and some recent experiments to monitor free T.D.I. from the decompositions of the foams by mass spectrometry have not been conclusive since additional experiments where free T.D.I. has been introduced (as a solution in toluene) into the mass spectrometer gives a distinct toluene spectrum but no spectrum of T.D.I. It is thought that the T.D.I. is lost by polymerization inside the heated inlet system of the mass spectrometer.

Current work is in progress to overcome the problem of the analysis of T.D.I. and to monitor the release of the material from the decomposition of the foam and will be reported shortly.

Further work, including experimental studies of the composition of the yellow smokes and studies of the thermal-oxidative decomposition and decomposition products of the foams will be recorded in future reports.

5. CONCLUSIONS

(1) At low temperatures (200 to 300°C) there is a rapid and complete loss of the T.D.I. unit of each foam as a volatile smoke leaving a polyol residue.

(2) The smoke (which is common to both foams) has been isolated as a yellow solid containing all the nitrogen of the original foams. The yellow smokes are stable under the conditions of this report to 750°C.

(3) Nitrogen-containing materials of small molecular weight are generated by the high temperature decomposition of the yellow smokes. The observed products from the high temperature decompositions of the foam and equivalent weights (on a nitrogen basis) of yellow smokes are in agreement.

(4) When decomposed at 800°C the foams (or equivalent amounts of yellow smokes) produce hydrogen cyanide, acetonitrile, acrylonitrile, pyridine and benzonitrile as the main nitrogen-containing products. At 900°C, all of these 5 products are formed but hydrogen cyanide and benzonitrile predominate. At 1000°C, hydrogen cyanide is virtually the only nitrogen containing product. At this temperature (1000°C) approximately 70 per cent of the available nitrogen has been recovered as hydrogen cyanide.

(5) If decomposed at temperatures in excess of 1000°C, it is suggested that virtually all of the nitrogen contents of the foams may be released as hydrogen cyanide.

6. REFERENCES

(1) BOTT, B., FIRTH, J. G., and JONES, T.A., Evolution of toxic gases from heated plastics, Br. Polym,J., 1969, I, pp 203-204.

(2) WOOLLEY, W. D., and FIELD, P., A preliminary study of the thermal decomposition of polyurethane foams by elemental ultramicroanalysis. Joint Fire Research Organization, Fire Research Note 880.

(3) DOMBROW, B. A., Polyurethanes, Reinhold Publishing Co., 1965.

(4) SAUNDERS, J. H., and FRISCH, K. C., Polyurethanes, Chemistry and Technology - Part 1, Chemistry, Interscience Publishers, 1962.

(5) GOLDING, B., Polymers and Resins, D. Van Nostrand Co. Inc., 1959.

(6) PHILLIPS, L. N., and PARKER, D. B. V. Polyurethanes, Iliffe Books Ltd., 1964.

(7) Hygienic Guide Series - Tolylene diisocyanate, American Industrial Hygiene Association, 14125 Prevost, Detroit 27, Michigan, U.S.A.

(8) WOOLLEY, W. D., A study and toxic evaluation of the products from the thermal decomposition of PVC in air and nitrogen. Joint Fire Research Organization, Fire Research Note 769, July 1969.

(9) WOOLLEY, W. D., and WADLEY, A. I., The thermal decomposition products of phenol-formaldehyde laminates. Part 1, the production of phenol and related materials, Joint Fire Research Organization, Fire Research Note 851, Dec. 1970.

(10) WOOLLEY, W. D., and WRIST, F., Coupled gas chromatography-mass spectrometry and its application to the thermal decomposition of cellulose, Joint Fire Research Organization, Fire Research Note 870, April 1971.

(11) CORNU, A., and MASSOT, R., Compilation of mass spectral data, Heyden and Son, 1966.

(12) DIETZ, W. A., Response Factors for gas chromatographic analyses, J. Gas. Chrom., 1967, 5 (2) pp 68-71.

(13) See reference 4 p 106.

(14) BACKUS, J. K., DARR, W. C., GEMEINHARDT, P. G., and SAUNDERS, J. H., Thermal decomposition of rigid urethane foams, J. Cellular Plastics, 1965, 1, pp 178-185.

(15) SAUNDERS, J. H., Thermal degradation and flammability of urethane foams, Proc. Conf. Natick (Cellular Plastics) 1966.

7 APPENDIX

a) Appendix 1. Integrator counts (arbitrary units) for the products from the thermal decomposition of polyester yellow product (2.5 mg) and foam (10 mg) for the calculations of Table 8.

Material	Peak Letter	Detector	Yellow Product			Foam		
			800°C	900°C	1000°C	800°C	900°C	1000°C
C_2 hydrocarbons	c, d	F.I.D.	1079 (3)*	1647 (3)	3923 (2)	∅	-	-
hydrogen cyanide	g	T.C.D.	1409 (1)	8490 (1)	2879 (2)	2085 (1)	1494 (2)	3242 (2)
acetonitrile	j	F.I.D.	1367 (2)	2226 (2)	1000 (2)	2709 (2)	5042 (2)	1818 (2)
acrylonitrile	k	F.I.D.	1060 (2)	2277 (2)	3738 (1)	-	-	-
benzene	n	F.I.D.	1300 (2)	1601 (3)	2204 (3)	[illegible]	-	-
pyridine	r	F.I.D.	8348 (1)	4531 (2)	3091 (1)	[illegible]	-	-
toluene	s	F.I.D.	8685 (1)	1200 (2)	5000 (0)	-	-	-
benzonitrile	x	F.I.D.	4046 (2)	1771 (3)	5947 (2)	1199 (3)	3001 (3)	7276 (2)

* number in brackets denotes the powers of ten; for example 1079 (3) = 1079000 arbitrary units

∅ not measured due to polyol interference

b) APPENDIX 2. Integrator counts (arbitrary units) for the products from the thermal decomposition of polyether yellow product (2.4 mg) and foam (10 mg) for the calculations of Table 9.

Material	Peak Letter	Detector	Yellow product			Foam		
			800°C	900°C	1000°C	800°C	900°C	1000°C
C_2 hydrocarbons	c,d	F.I.D.	7467 (2)*	7806 (2)	5385 (2)	∅	-	-
hydrogen cyanide	g	T.C.D.	1203 (1)	7435 (1)	2860 (2)	2885 (1)	1271 (2)	2734 (2)
acetonitrile	j	F.I.D.	1717 (2)	2045 (2)	1197 (2)	2879 (2)	4013 (2)	1949 (2)
acrylonitrile	k	F.I.D.	1228 (2)	2098 (2)	4437 (1)	-	-	-
benzene	n	F.I.D.	1412 (2)	8443 (2)	2247 (3)	-	-	-
pyridine	r	F.I.D.	7274 (1)	2569 (2)	1569 (1)	-	-	-
toluene	s	F.I.D.	1034 (2)	1377 (2)	7500 (0)	-	-	-
benzonitrile	x	F.I.D.	5102 (2)	1445 (3)	5882 (2)	1058 (3)	3252 (3)	5909 (2)

* number in brackets denotes the powers of ten; for example 7467 (2) = 746700 arbitrary units

∅ not measured due to polyol interference

10780 FR 881

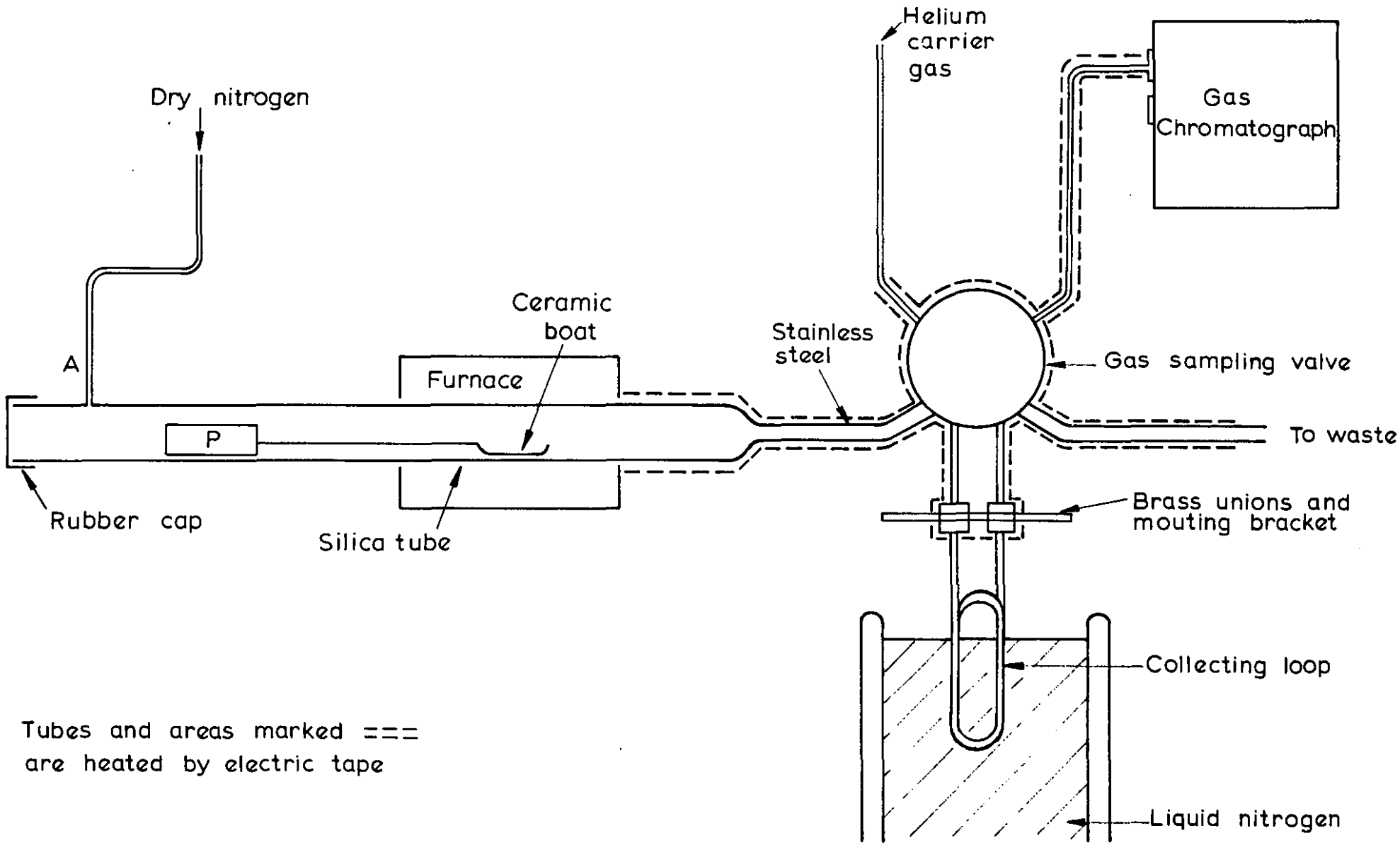


FIG. 1. THE DECOMPOSITION SYSTEM

10781 FR 881

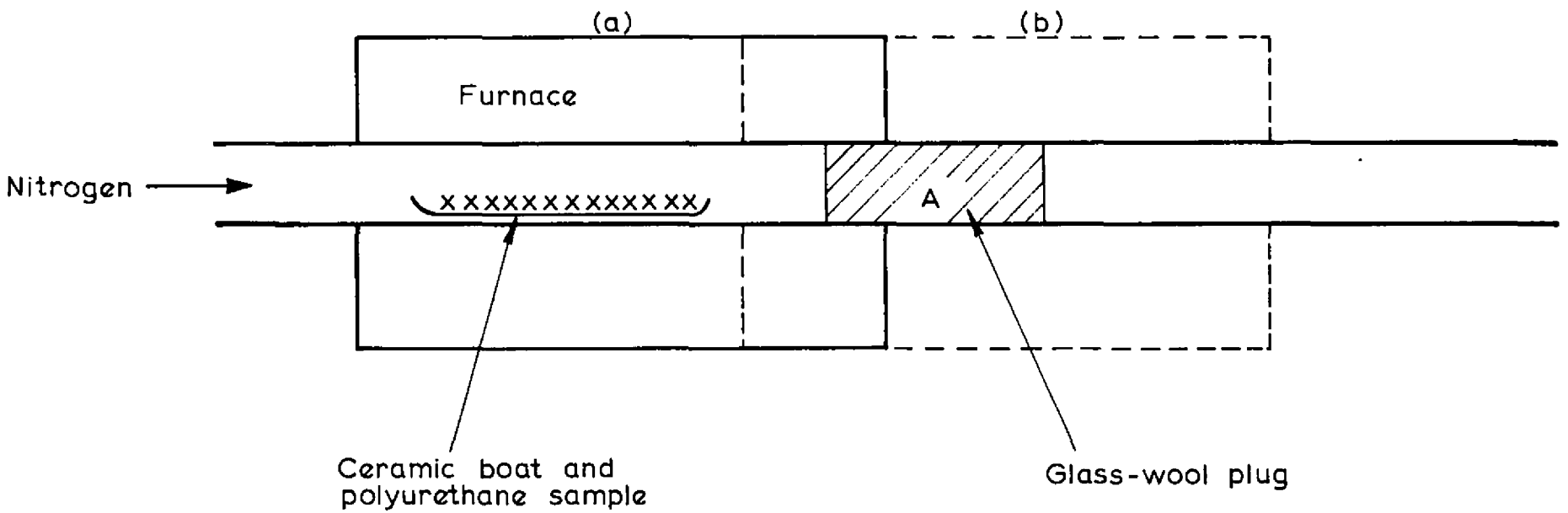


FIG. 2. APPARATUS FOR SMOKE COLLECTION (a) AND SMOKE VOLATILITY TESTS (b)

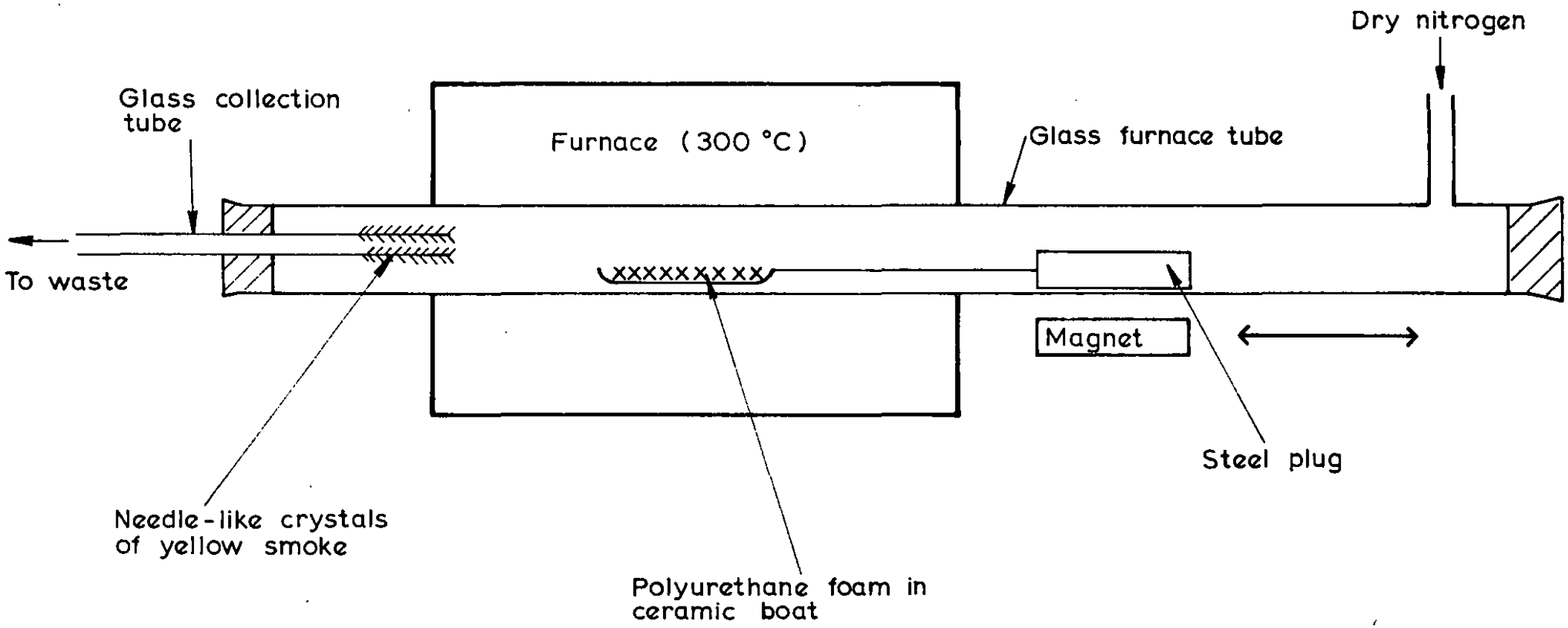


FIG. 3. FURNACE SYSTEM FOR COLLECTING YELLOW SMOKES FROM POLYURETHANE FOAMS

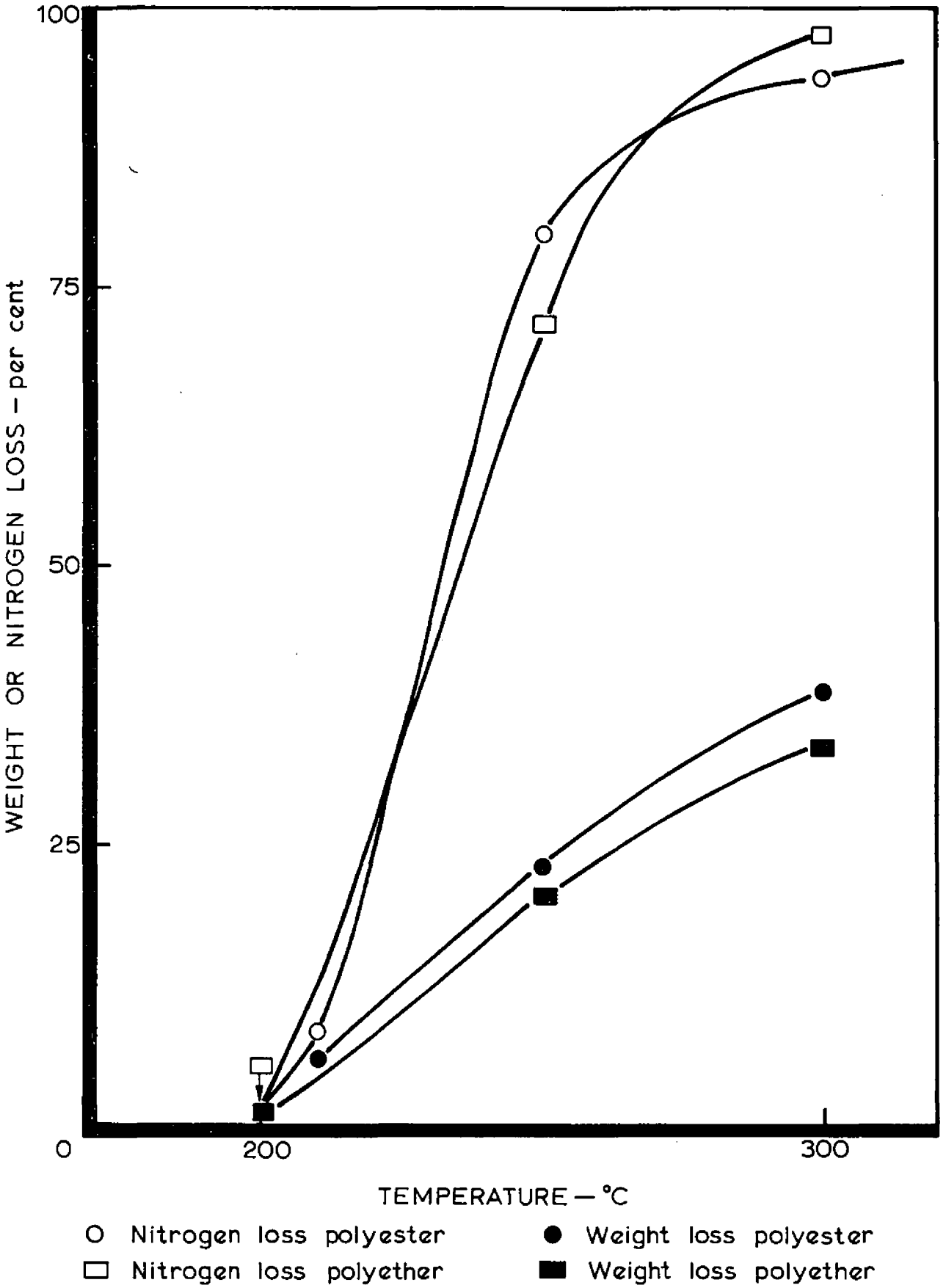
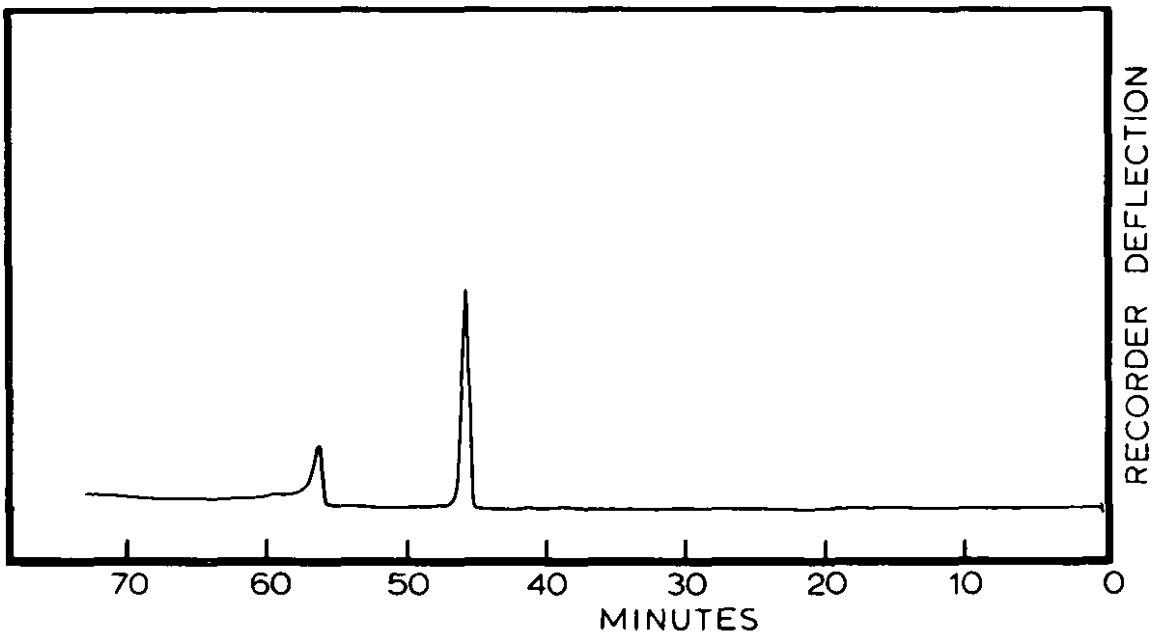
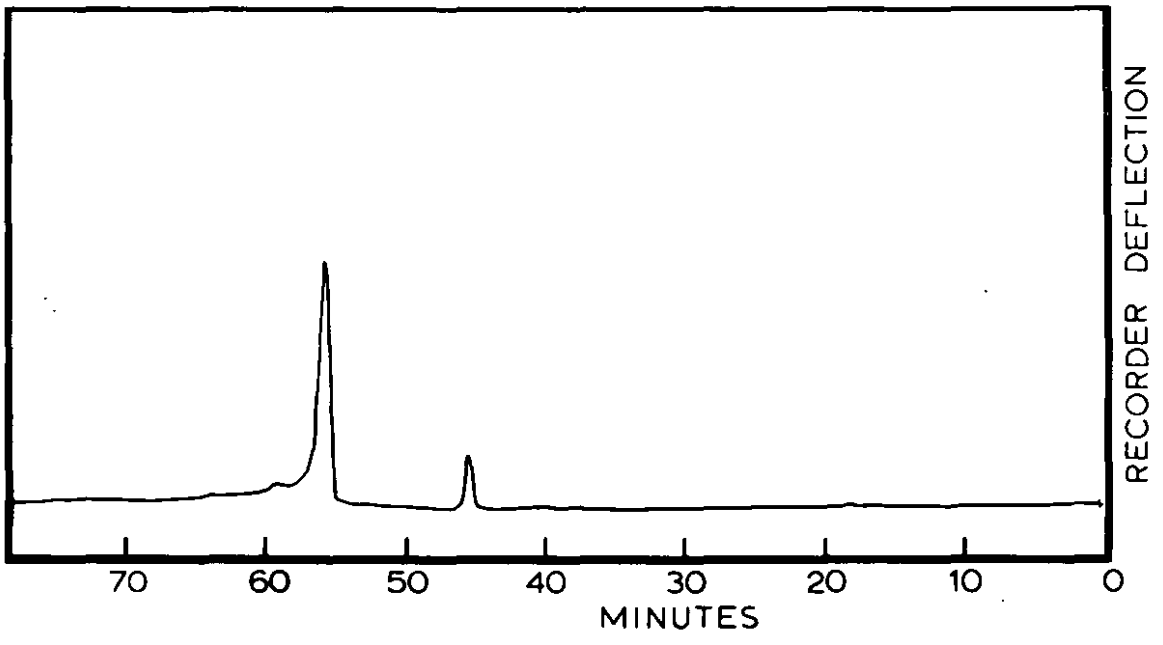


FIG. 4. COMPARISONS BETWEEN THE WEIGHT LOSSES AND THE NITROGEN LOSSES DURING THE THERMAL DECOMPOSITION OF POLYURETHANE FOAMS BETWEEN 200 AND 300 °C

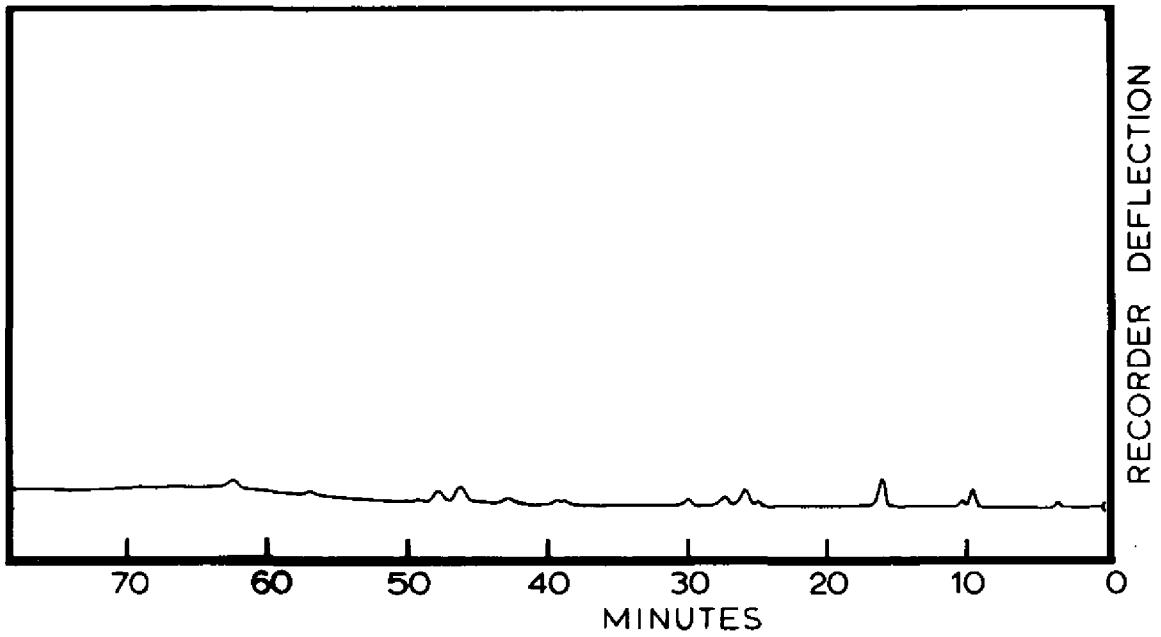


FOAM

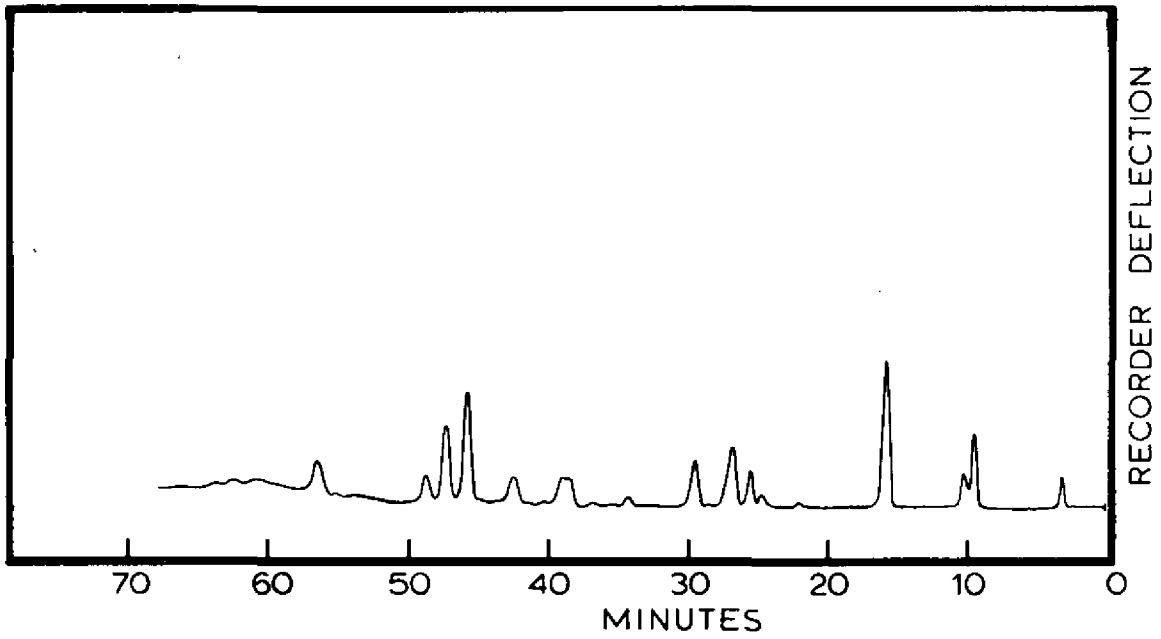


POLYOL

FIG. 5. CHROMATOGRAMS (F.I.D.) OF THE DECOMPOSITION PRODUCTS OF POLYESTER FOAM AND POLYOL AT 300 °C

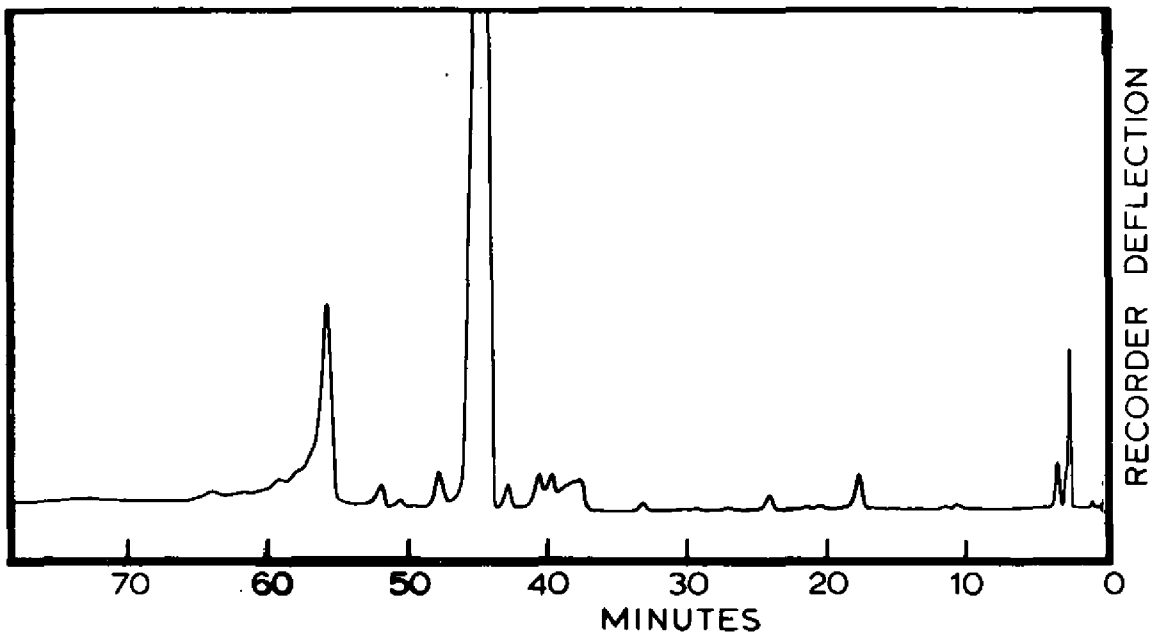


FOAM

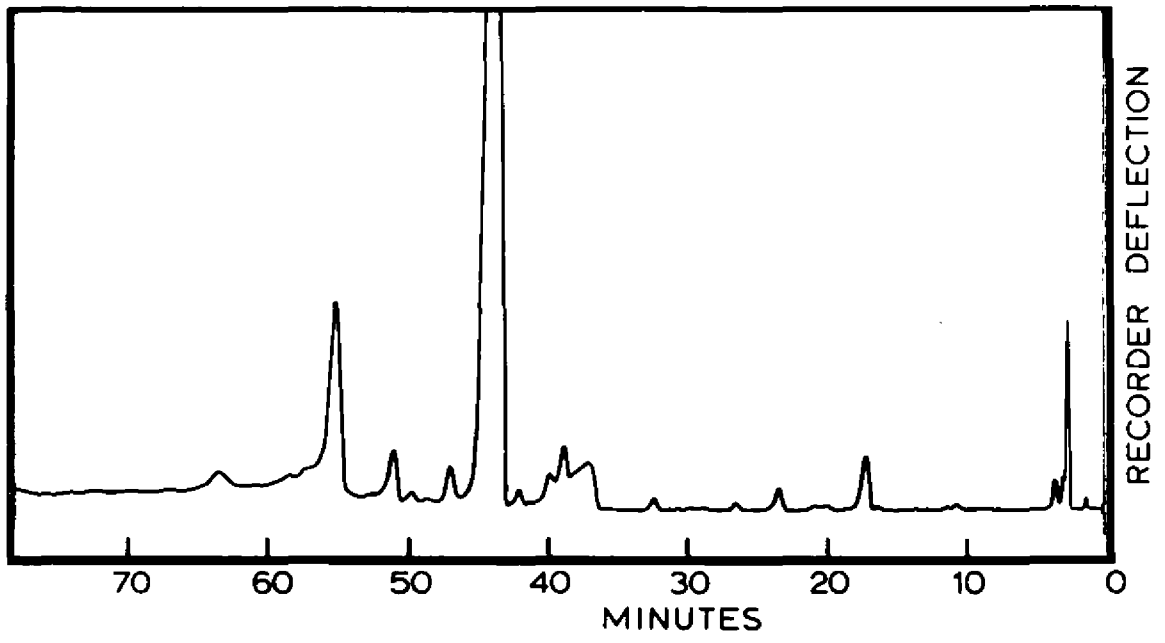


POLYOL

FIG. 6. CHROMATOGRAMS (F.I.D.) OF THE DECOMPOSITION PRODUCTS OF POLYETHER FOAM AND POLYOL AT 300°C

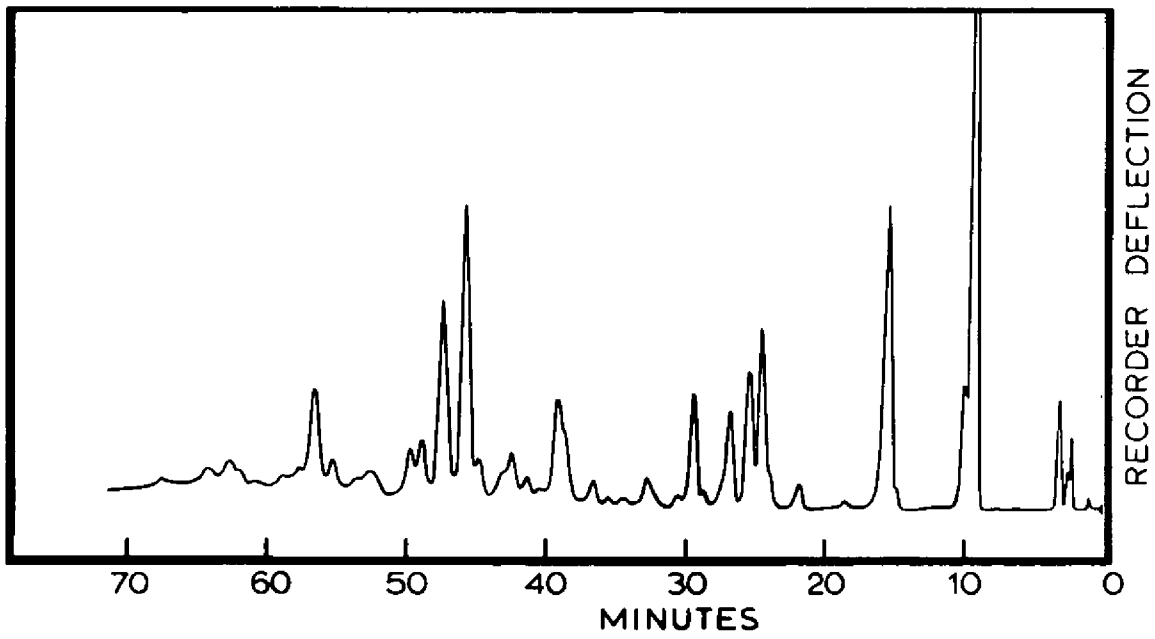


FOAM

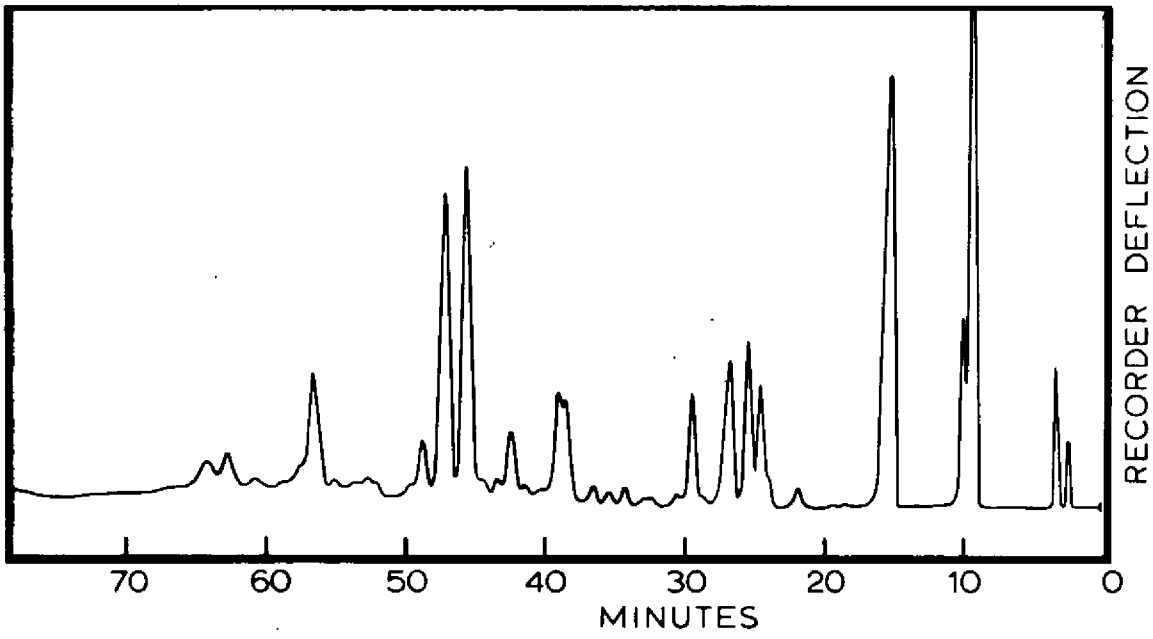


POLYOL

FIG. 7. CHROMATOGRAMS (F.I.D.) OF THE DECOMPOSITION PRODUCTS OF POLYESTER FOAM AND POLYOL AT 400°C

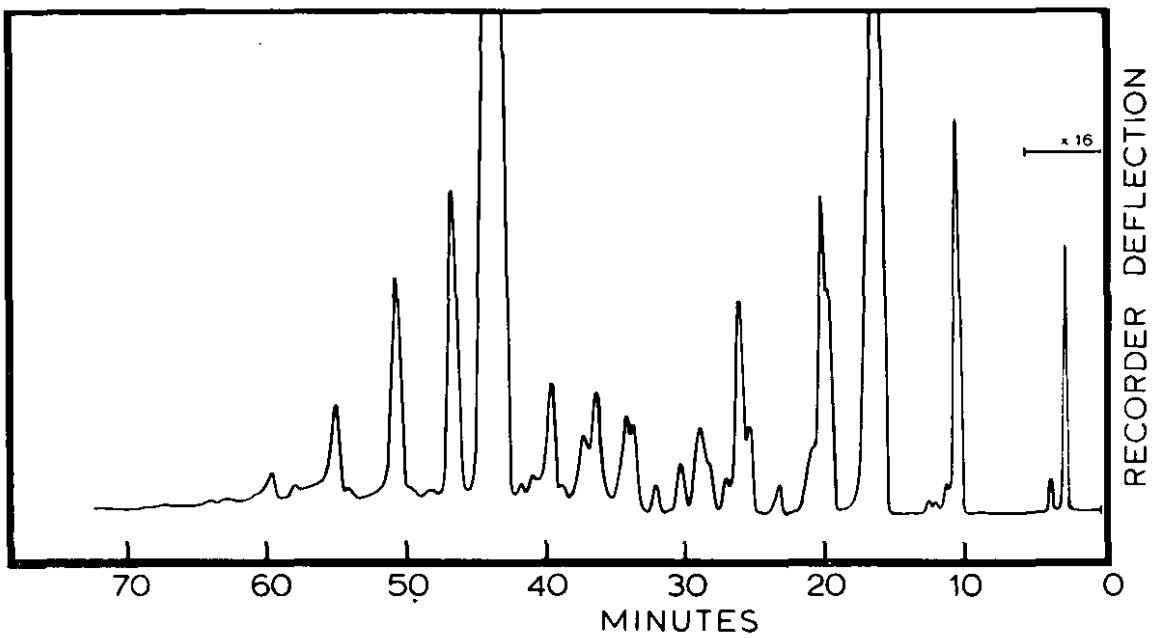


FOAM

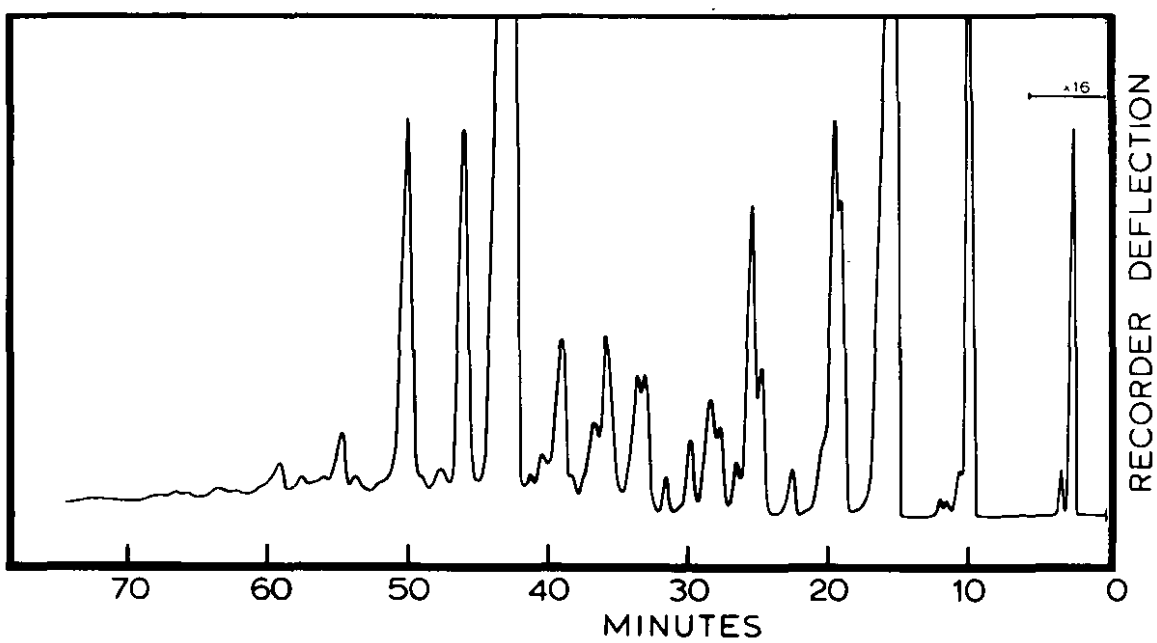


POLYOL

FIG. 8. CHROMATOGRAMS (F.I.D.) OF THE DECOMPOSITION PRODUCTS OF POLYETHER FOAM AND POLYOL AT 400°C

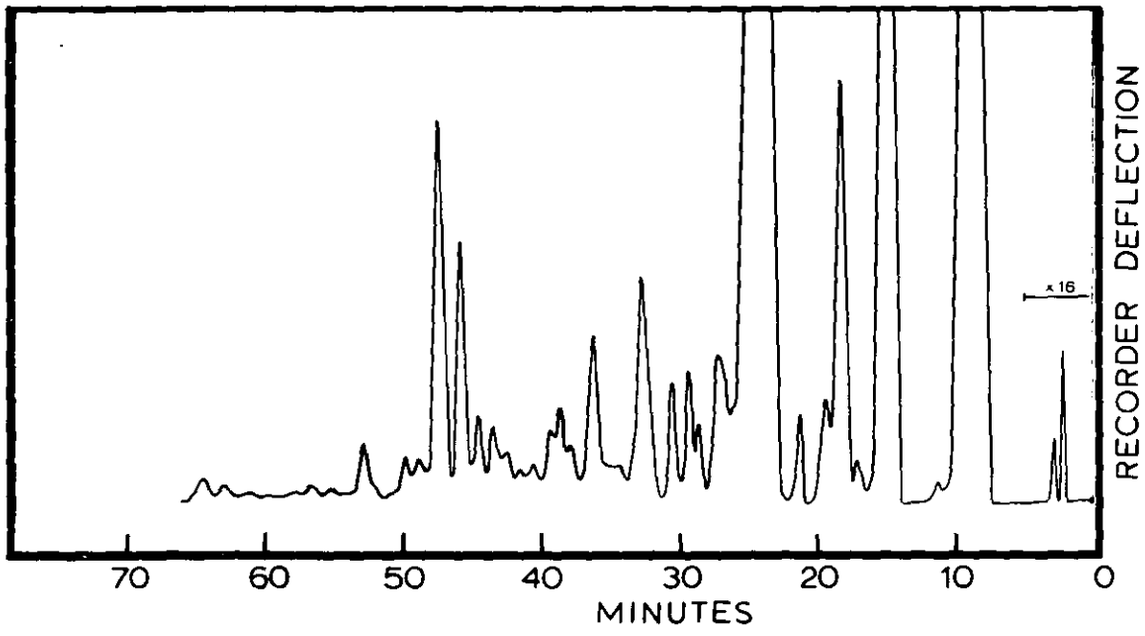


FOAM

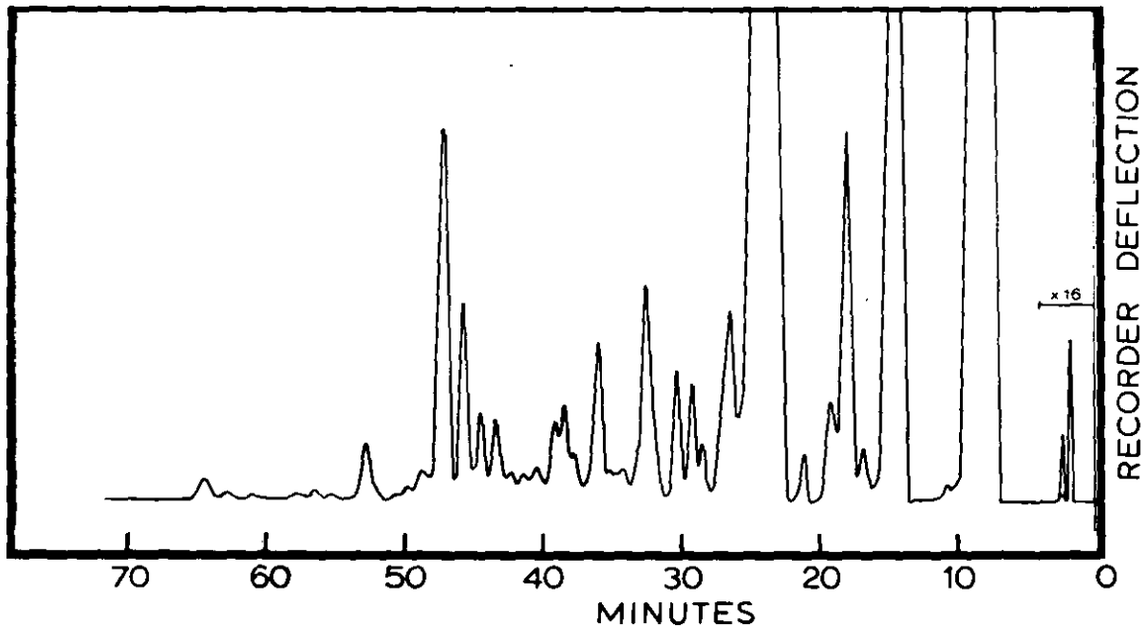


POLYOL

FIG. 9. CHROMATOGRAMS (F.I.D.) OF THE DECOMPOSITION PRODUCTS OF POLYESTER FOAM AND POLYOL AT 600°C

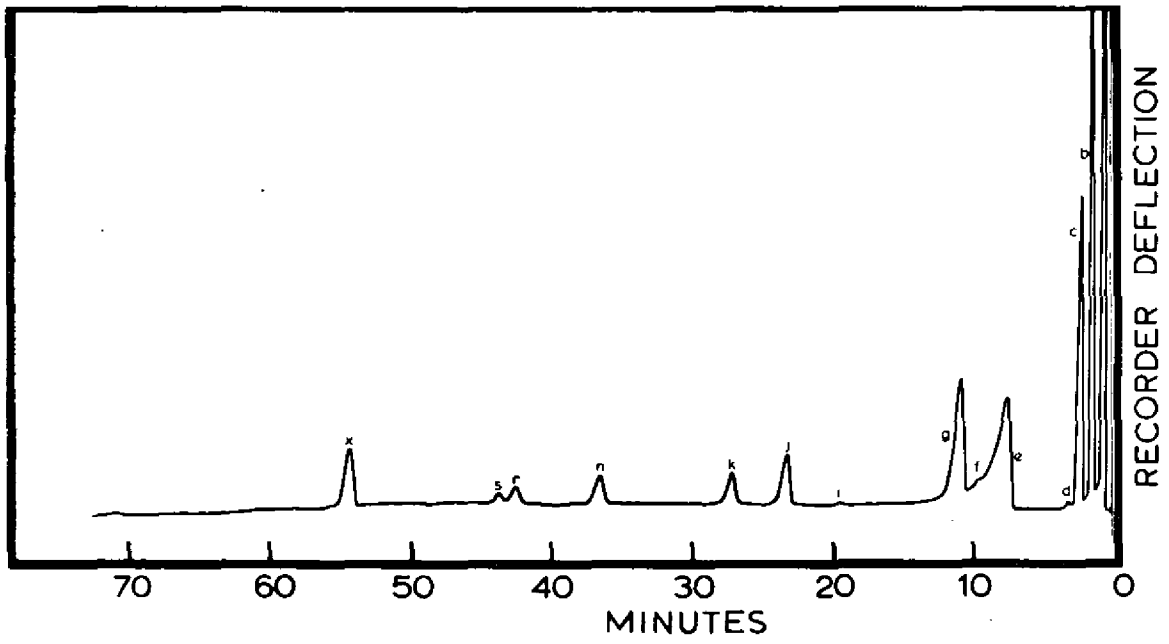


FOAM

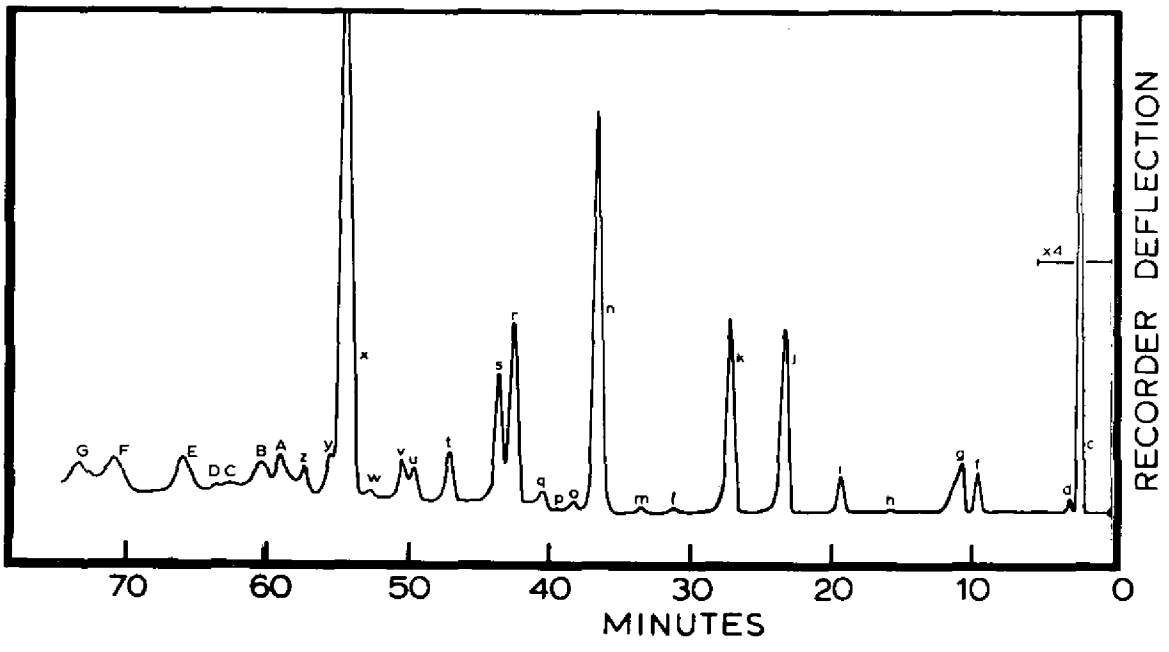


POLYOL

FIG. 10. CHROMATOGRAMS (F.I.D.) OF THE DECOMPOSITION PRODUCTS OF POLYETHER FOAM AND POLYOL AT 600°C

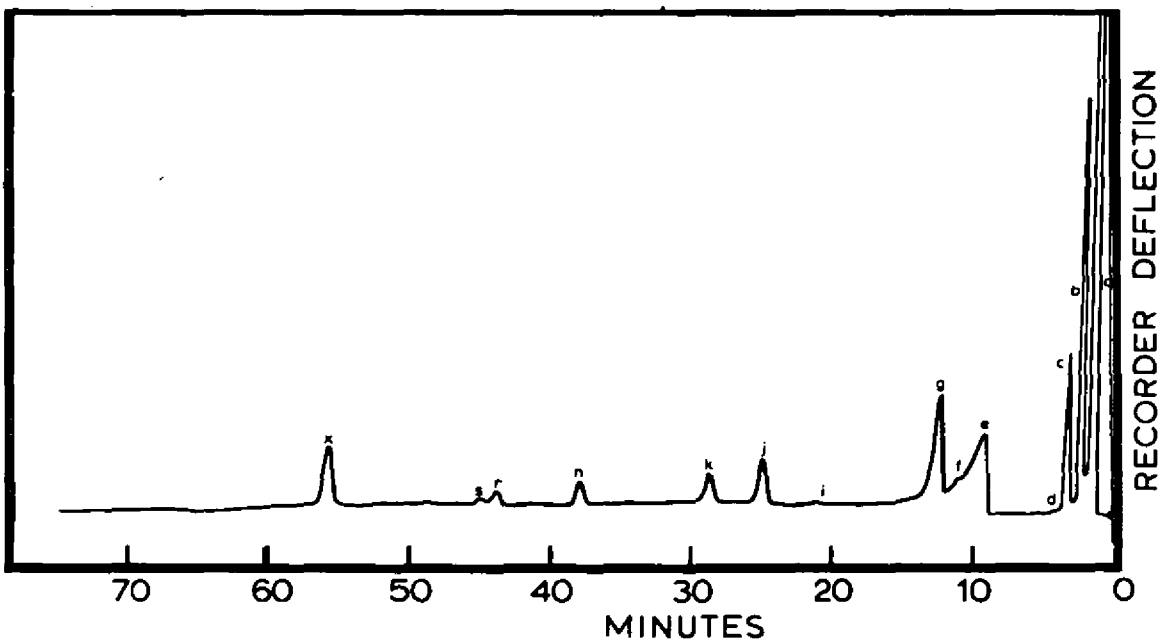


THERMAL CONDUCTIVITY DETECTION

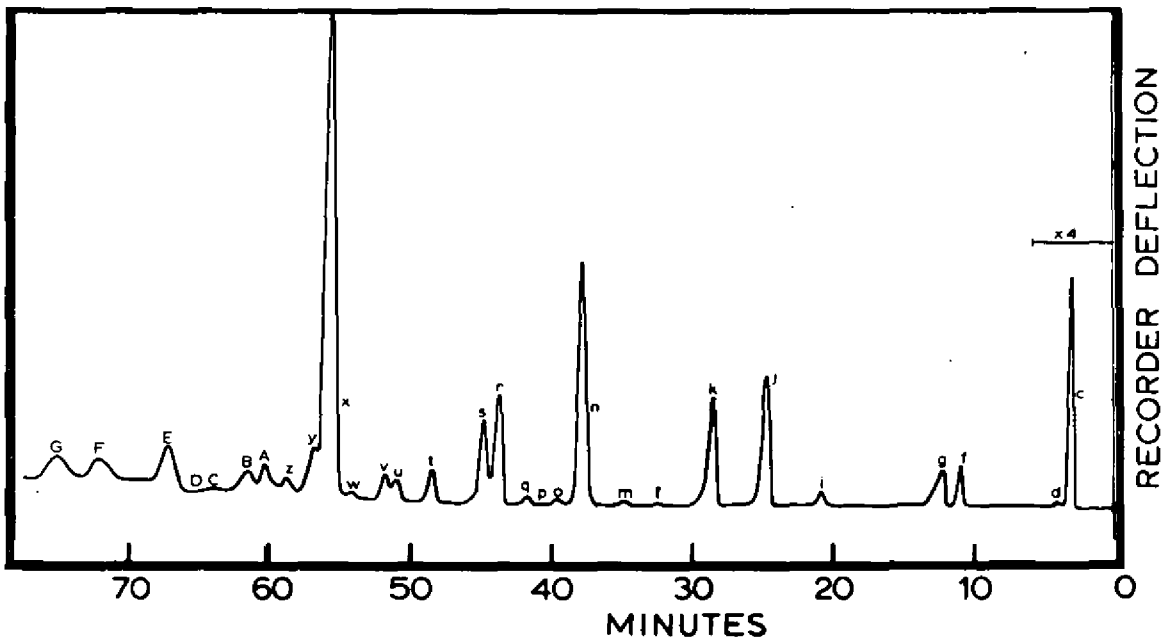


FLAME IONIZATION DETECTION

FIG. 11. CHROMATOGRAMS (F.I.D. AND T.C.D.) OF THE DECOMPOSITION PRODUCTS OF THE YELLOW PRODUCT (POLYESTER) AT 850 °C

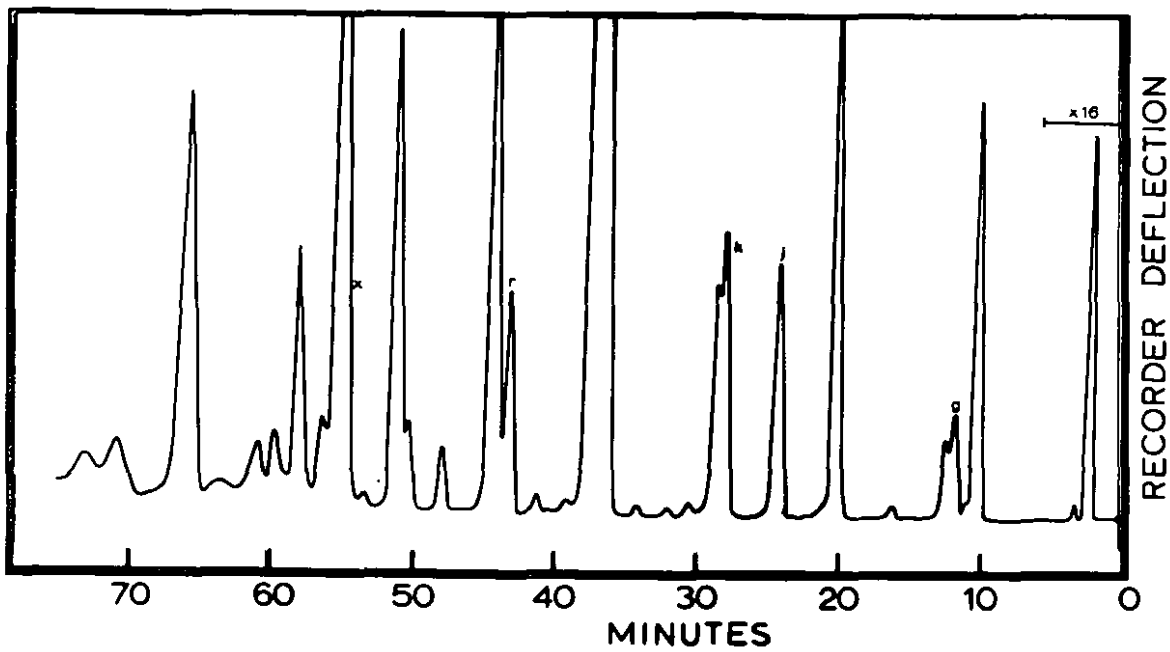


THERMAL CONDUCTIVITY DETECTION

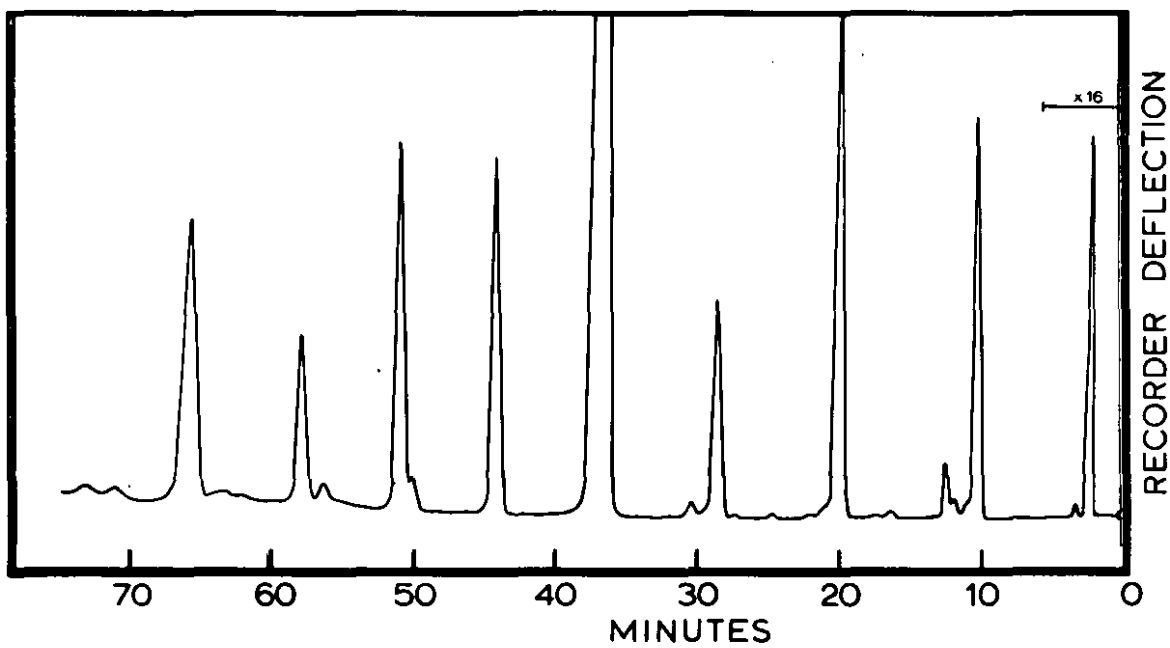


FLAME IONIZATION DETECTION

FIG. 12. CHROMATOGRAMS (F.I.D. AND T.C.D.) OF THE DECOMPOSITION PRODUCTS OF THE YELLOW PRODUCT (POLYETHER) AT 850 °C

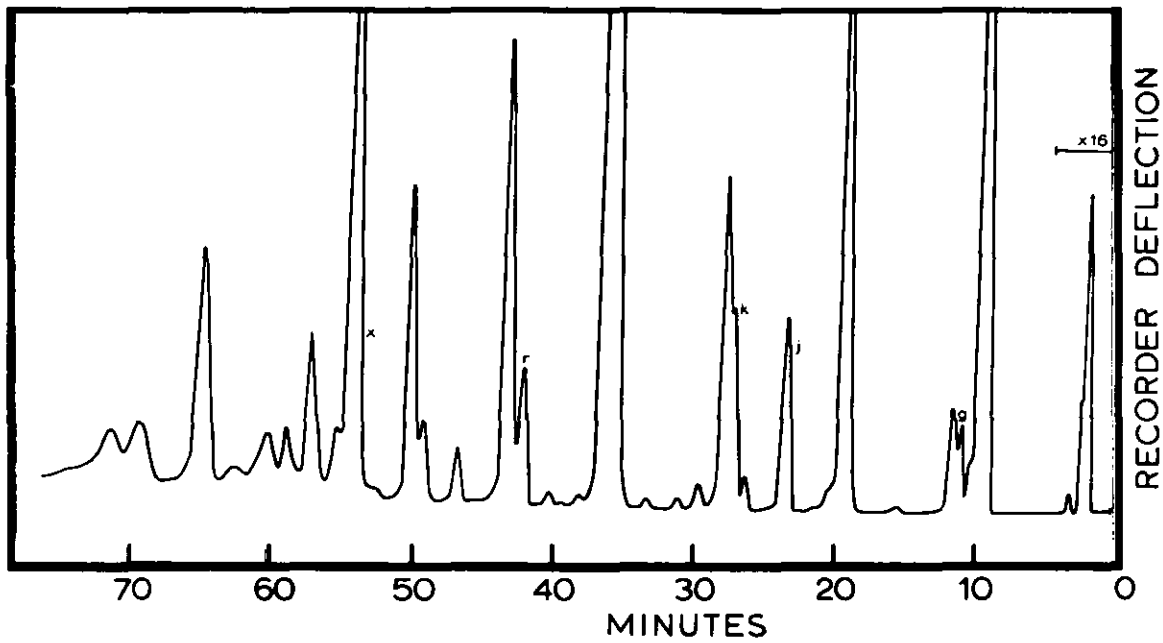


FOAM

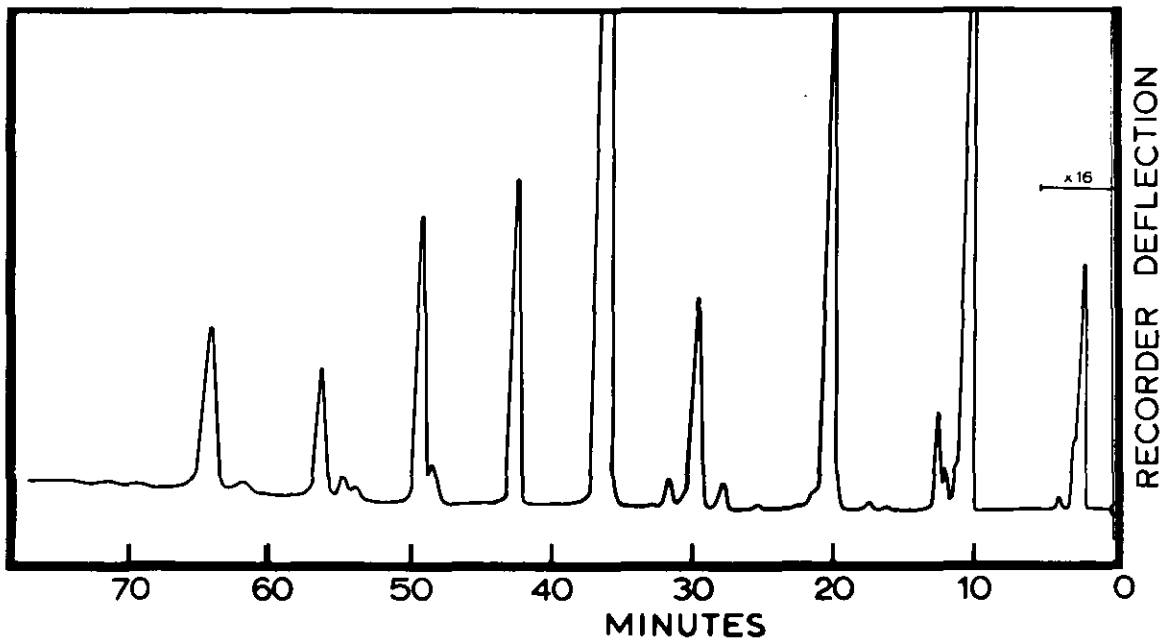


POLYOL

FIG. 13. CHROMATOGRAMS (F.I.D.) OF THE DECOMPOSITION PRODUCTS OF POLYESTER FOAM AND POLYOL AT 850°C



FOAM



POLYOL

FIG. 14. CHROMATOGRAMS (F.I.D.) OF THE DECOMPOSITION PRODUCTS OF POLYETHER FOAM AND POLYOL AT 850°C

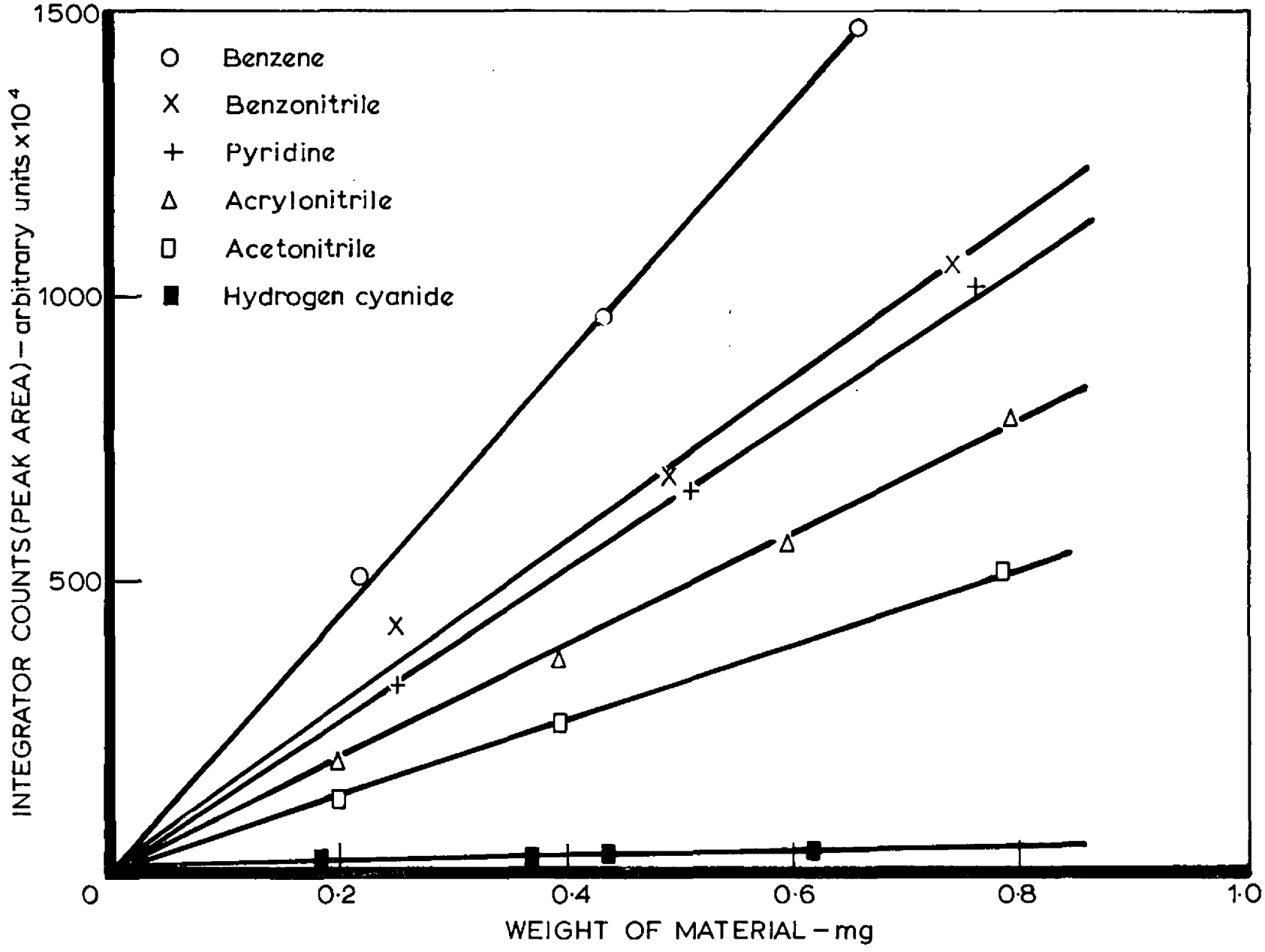


FIG.15 CHROMATOGRAPHIC CALIBRATION DATA (F.I.D)

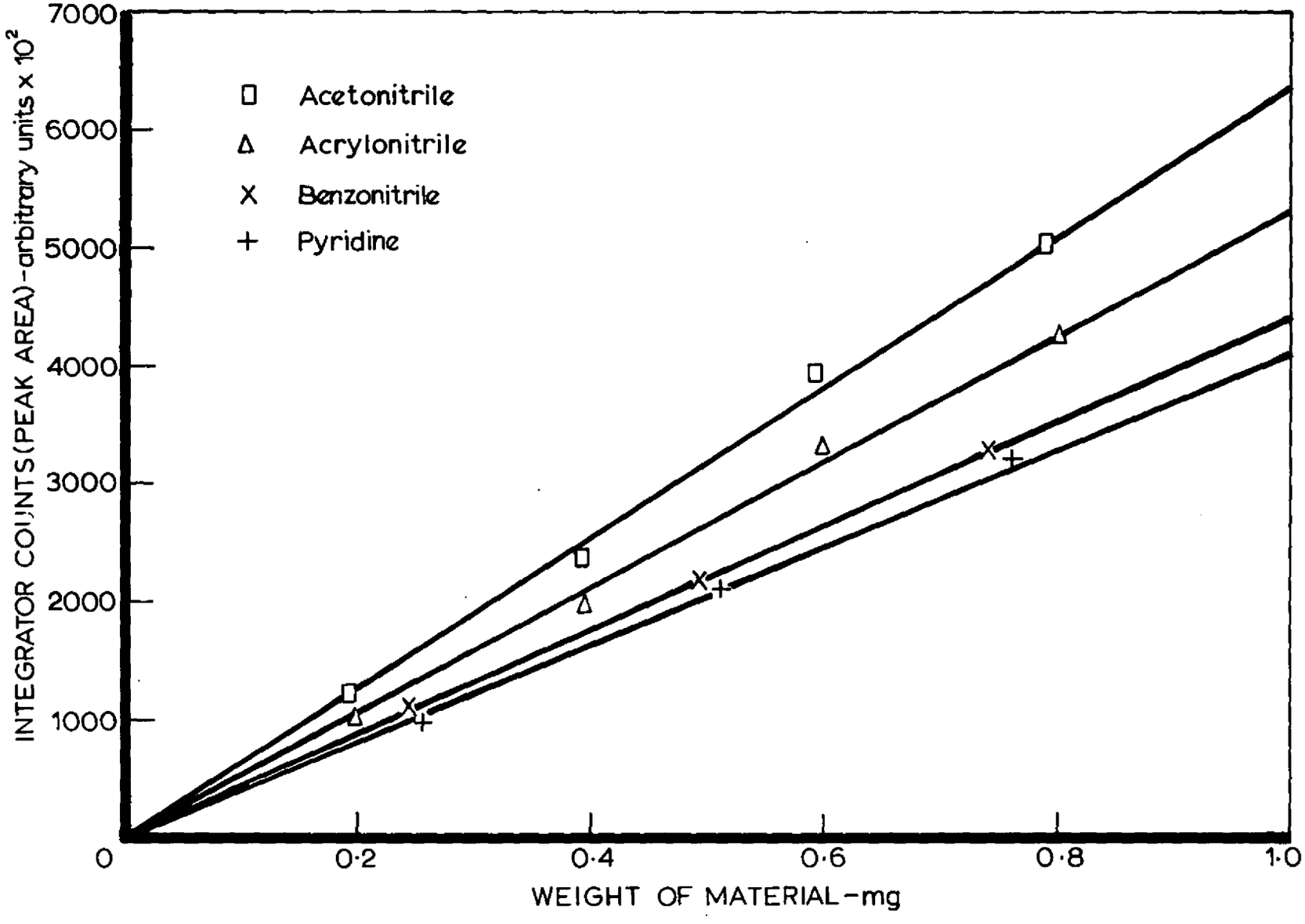


FIG.16. CHROMATOGRAPHIC CALIBRATION DATA (T.C.D)

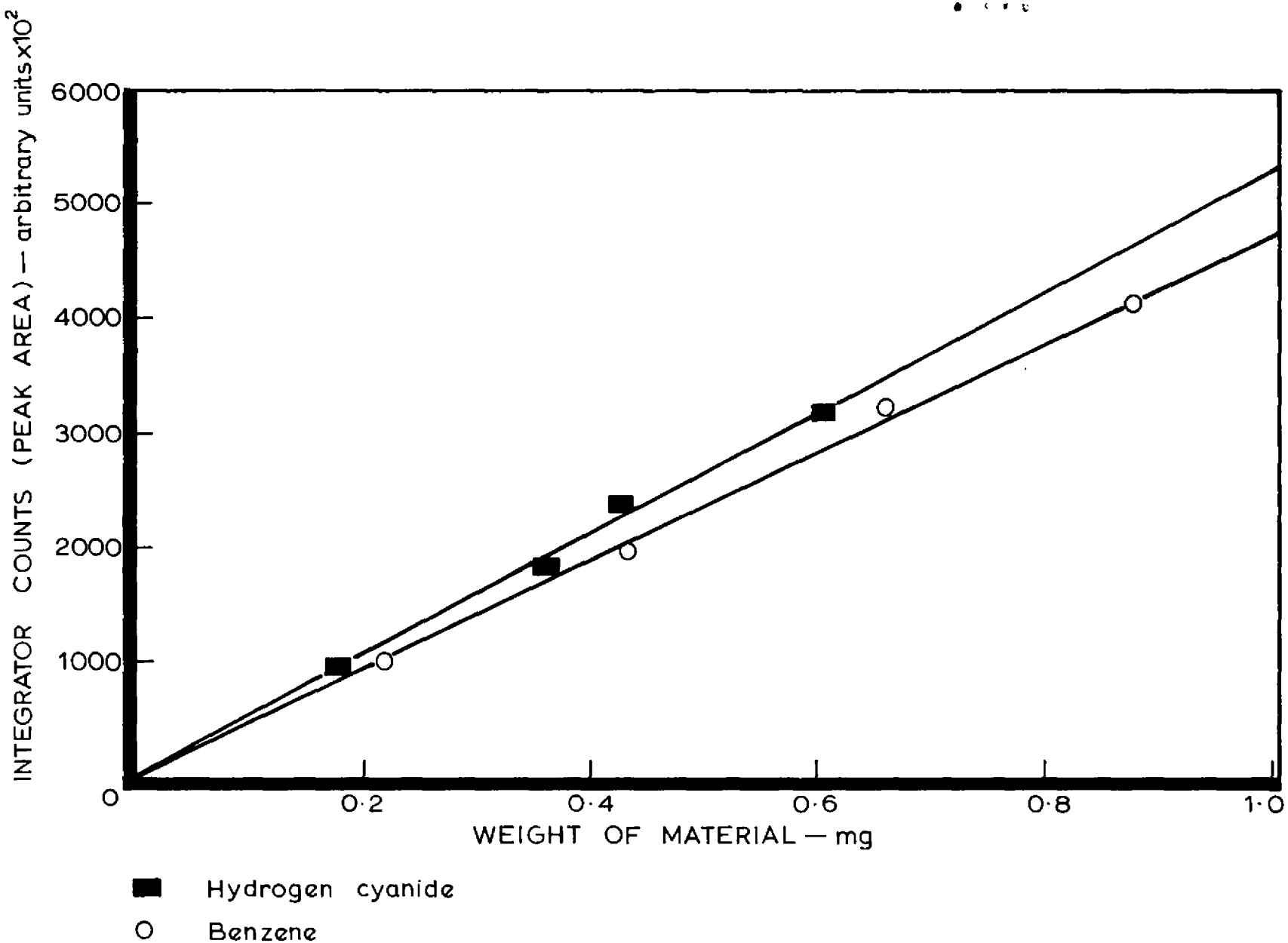


FIG. 17. CHROMATOGRAPHIC CALIBRATION DATA (T.C.D.)