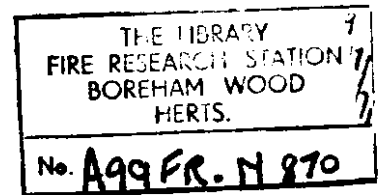


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# Fire Research Note

## No 870

COUPLED GAS CHROMATOGRAPHY-MASS SPECTROMETRY  
AND ITS APPLICATION TO THE THERMAL DECOMPOSITION  
PRODUCTS OF CELLULOSE

by

W. D. WOOLLEY and F. N. WRIST

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Fire Research Station,  
Borehamwood,  
Herts.  
Tel. 01-953-6177

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SUMMARY

An analytical system, consisting of a coupled gas chromatograph - mass spectrometer unit linked to an on-line decomposition furnace has been constructed for studies of the thermal decomposition products of organic materials. The system has been evaluated by a qualitative study of the decomposition products of cellulose in nitrogen and air atmospheres. Some chromatographic experiments using flame retarded cellulose (mono ammonium phosphate) are given and some general observations on the action of this flame retardant are recorded.

KEY WORDS: Fire retardant, gas chromatography, mass spectrometry, pyrolysis.

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## 1. INTRODUCTION

Studies of the decomposition products of various common plastics by gas chromatography and mass spectrometry have been outlined in a number of earlier papers<sup>1-4</sup>. In this earlier work a special apparatus was constructed so that the volatile decomposition products released during the thermal and thermal oxidative decomposition of the plastics could be collected in a refrigerated trap coupled on-line to a research gas chromatograph. In this way the many volatile decomposition products could be introduced very simply into the chromatograph without laborious solvent extraction methods. The research chromatograph was fitted with simultaneous flame ionization and thermal conductivity detectors for product evaluation and coupled directly to an automatic electronic integrator with print-out facilities for the quantitative analysis of the products.

For the identification of the components eluted from the chromatograph, an AEI MS 10c2 mass spectrometer was available. Basically this instrument is a low resolution unit (resolution 1 in 350 at 10 per cent valley) with a scan rate of several minutes per decade (a decade being masses of say 1 to 10, 10 to 100 etc). With packed columns, materials are generally eluted from a gas chromatograph at intervals of the order of 1 minute or less and consequently this mass spectrometer cannot be coupled directly to the gas chromatograph. As a result, a special technique was developed for the collection and storage of small amounts of material, as they are eluted from the chromatograph, for future mass spectrometric analysis<sup>5</sup>. These samples could then be introduced into the mass spectrometer via a conventional batch inlet system whenever mass spectrometer free time was available. In this decomposition system, the weak link in the overall unit is the incompatibility between the gas chromatograph and the mass spectrometer. As a result the existing MS 10c2 mass spectrometer was upgraded to a fast scanning MS 20 complete with all the necessary interface equipment for direct coupling to a gas chromatograph.

This report outlines the operation of the complete analytical system and evaluates the new gas chromatograph - mass spectrometer link by studying the thermal and thermal-oxidative decomposition products of cellulose with and without added flame retardants. Cellulose was chosen for this evaluation in order to provide background information for a current research project involving flame retardants such as ammonium phosphate.

For this evaluation, mass spectrometric identifications of the decomposition products of untreated and flame retardant samples of cellulose were undertaken. During the work a number of interesting features about the action of flame retardants became clear and are recorded. It must, however, be emphasised that this report is not designed to present a detailed account of the decomposition of cellulose or to investigate the action of flame retardants.

The report also includes briefly a recent modification to the analytical unit, consisting of a pre-column system (molecular sieve and silica gel columns) with injection ports built into the inlet of the research chromatograph for the analysis of permanent combustion gases ( $O_2$ ,  $N_2$ , CO and  $CO_2$ ). Details of this modification and a new technique for interpreting the integrator data directly with a small computer during these permanent gas analyses have been recorded in a separate publication<sup>6</sup> but will be mentioned here in order to give a complete picture of the analytical system.

## 2. EXPERIMENTAL

### (i) Apparatus

A block diagram of the complete decomposition and analytical system is shown in Fig. 1. For convenience the system has been divided into four main sections and each section will be considered separately.

#### (a) The decomposition system

The decomposition system has been outlined in detail in a number of earlier reports<sup>1-4</sup> and will be described very briefly here. Essentially the decomposition system consists of a tube furnace (0 to 1000°C) fitted with a silica tube (20 mm o. d.) coupled via a short heated tube to a heated stainless steel gas sampling valve. The sample loop of the valve consists of a length of stainless steel tubing (3.2 mm o.d.) formed into a double loop and immersed into a refrigerant (either liquid nitrogen directly (-196°C) or isopentane (F.Pt. -160°C) cooled with liquid nitrogen). Samples

of the material under investigation (usually 15 mg) are introduced into the furnace in a stream of air or nitrogen and the decomposition products are carried to the sampling loop where the condensable products are trapped inside the loop by freezing. At the end of a decomposition experiment (usually 15 to 30 mins), the gas sampling valve is turned to the inject position to divert the chromatographic helium flow through the loop and the loop is then heated quickly to 200°C by direct electrical heating (using a 10 volt, 50 amp transformer) to vaporise the condensed products into the chromatograph.

(b) The chromatographic unit

The chromatograph is a Hewlett Packard 5750 research unit, fitted out as a dual column instrument with full temperature programming facilities with output flow splitters for the simultaneous operation of thermal conductivity and flame (hydrogen) ionization detection. In normal chromatography the splitters are arranged to feed the two detectors in the flow ratios of 1 : 1. During mass spectrometric experiments a further splitter output (normally blocked at termination point T) is utilised to give a triple output of the main column to thermal conductivity, flame ionization and mass spectrometry in the ratios of 1 : 1 : 1. Because of the reduction of detector sensitivity during mass spectrometric analysis, quantitative chromatographic measurements are normally recorded with the mass spectrometer disconnected from the chromatograph.

Chromatographic data from the thermal conductivity and flame ionization detectors are recorded simultaneously with the dual channel recorder R. Peak areas for quantitative studies are determined by the Hewlett Packard 3370A electronic integrator coupled on-line to the chromatograph. The integrator is a single channel unit and can be switched to either detector as required. In operation, peak areas and retention times are automatically determined and printed. The attenuation of the recorder presentation is independent of the integrator coupling.

(c) The pre-column system

The pre-column system<sup>6</sup> is built into the helium stream of the reference column prior to the normal inlet port of the chromatograph. The system consists of a molecular sieve (M.S.) and a silica gel column (S.G.) with individual injection ports X and Y respectively. In operation, gaseous samples (approximately 0.25 to 0.5 ml) are injected into port X for the

separation of oxygen, nitrogen and carbon monoxide with molecular sieve and into port Y for the separation of carbon dioxide by the silica gel. After separation the gases pass unchanged through the chromatographic reference column (usually Porapak Q at 80°C) and are analysed by thermal conductivity detection with integration and print-out facilities for the peak areas. To date approximately 300 permanent gas analyses have been performed with the pre-column unit using a short programme in an electronic desk computer to calculate the gas percentages directly from integrator counts.

(d) The mass spectrometer

For mass spectrometric identifications of materials eluted from the chromatograph, the mass spectrometer is coupled, with a length of heated stainless steel capillary tubing, to the termination point T of the chromatographic splitter block. In this way, one third of the gas stream passing through the main column of the chromatograph is fed to a helium separator (Biemann type) and then directly to the ion source of the mass spectrometer.

The helium separator is essentially a sample enrichment device, designed to preferentially remove the helium gas and hence allow the eluted components (of relatively large molecular weight in comparison with helium) to pass into the analyser tube. The separator is shown diagrammatically in Fig. 2.

The helium carrier gas, together with the sample eluted from the chromatograph enter the separator via the heated capillary tube as shown. The helium diffuses through the porous (fritted) glass and is pumped to waste with a rotary oil pump. A proportion of the remaining gas, enriched in sample, passes through the exit leak into the mass spectrometer. The efficiency of the enrichment process and the percentage loss of sample through the fritted glass depends upon the molecular weight of the sample and the operating temperature of the separator. During an analysis the capillary inlet, the separator itself and the tube to the mass spectrometer must be maintained at a sufficiently high temperature in order to prevent the condensation or absorption of materials prior to their entry into the analyser tube. This type of separator can readily handle helium flow rates of up to 50 ml/min as is required during chromatography with packed columns.

The mass spectrometer used in this work is a fast scanning organic version of the AEI MS20 (termed 'Rapide') and is essentially a low resolution unit (resolution approximately 1 in 350 at 10 per cent valley) with magnetic



scanning. Fast analytical response is achieved by the use of an electron multiplier as an ion detector built into the main analyser tube, coupled to fast amplifiers feeding a three channel ultraviolet recorder (Fig. 1.) The recorder provides three presentations of mass spectra at sensitivities of 1, 10 and 100. Scanning speeds may be varied from 1 to 2000 sec/mass-decade (a decade being masses of say 1 to 10, 10 to 100 etc). A filter is provided to eliminate some background noise with slow scanning speeds. This filter must be removed for scan speeds in excess of 5 sec/mass-decade.

The mass spectrometer is also fitted with a separate amplifier and detector system (slow response) to provide a total ion monitor during experiments. This total ion monitor provides, by meter presentation, a check on the total number of ions generated in the ion source and hence gives a direct visual indication of components entering the analyser tube from the separator. This is necessary because there is a distinct time lag (about 10 sec) between the chromatographic detection of a component and its arrival at the mass spectrometer analyser tube.

On installation the mass spectrometer gave a resolution of 1 in 475 (at 10 per cent valley). The minimum quantity of material from the chromatograph required to give an identifiable spectrum is quoted as being about 10 nanograms, i.e.  $10^{-8}$  g.

A general view of the analytical laboratory is shown in Fig. 3. For convenience, the decomposition apparatus, the chromatograph and the mass spectrometer are labelled A, B and C respectively. Fig. 4 shows a view of the main analyser tube with the electron multiplier D and the helium separator E.

#### (ii) Experimental details for cellulose studies

Samples of cellulose\* or flame retarded cellulose (15-mg samples) were decomposed at temperatures between 250 and 500°C in a flow of air or nitrogen (100 ml/min at 20°C) for 15-minute periods. The decomposition products were collected prior to chromatography using liquid nitrogen (-196°C) as a refrigerant for the experiments involving nitrogen and isopentane (-160°C) for the experiments in air. Chromatographic separation of the products was undertaken using stainless steel columns (3.2 mm o.d. x 2 m) packed with Porapak Q, temperature programmed from 50 to 260°C at 4°C/min with a helium flow rate of 30 ml/min. For sensitivity reasons the products were monitored using flame ionization detection.

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\* in the form of low ash content filter paper.

Mass spectra were recorded at 70 ev at a scan rate of 5 sec/decade. The helium separator was operated in all experiments at 110°C. Spectra were interpreted using the data compiled by Cornu and Massot<sup>7</sup>.

Certain materials, identified by mass spectrometry, were confirmed by direct chromatographic seeding experiments. For this seeding technique a small amount of the material is introduced into the furnace with a cellulose sample during a decomposition experiment. An increase in the peak height of the component without doublet formation confirms the identification.

Flame retardant samples of cellulose were prepared by coating a sheet of cellulose filter paper with a sufficient volume of aqueous mono-ammonium phosphate (M.A.P.) to give, after drying, a 10 per cent add-on weight. Cellulose samples weighing 15 mg were used in all decomposition experiments (i.e. 15 mg cellulose or 15 mg cellulose + 1.5 mg M.A.P.).

### 3. RESULTS

#### (i) Analyses of the decomposition products of cellulose by gas chromatography - mass spectrometry

A chromatographic trace (flame ionization detection - F.I.D.) of the decomposition products of cellulose at 500°C (15-minute period) in nitrogen with product collection at -196°C is shown in Fig. 5\*. During this chromatographic analysis, mass spectra were recorded as each component (as numbered in Fig. 5) entered the analyser tube of the mass spectrometer and were interpreted using the data compiled by Cornu and Massot<sup>7</sup>. With some components, identifications were not possible due to overlap of chromatographic peaks, small mass spectra or interpretation difficulties but the mass of the molecular ion (i.e. the molecular weight), if distinct in the spectrum, is given. For convenience, Table 1 summarises the components identified, together with the chemical formulae and molecular weights. Also shown in Table 1 is the positive confirmation of a number of readily available compounds by direct seeding experiments.

It should be noted that the chromatographic trace of Fig. 5 is recorded, for sensitivity reasons, by flame ionization detection (F.I.D.) and hence only materials with a C - C or C - H bond (i.e. organic) are detected. The mass spectrometer is an 'absolute' detector and records all materials eluted

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\* The time scale (in minutes) of all chromatographic traces recorded in this report refers to the chromatographic analysis time. This is in no way connected with the 15-minute decomposition period.

from the column. Peak 1 of Fig. 5 is a small amount of methane eluted with approximately the same retention time as carbon dioxide. The carbon dioxide (not detected by F.I.D.) in the mass spectrometer masks the methane spectrum. In a similar manner, peak 4, eluted between peaks 3 and 5 in Fig. 5 is water, which is not detected by F.I.D. but gives a distinct response on the total ion monitor.

Table 1. The decomposition products of cellulose at 500°C in nitrogen as analysed by gas chromatography - mass spectrometry

Peak identification	Component name	Chemical formula	Mol. wt	Direct seeding confirmation
1	carbon dioxide <sup>δ</sup>	CO <sub>2</sub>	44	positive
2	ethylene	C <sub>2</sub> H <sub>4</sub>	28	positive
3	ethane	C <sub>2</sub> H <sub>6</sub>	30	positive
4	water <sup>δ</sup>	H <sub>2</sub> O	18	positive
5	propene	C <sub>3</sub> H <sub>6</sub>	42	positive
6	formaldehyde	HCHO	30	☒
7	propyne or propadiene*	C <sub>3</sub> H <sub>4</sub>	40	☒
8	acetaldehyde	CH <sub>3</sub> CHO	44	positive
9	butene*	C <sub>4</sub> H <sub>8</sub>	56	☒
10	furan	C <sub>4</sub> H <sub>4</sub> O	68	☒
11	acrolein	C <sub>2</sub> H <sub>3</sub> CHO	56	☒
12	acetone	CH <sub>3</sub> COCH <sub>3</sub>	58	positive
13	cyclopentene	C <sub>5</sub> H <sub>8</sub>	68	☒
14	allyl alcohol	C <sub>3</sub> H <sub>5</sub> OH	58	☒
15	not identified	(C <sub>4</sub> H <sub>6</sub> O) <sup>≠</sup>	70	☒
16	acetic acid	CH <sub>3</sub> COOH	60	positive
17	crotonaldehyde	C <sub>3</sub> H <sub>5</sub> CHO	70	☒
18	acetol	CH <sub>3</sub> COCH <sub>2</sub> OH	74	☒
19	not identified	-	≠	☒
20	not identified	-	≠	☒
21	not identified	-	92	☒
22	not identified	-	102	☒
23	furfural	C <sub>4</sub> H <sub>3</sub> OCHO	96	☒
24	not identified	-	98	☒
25	not identified	-	96	☒
26	not identified	-	98	☒
27	methyl furfural	CH <sub>3</sub> C <sub>4</sub> H <sub>2</sub> O <sub>2</sub> CHO	110	☒

<sup>δ</sup> not detected by F.I.D. (see text)

☒ not confirmed by seeding

\* isomeric configuration not clear by mass spectrometry

≠ possible molecular formula (see text)

≠ molecular ion not clear in spectrum

A chromatographic trace of the decomposition products of cellulose obtained under similar conditions as given above (i.e. a 15-minute period at 500°C) but in an air atmosphere with product collection at -160°C (isopentane) is given in Fig. 6. As in the nitrogen case, mass spectra were recorded as each component (lettered for identification in Fig. 6) entered the analyser tube. The peak identifications, component names, chemical formulae and molecular weights are summarised in Table 2. Also recorded are the equivalent component numbers for the nitrogen experiment.

In Table 2, the first recorded component (water) was detected by the total ion monitor. It was not possible in this experiment to record the first real peak (carbon dioxide) since the residual air (furnace carrier gas) in the collection trap is injected into the chromatograph with the decomposition products and is eluted rapidly from the Porapak Q column. This air enters the mass spectrometer and can damage the hot filament (i.e. electron source) by oxidation. Consequently, the mass spectrometer filament is usually turned off during this period. This problem is not present with the nitrogen atmospheres.

Table 2

The decomposition products of cellulose at 500°C in air  
as analysed by gas chromatography-mass spectrometry

Peak identification	Component name	Chemical formula	Mol wt	Equivalent nitrogen peak
a*	water $\beta$	H <sub>2</sub> O	18	4
b	methanol	CH <sub>3</sub> OH	32	-
c	acetaldehyde	CH <sub>3</sub> CHO	44	8
d	acrolein	C <sub>2</sub> H <sub>3</sub> CHO	56	11
e	acetone	CH <sub>3</sub> COCH <sub>3</sub>	58	12
f	allyl alcohol	C <sub>3</sub> H <sub>5</sub> OH	58	14
g	acetic acid	CH <sub>3</sub> COOH	60	16
h	crotonaldehyde	C <sub>3</sub> H <sub>5</sub> CHO	70	17
i	pyruvaldehyde	CH <sub>3</sub> COCHO	72	-
j	furfural	C <sub>4</sub> H <sub>3</sub> OCHO	96	23

\* the first peak (CO<sub>2</sub>) not analysed in experiments in air (see text)

$\beta$  not detected by F.I.D.

(ii) Chromatographic experiments with cellulose and flame retarded cellulose

The decomposition products of cellulose and flame retarded cellulose (mono ammonium phosphate) were studied by chromatography only at temperatures between 250 and 400°C in nitrogen and between 200 and 300°C in air. In all cases the decomposition period was limited to 15 minutes.

Figures 7, 8, 9 and 10 show the chromatographic traces (F.I.D.) of the decomposition products of the cellulose and flame retarded cellulose in nitrogen with product collection at -196°C at temperatures of 250, 300, 350 and 400°C respectively. All traces are shown on recorder range 1. It should be noted that the recorder was attenuated to range 4 (range 4 less sensitive than range 1) for the chromatographic traces of Figs. 5 and 6.

Figures 11 and 12 show the equivalent chromatographic traces of the cellulose and flame retarded cellulose in air at temperatures of 250 and 300°C with product collection at -160°C. For direct comparison purposes the traces are shown on recorder range 1.

(iii) Mass spectrometry of the decomposition products of flame retarded cellulose

Since the presence of the ammonium phosphate in the cellulose appeared to give a distinct simplification of the chromatographic traces, a repeat of the decomposition experiment (using the flame retarded cellulose) at 300°C in nitrogen was undertaken with mass spectrometric analysis of the 4 main products as numbered in Fig. 8. The relevant identifications are given in Table 3.

Table 3

The decomposition products of flame retarded cellulose  
at 300°C in nitrogen as analysed by  
gas chromatography-mass spectrometry

Peak identification	Component name	Chemical formula	Mol wt
1	methyl ethyl ketone	$\text{CH}_3 \text{CO} \text{C}_2\text{H}_5$	72
2	furfural	$\text{C}_4\text{H}_3\text{O} \text{CHO}$	96
3	methyl furfural	$\text{CH}_3\text{C}_4\text{H}_2\text{O} \text{CHO}$	110
4	-	-	117*

\* Not clear (see text)

Components 1, 2 and 3 were identified readily from the mass spectra. Component 4 gave a distinct mass spectrum but with certain irregularities. The spectrum shows distinct  $98^+$  and  $96^+$  fragments which could be furan derivatives (furfuryl alcohol  $98^+$  or furfural  $96^+$ ) but the molecular ion at  $117^+$  is inconsistent with the other fragmentation ions. Also the parent ion intensity is unusually low for the general type of compound encountered in this report. Component 4 may well be a mixture of components.

#### 4. DISCUSSION

##### (i) General discussion of experimental techniques

The report shows that the gas chromatograph-mass spectrometer unit, particularly when linked to an on-line decomposition system, is a very powerful and versatile tool for the analysis of the decomposition products of organic building materials. Mass spectra can be recorded satisfactorily as components are eluted from the chromatograph and the component resolution of the mass spectrometer is similar to that of the chromatograph, i.e. there is little or no tailing or spreading of component peaks in the interface equipment. There are, however, some problems in interpreting mass spectra firstly where the mass spectrum is small, secondly where there is inadequate resolution of components in the chromatograph, thirdly where there is inadequate reference data available, and fourthly where mass spectra of isomeric compounds are



very similar. However, the common problem of column bleed in coupled gas chromatography does not appear to be a significant problem with the porous polymer column materials (Porapak Q) used in this report.

(ii) Discussion of the decomposition products of cellulose

Approximately 30 components (Fig. 5) have been detected during the thermal decomposition of cellulose at 500°C in nitrogen and out of the 27 examined by mass spectrometry, 19 have been identified and the molecular weights of an additional 6 recorded. Of the 19 materials identified, 8 were readily available in the laboratory and all gave positive confirmation by direct seeding techniques.

In the decomposition at 500°C in air (Fig. 6), 10 components were analysed and identified by mass spectrometry. Two of these components (methanol and pyruvaldehyde) were not detected in the nitrogen atmosphere.

In general the products from both the nitrogen and air atmospheres at 500°C are saturated and unsaturated aldehydes, acids, ketones, alcohols and heterocyclic compounds. In the nitrogen atmosphere there are additional unsaturated and saturated aliphatic hydrocarbons (which may be derived from the dehydration of oxygenated species).

The chromatographic studies of the products from the decomposition of the normal and flame retarded cellulose in nitrogen and air show a number of interesting features relevant to the action of the flame retardant. At low temperatures in nitrogen (250°C as in Fig. 7) the flame retardant produces a distinct increase in the quantities\* of flammable vapours (consequently the retarded material is more prone to decomposition than the normal cellulose). Also, rather than producing a varied mixture of products the retardant is selective and generates only 4 main components. The increase in temperature from 250 to 350°C (see Figs. 7, 8 and 9) produces an increase in the quantity of volatiles from the normal cellulose but approximately the same quantity from the flame retarded cellulose. At these temperatures the retardant is again selective in favouring the formation of the four components.

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\* The peak area for a particular material in a chromatographic trace (F.I.D.) is a measure of the quantity generated during the decomposition.

At 400°C, the normal material generates greater quantities of volatiles than the flame retarded cellulose. Also, the retardant is now more selective than at lower temperatures and produces only 2 main components.

In air, the volatiles at 250°C (Fig. 11) from the normal cellulose are small in quantity; the flame retarded cellulose is again more prone to decomposition and apparently produces the same 4 components in similar amounts to those of the nitrogen experiment at 250°C. At 300°C in air (Fig. 12), the products from the normal cellulose are greater in quantity than in the nitrogen case but the oxidative route has selected 3 main components, 2 of which could well be peaks 3 and 4 of the flame retarded grade (see Fig. 8). The flame retarded cellulose at 300°C in air (Fig. 12) produces less volatiles (quantitatively) than the normal material.

Of the 4 main components generated during the decomposition of the flame retarded cellulose, 3 have been identified by mass spectrometry as methyl ethyl ketone, furfural and methyl furfural. The action of the ammonium phosphate appears to be of a selective nature by specifically favouring a particular decomposition route. The action is sufficiently powerful to override the selective oxidative route. There may, however, be similarities between the oxidative and flame retardant action. Also, although the flame retarded material is more prone to decomposition and generates greater quantities of products than the normal cellulose at low temperatures (250°C), the reverse is true at higher temperatures.

### (iii) Comparisons of the cellulose results with other work

In recent years a number of workers have studied the decomposition products of cellulose<sup>8</sup>. In 1969, Lipska and Wodley<sup>9</sup> studied the decomposition products of cellulose and treated cellulose (2 per cent potassium bicarbonate) by gas chromatography and mass spectrometry.

More recently Lipska et al<sup>10</sup> extended this work to cover the action of ammonium phosphate (2 per cent) and certain chemical treatments.

Unfortunately their work is not directly comparable with the data of the present report because of the different levels of flame retardants used. However, the results of Lipska et al for the decomposition products of the normal cellulose together with their reported selectivity of flame retardants (including ammonium phosphate) in product formation are in good agreement with the finding of this present report.

From their studies, Lipska et al<sup>11</sup> suggested the following model to explain their experimental observations. Cellulose, irrespective of its molecular weight decomposes rapidly above about 275°C with rupture of the glucosan units in an unzipping manner. Approximately 60 per cent of the severed glucosan units rearrange to form laevoglucosan and the remaining severed glucosans enter into char formation reactions with the release of H<sub>2</sub>O, CO, CO<sub>2</sub> and H<sub>2</sub>. Most of the observed pyrolysis products result from the decomposition of the laevoglucosan and other reactions among the decomposition products.

Lipska et al<sup>11</sup> show that the flame retardants (including ammonium phosphate) increase the rate of decomposition by increasing the rate of the unzipping process. Also, the retardants alter the decomposition route of the laevoglucosan (not the cellulose) giving preference to char formation routes. The decrease in flammability of retarded cellulose was explained as resulting from an increase in the dilution of the carbon rich laevoglucosan vapour with the carbon lean gases released during char formation.

## 5. CONCLUSIONS

1. Gas chromatography-mass spectrometry, particularly when coupled to an on-line decomposition system, is a powerful and versatile analytical tool for studies of the decomposition products of organic building materials.
2. With the system, mass spectra can be recorded as materials are eluted from the chromatograph. There appears to be little or no loss in chromatographic resolution in the interface equipment of the gas chromatograph-mass spectrometer.
3. There are some problems of mass spectrometric identifications of materials particularly:-
  - (a) Where there is poor separation of materials in the chromatograph.
  - (b) Where there is insufficient mass spectrometric reference data.
  - (c) Where the mass spectra of isometric materials are very similar.
4. The thermal decomposition of cellulose produces a complex mixture of hydrocarbons, aldehydes, acids, ketones, alcohols and heterocyclic compounds. This is in good agreement with other experimental work.
5. Ammonium phosphate alters the general decomposition pattern of products and selectively generates only 4 main products.

6. The flame retarded material is more prone to decomposition and produces a greater quantity of products (as measured by F.I.D.) than the normal cellulose at low temperatures. At higher temperatures (i.e. above 250°C) the flame retarded cellulose produces a smaller quantity of products than the normal cellulose.

#### 6. ACKNOWLEDGMENTS

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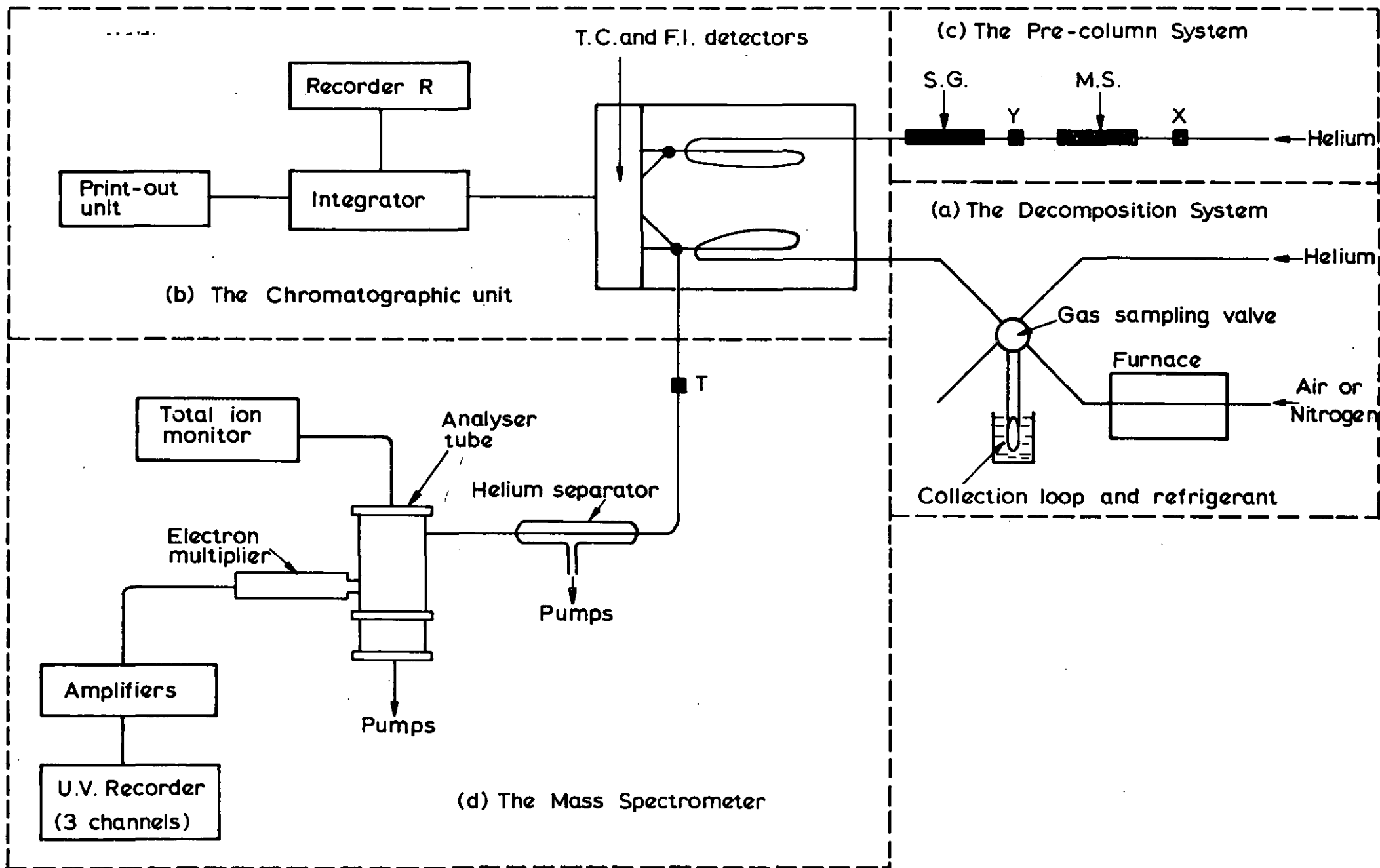
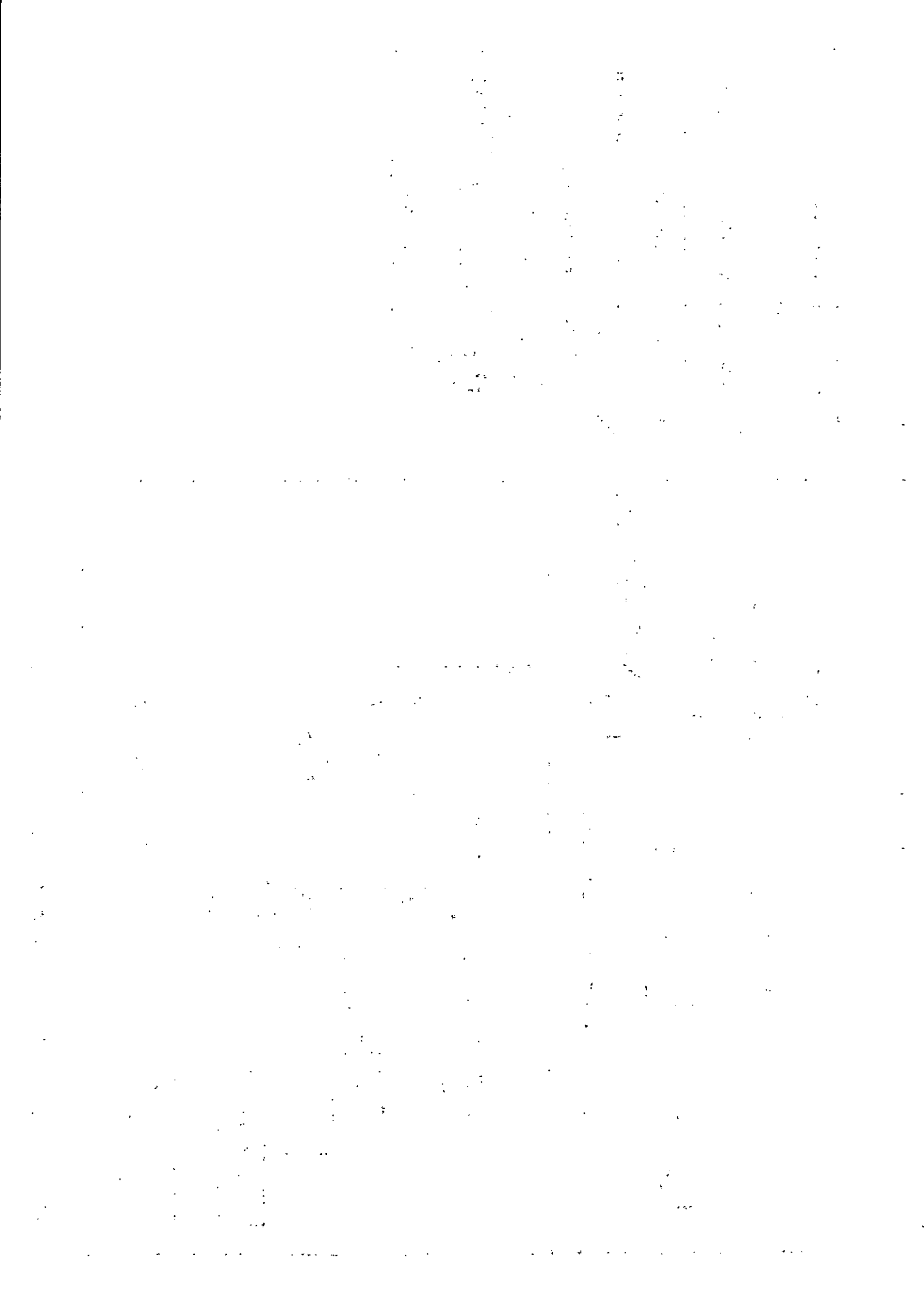


FIG. 1. BLOCK DIAGRAM OF THE COMPLETE DECOMPOSITION SYSTEM



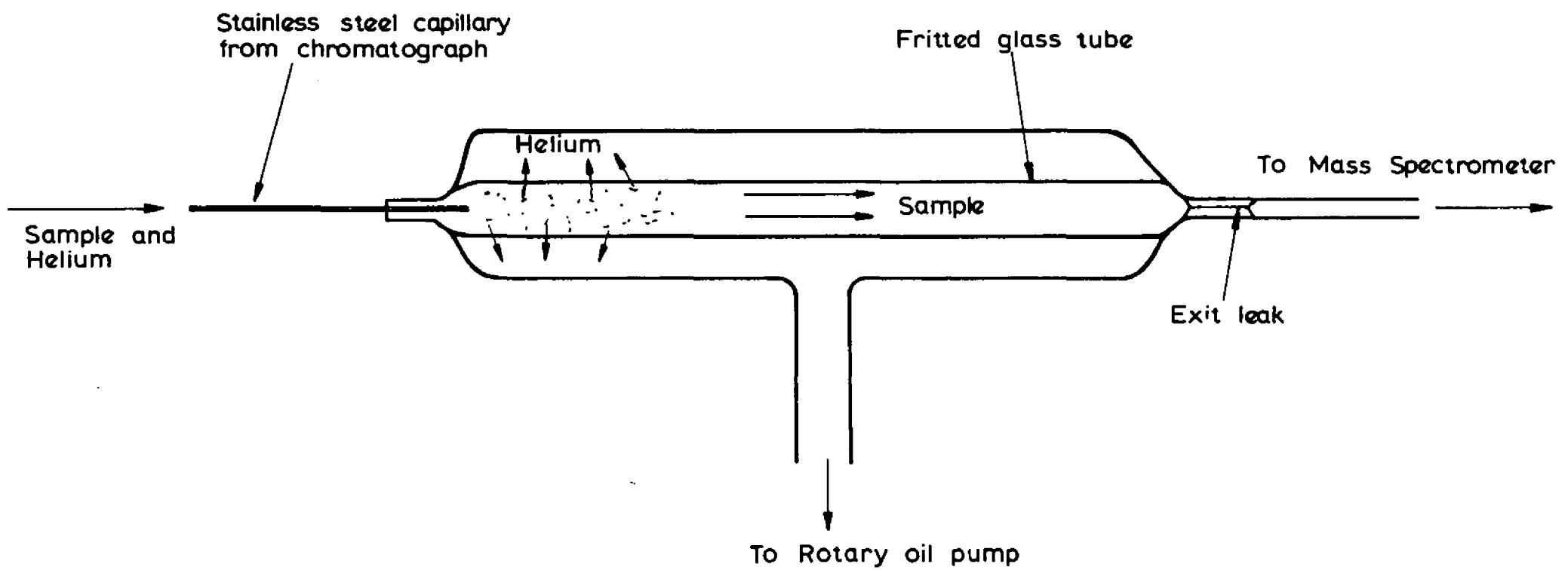
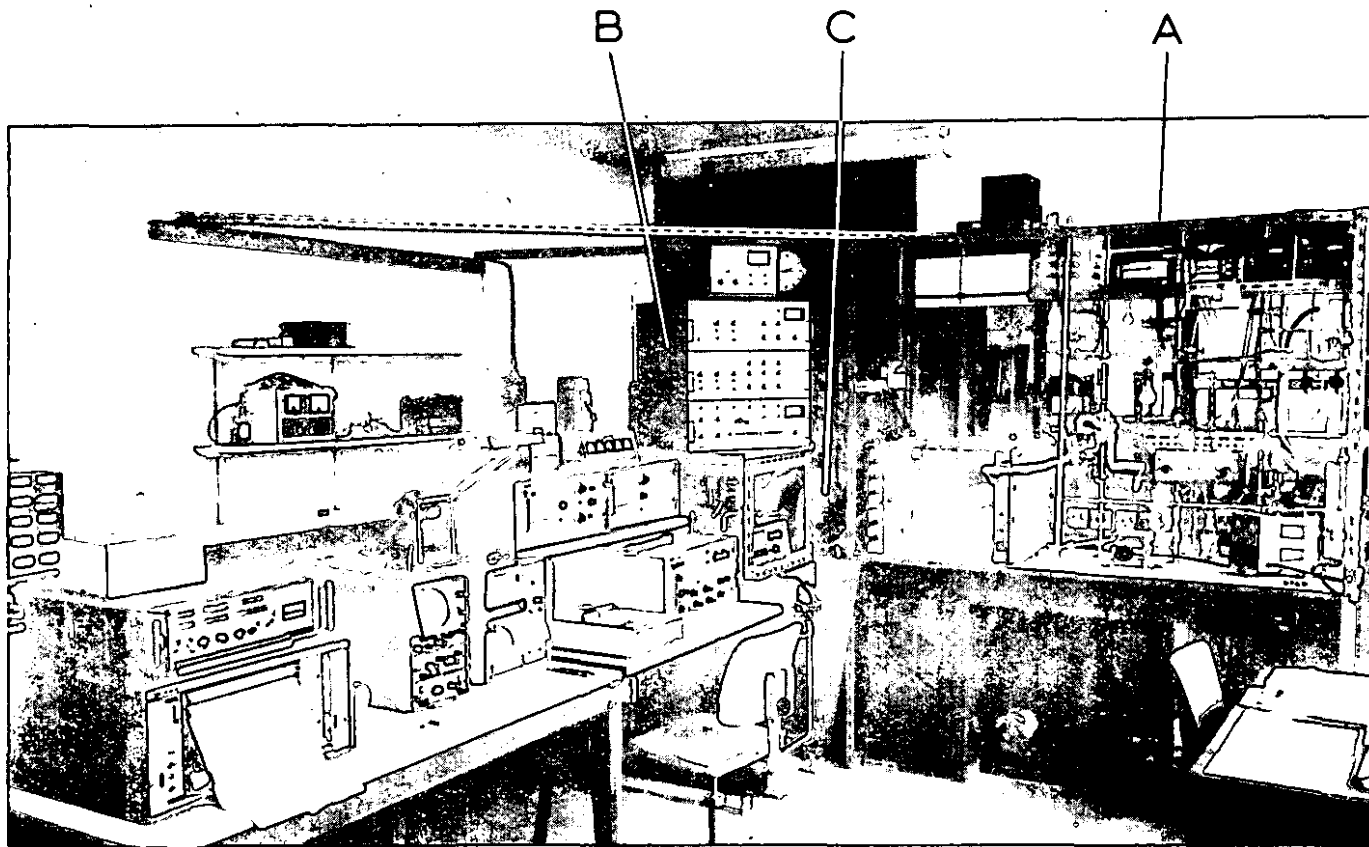


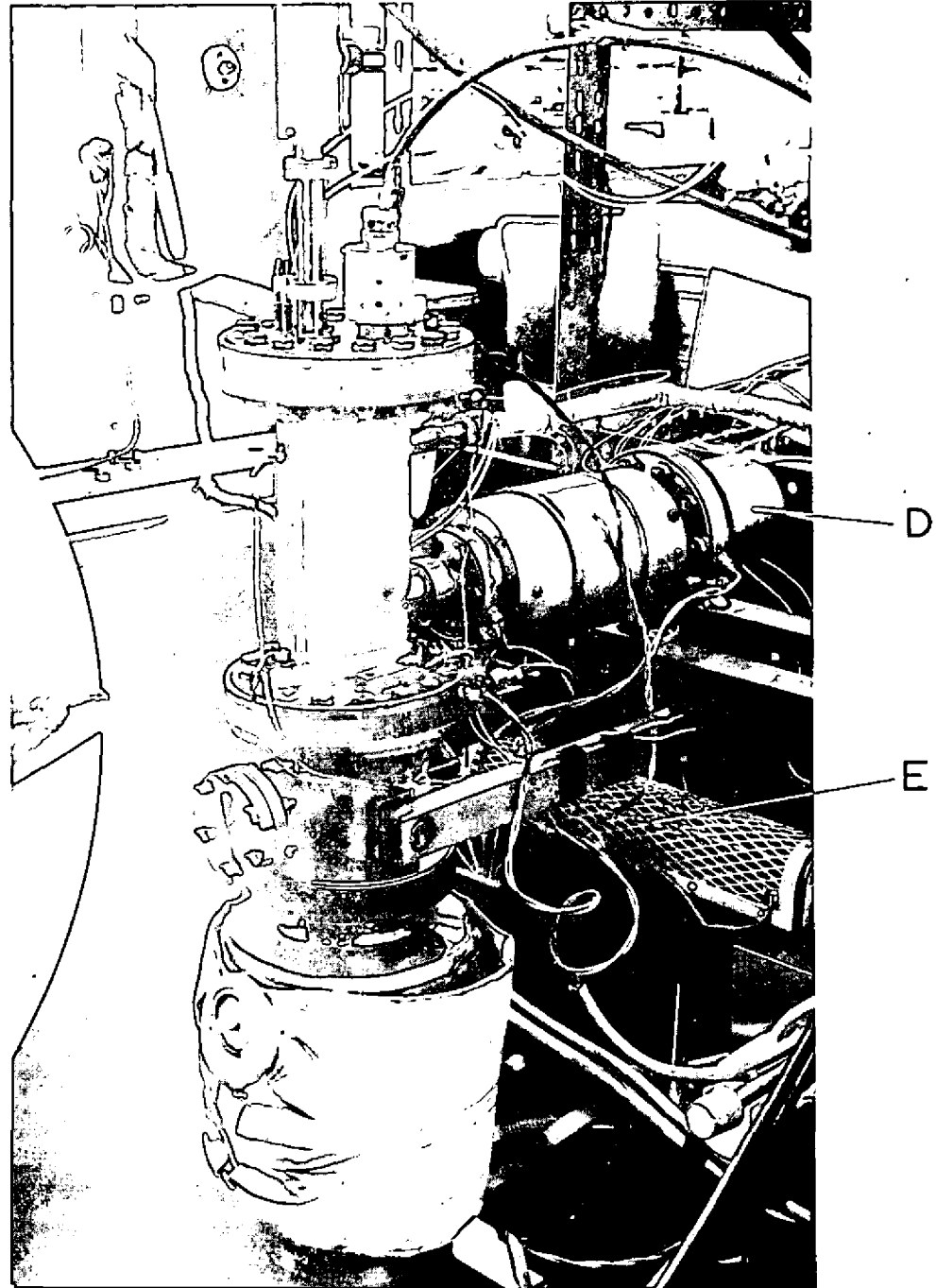
FIG. 2. THE HELIUM SEPARATOR





- A The decomposition apparatus
- B The chromatograph
- C The mass spectrometer

FIG. 3. A GENERAL VIEW OF THE ANALYTICAL LABORATORY



- D Electron multiplier
- E Helium separator

FIG. 4. THE MAIN ANALYSER TUBE

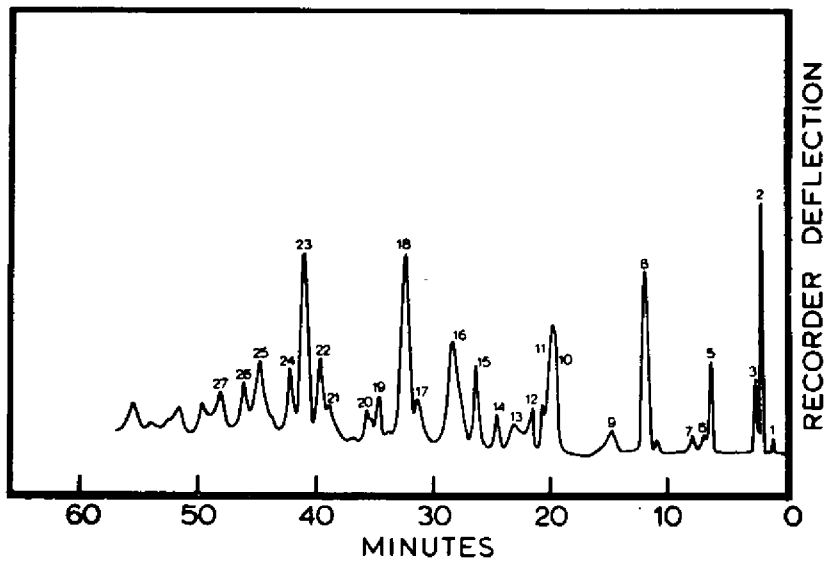


FIG. 5. THE DECOMPOSITION PRODUCTS OF CELLULOSE AT 500°C IN NITROGEN. (RECORDER RANGE 4)

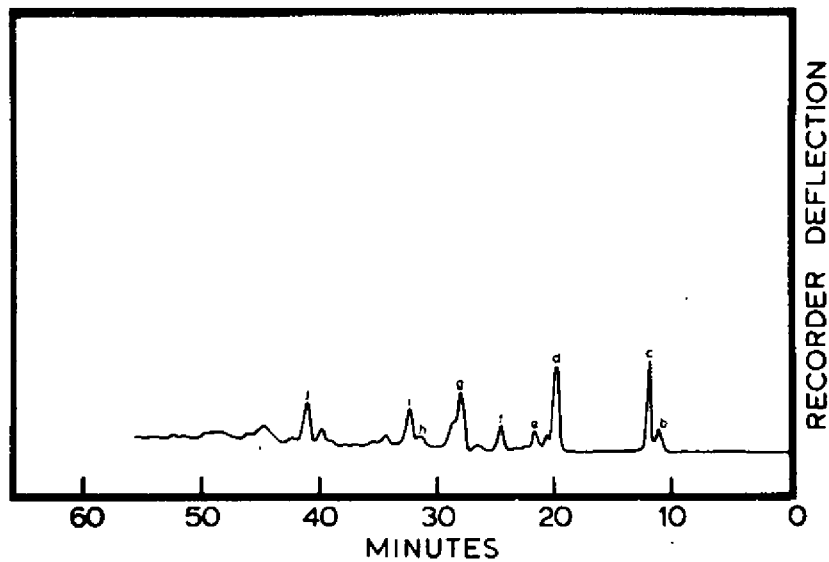
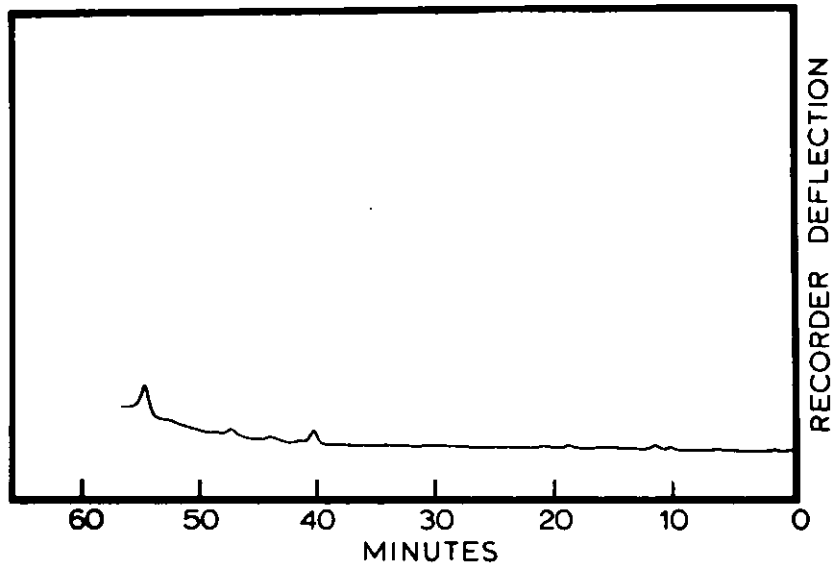
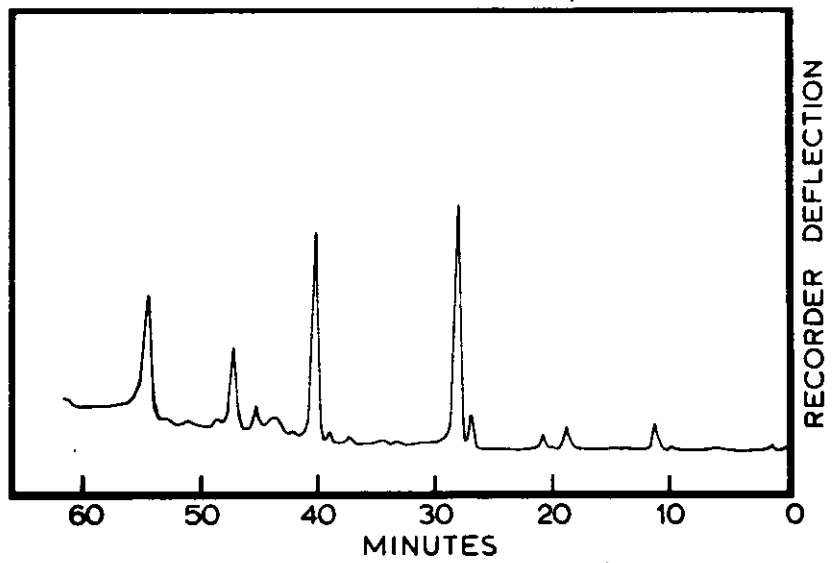


FIG. 6. THE DECOMPOSITION PRODUCTS OF CELLULOSE AT 500°C IN AIR. (RECORDER RANGE 4)

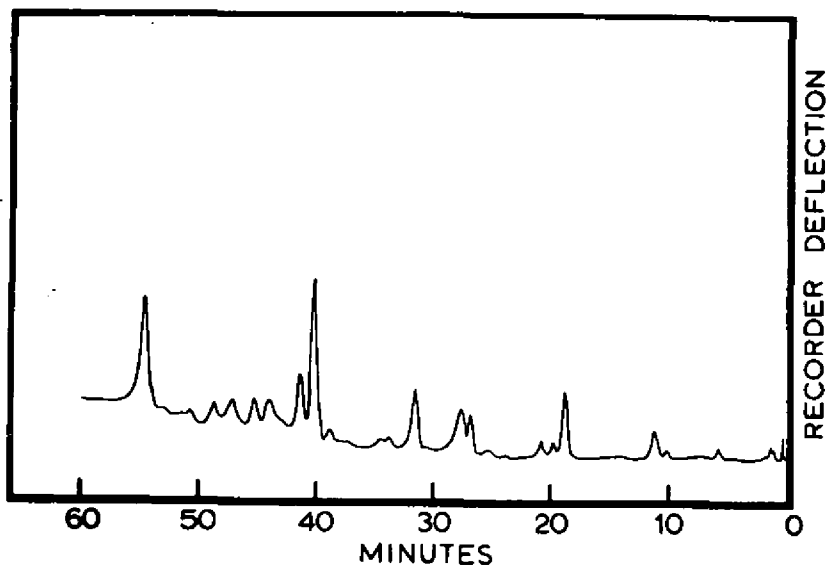


NORMAL CELLULOSE

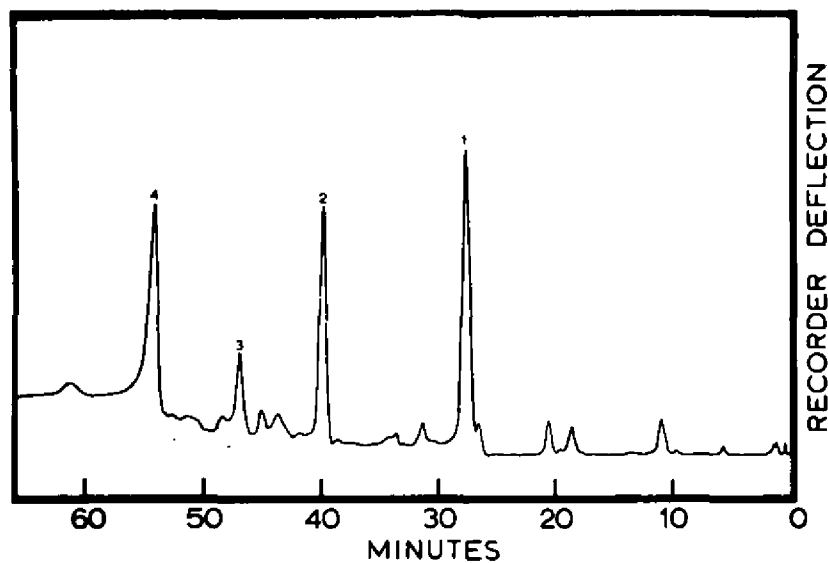


FLAME RETARDED

FIG. 7. THE DECOMPOSITION PRODUCTS OF CELLULOSE AT 250°C IN NITROGEN

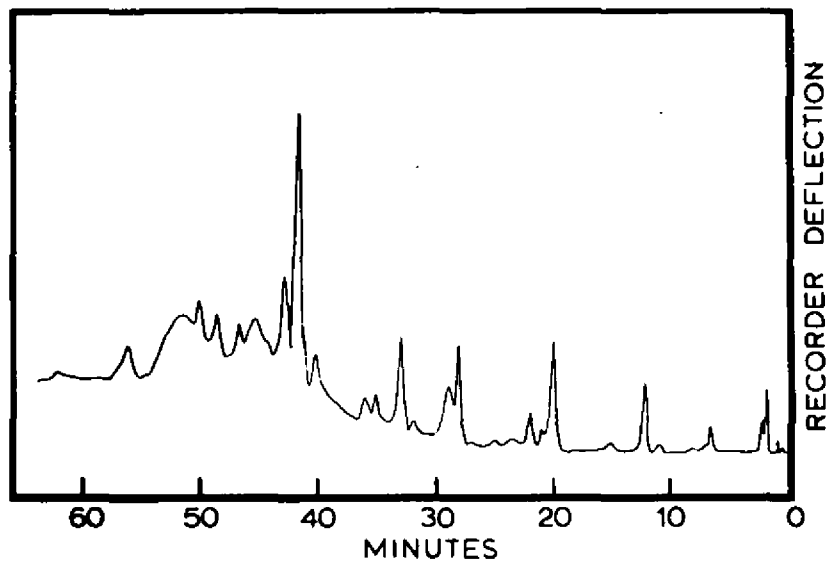


NORMAL CELLULOSE

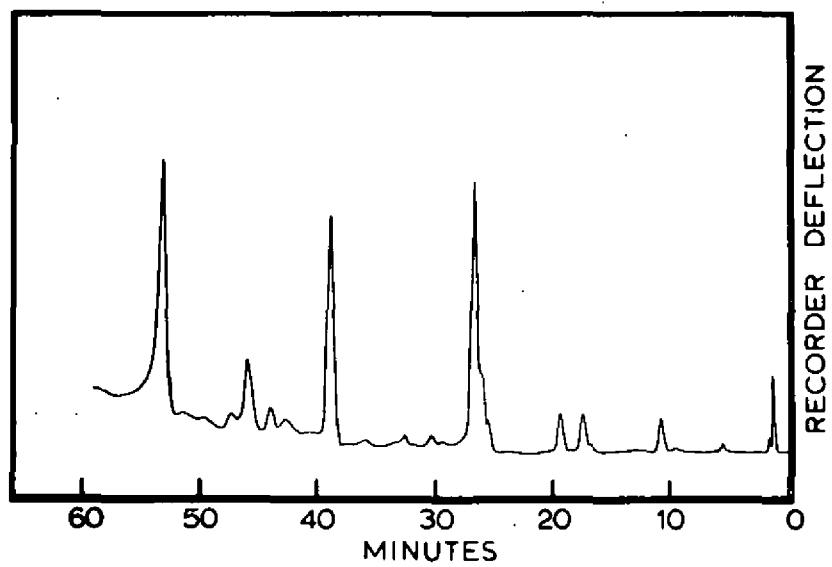


FLAME RETARDED

FIG. 8. THE DECOMPOSITION PRODUCTS OF CELLULOSE AT 300°C IN NITROGEN

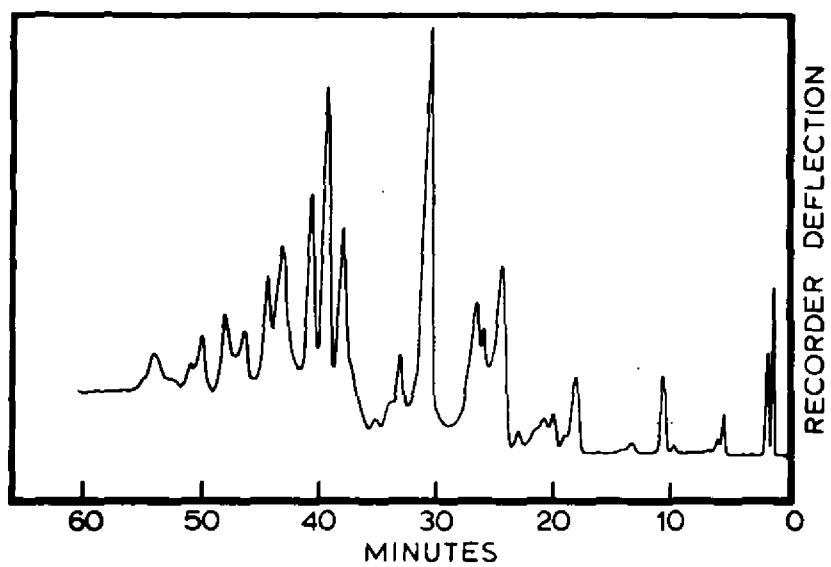


NORMAL CELLULOSE

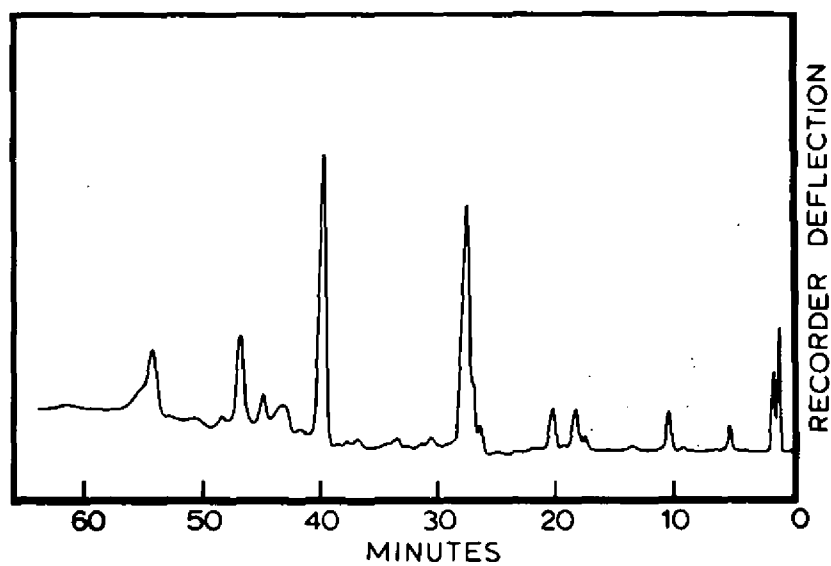


FLAME RETARDED

FIG. 9. THE DECOMPOSITION PRODUCTS OF CELLULOSE AT 350°C IN NITROGEN

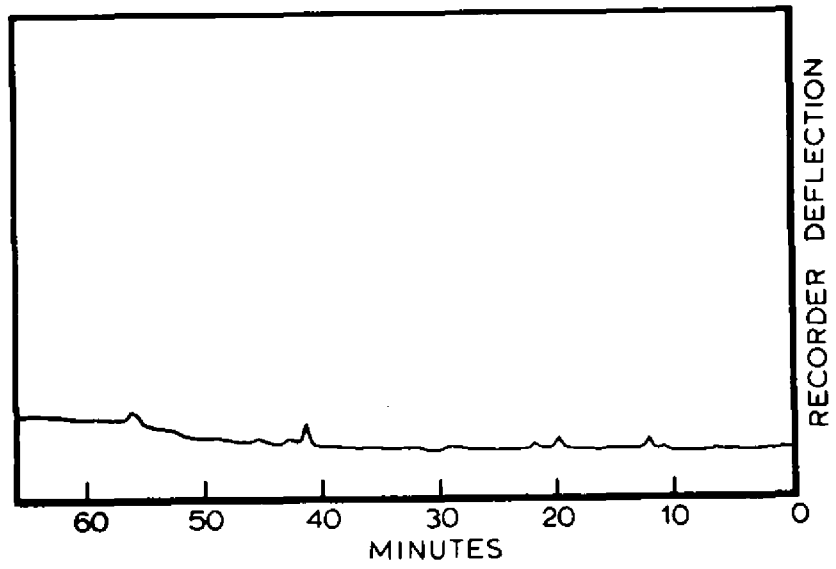


NORMAL CELLULOSE

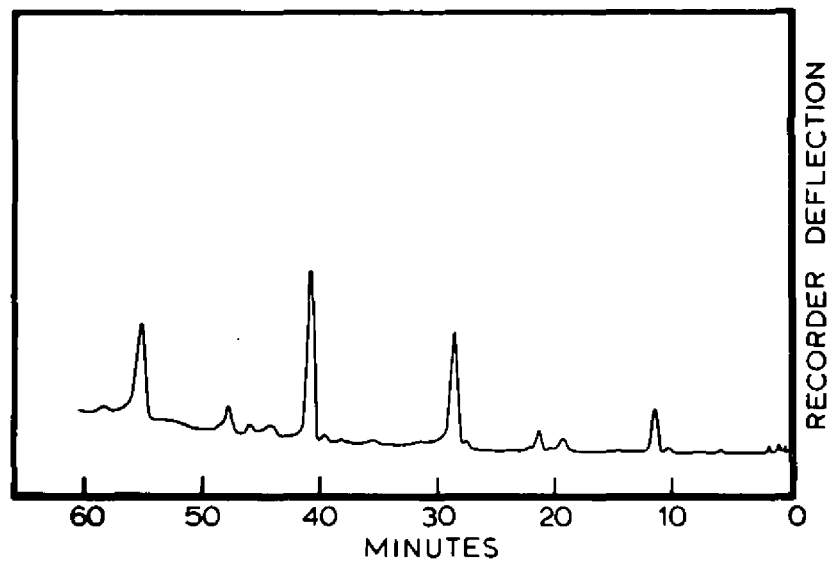


FLAME RETARDED

FIG. 10. THE DECOMPOSITION PRODUCTS OF CELLULOSE AT 400°C IN NITROGEN



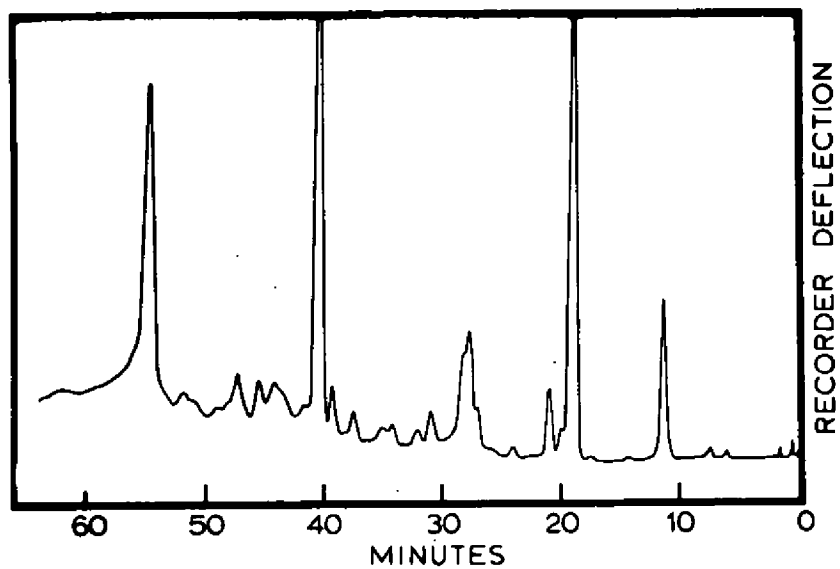
NORMAL CELLULOSE



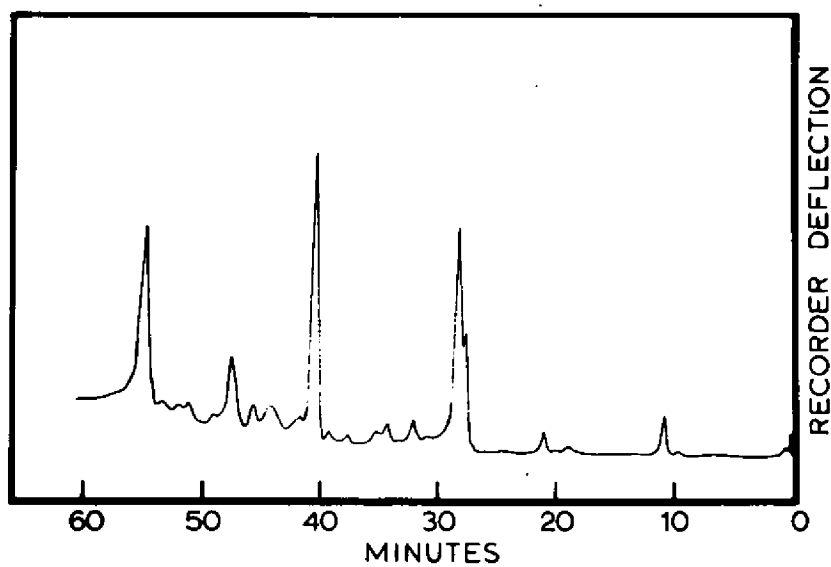
FLAME RETARDED

FIG. 11. THE DECOMPOSITION PRODUCTS OF CELLULOSE AT 250°C IN AIR





NORMAL CELLULOSE



FLAME RETARDED

FIG. 12. THE DECOMPOSITION PRODUCTS OF CELLULOSE AT 300°C IN AIR

