

A STUDY OF THE DECOMPOSITION PRODUCTS OF POLYURETHANE FOAM RELATED TO AIRCRAFT CABIN FLASH FIRES

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16. Abstract A laboratory model of a flash fire cell using a high voltage arc as an ignition source was assembled and tested. The cell is designed to pyrolyze the sample in air while measuring the time of onset of a flash fire and simultaneously allowing withdrawal of gas samples for analysis. Some of the low molecular weight products produced from the pyrolysis of flexible polyether type urethane foams were identified. The flash fire cell was used to compare the flash fire potential of polymers of potential interest to the aircraft industry. Studies of the role of smoke in flash fire produced in the pyrolysis of flexible urethanes were undertaken. Flash fires in the cell were recorded on 16 mm motion picture film.			
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PREFACE

This report represents the third in a series of NBS reports under the joint sponsorship of NBS and FAA. The development of a method of assessing the flash fire potential of polymeric materials and methods of identification of the pyrolysis gas components responsible for flash fires are described.

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TABLE OF CONTENTS

	Page
INTRODUCTION	1
Purpose	1
Background	1
DISCUSSION	2
Flash Fire Cell	2
Design Criteria	2
Laboratory Model Construction	2
Ignition Source	2
Pyrolysis Unit	5
TEST PROCEDURE	6
Materials	6
Pyrolysis and Combustion Gas Analysis	7
Gas Chromatographic Equipment	7
Infrared Analysis	9
EXPERIMENTAL RESULTS	10
Combustible Gas Analysis	10
Gas Analysis	10
Analysis of Smoke	19
Intercomparison of Materials - Flash Fire Potential	27
SUMMARY OF RESULTS	31
Gas Analysis and Smoke Characterization	31
Development of Flash Fire Cell	31
CONCLUSIONS	32
APPENDIX References	33

LIST OF ILLUSTRATIONS

Figure		Page
1	Flash fire apparatus	3
2	Schema of flash fire cell	4
3	Instrumentation for gas analysis	8
4	Total combustible gases evolved from polyurethane foam heated in nitrogen as a function of temperature	11
5	Chromatograms of flexible foam decomposition products in air before onset of flash fire	12
6	Chromatogram of same mixture as Figure 5, but with "air" peak resolved only	13
7	Pyrogram of orange smoke deposit from flexible urethane	21
8	Pyrogram of acetone extract of orange smoke deposit	22
9	Pyrogram of original unretarded urethane foam	23
10	Infrared spectrogram of smoke condensate in potassium bromide. (Strong 9 μm absorption characteristic of polyether type urethane)	24
11	Infrared spectrogram of acetone extract of smoke condensate in potassium bromide. (Strong 9 μm absorption characteristic of polyether type urethane)	25
12	Infrared spectrogram of acetone extract of smoke condensate in carbon tetrachloride. (* solvent absorption)	26

LIST OF TABLES

Table		Page
I	Weight Percent Composition of Polyurethane Pyrolysis Products	16
II	Polyurethane Pyrolysis Products	17
III	Lower Limits of Flammability of Pyrolysis Products in Air	18
IV	Elemental Analysis of the Orange Smoke and Polyurethane Foam	28
V	Intercomparison of Materials - Flash Fire Potential	29

INTRODUCTION

Purpose

The purpose of this project was to develop a laboratory model for assessing flash fire potential of aircraft interior plastics and to obtain analytical data on the composition of gases producing flash fires.

Background

This report covers the time interval March 1971 through June 1972. Previous NBS reports on the first phase of this program described exploratory experiments on fire growth in model enclosures and an extensive investigation of smoke and gases produced by testing aircraft interior materials in the smoke test chamber [1]. While these data are helpful in evaluating potential hazards of various materials, the complex phenomena of flash fires as they might relate to aircraft cabins are not well defined. In this work, a flash fire appears to involve gas phase combustion reactions from the products of the thermal decomposition of solid organic materials within the cabin enclosure. The above studies on a gross macroscopic level have limited value in arriving at a detailed understanding of flash fires or flashover conditions [2,3]. Meaningful design of large scale tests requires some understanding of the fundamental processes involved and identification of the important variables. Carefully designed laboratory models should provide a practical approach to the analysis of these complex systems while affording the opportunity to obtain precise quantitative data on combustion products and reactions.

The initial reactions of interest in this study include a low temperature pyrolysis reaction in the condensed phase to produce a combustible gas mixture. Subsequent pyrolysis of organic compounds in the gas phase may then occur. Propagation of flame in the gas phase will depend on the composition of the combustibles and ratio of combustibles to air. In addition to these important variables the rate of heating, source of ignition, and type of heating have been considered in designing a laboratory model. This report describes: (a) the successful design and construction of a laboratory model for producing flash fires; (b) preliminary comparisons of various polymers to assess the usefulness of the apparatus for measuring flash fire potential of materials; and (c) the analysis of pyrolysis gases evolved from flexible polyurethane.

DISCUSSION

Flash Fire Cell

Design Criteria

Design criteria for the laboratory model included:

1. An arrangement for varying the method of heating the sample to be pyrolyzed. Methods considered included burner heating, electric furnace, and laser radiation.
2. Variable sources of ignition remote from the site of solid and gas pyrolysis.
3. Capability of monitoring gas composition during the experiment by means of infrared absorption spectrophotometry.
4. Sampling ports for removal of gas samples for analysis by means of gas chromatography with a minimum perturbation of the cell contents.
5. Transparent cell to allow measurement of flame front and time of initiation of flash fire.
6. Positional flexibility to allow measurement of the effect of orientation of the cell in gravitational field on the flash fire.

Laboratory Model Construction

The cell was constructed of a pyrex cylinder 50 cm (approx. 20 in.) in length and 5 cm (approx. 2 in.) in diameter (Figures 1 and 2). With a total volume of approximately 1 liter, each end of the glass cylinder had as an integral part "O" ring flanges filled with neoprene "O" rings and polymethyl methacrylate windows fastened with spring loaded clamps. This arrangement allowed for safe pressure release resulting from the explosions generally accompanying the flash fire. The pyrolysis sample holder (B) was connected to the main cell body by a glass "O" ring flange. The "O" ring connection facilitated rapid removal for cleaning and sample replacement. Fittings were provided for rapid gas sampling into evacuated bulbs (A,C,D) and for removal or adjustment of the ignition source (E).

Ignition Source

The ignition source was a 10 KV AC arc, about 1 cm in

The polyol in this instance was a polymer formed from glycerol and ethylene oxide. The essential point is that it have a number of OH groups available to react with the isocyanate. The density of the foam was approximately 2.0 pounds per cubic foot (0.032 grams per cubic centimeter) and utilized water as a blowing agent. The foam was prepared from the following formulation: a trifunctional, 3000 m.w. polyether polyol (a propylene oxide adduct of glycerol), water, a polydimethylsiloxane-polyoxyalkylene block copolymer, amine catalyst, stannous octoate, and a blend of 2,4 and 2,6 toluene diisocyanates.

The majority of tests where the urethane sample is not specified employed a polyether diisocyanate type urethane provided by the FAA. These were both fire retarded and unretarded samples although the type of retardant was not identified. In tests where retarded samples received from FAA were employed no measurable differences from unretarded foam were noted.

Pyrolysis and Combustion Gas Analysis

Gas samples were collected both before and after flash-over. A 500 ml evacuated bulb fitted with a hypodermic needle and rubber septum was used. Samples were then transferred through an evacuated manifold equipped with manometers to the sampling inlet valve of a gas chromatograph. (Figure 3)

Gas Chromatographic Equipment

A gas chromatograph equipped with two thermal conductivity (TC) and two flame ionization detectors (FID), and two column ovens with temperature programming capabilities was used for separation and identification of the gaseous pyrolysis products (Figure 3). A sampling valve in conjunction with a 2 or 5 ml loop was used for transferring gas samples from the sampling bulb into the gas chromatograph.

The dual column gas chromatographic technique was used for simultaneous resolution of air components and low-boiling hydrocarbons. A 5 foot Porapak Q stainless steel column, 50/80 mesh, 1/4 inch in diameter was connected in series with a 5 foot molecular sieve 5A copper column, 60/80 mesh, 1/4 inch in diameter with the aid of a 4-way switching valve. The Porapak Q column was in one oven and during the analysis the temperature was programmed from 60 to 200 °C (140-392 °F) by holding the column oven constant at 60 °C (140 °F) for 4 minutes. Then the temperature was raised at a rate of 10 °C (18 °F)/minute. Baseline drift during temperature programming was eliminated by using an identical reference column.

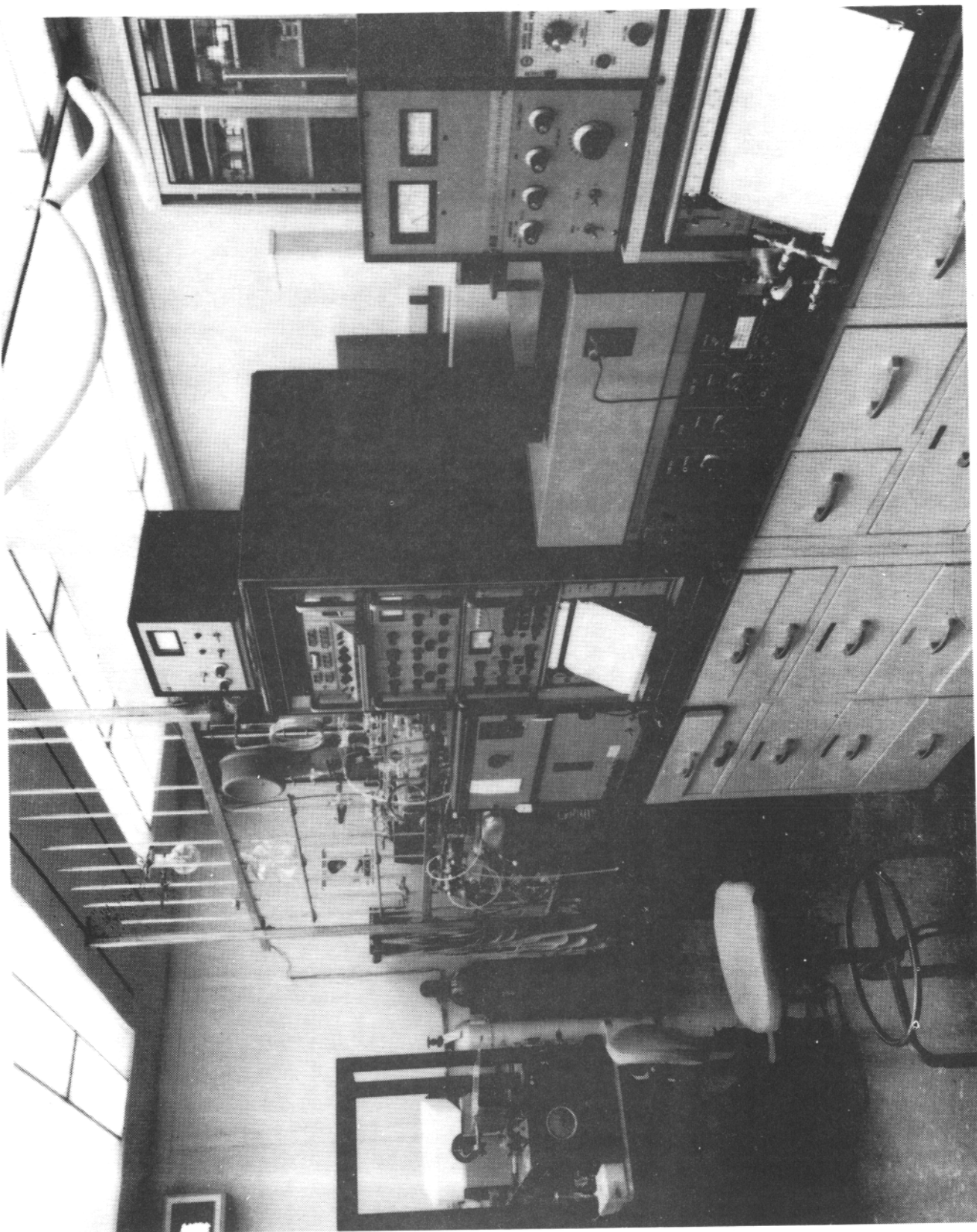


FIGURE 3. INSTRUMENTATION FOR GAS ANALYSIS.

Helium was used as a carrier gas at a flow rate of 60 ml/min. at 62 psi. The eluted gases were detected by one thermal conductivity and two flame ionization detectors held at 200 °C (392 °F). Since the first column did not resolve the air and methane peaks at these experimental conditions, the combined peak was allowed to enter the molecular sieve column and the 4-way valve was switched before heavier components, particularly carbon dioxide, were eluted from the Porapak Q column. A matching restriction valve consisting of a micrometer valve was connected to the exit of the 4-way valve to eliminate excessive pressure change. The molecular sieve column was held isothermally in the second oven at 90 °C (194 °F) and the permanent gases and methane were detected by the second thermal conductivity detector. During the preliminary runs the dual column facility was not available and the sample gas mixture entered directly into the molecular sieve column held at 75 °C (167 °F). The filament currents of the thermal conductivity detectors were kept constant at either 100 or 150 milliamperes. Two recorders, 1 millivolt full scale sensitivity, were used. For analysis of nonvolatile samples the gas chromatograph was equipped with a pyrolysis unit consisting of an electrode with platinum-rhodium filament and a variable power supply.

A temperature of 1000 °C (1832 °F) was used for pyrolyzing samples of polyurethane foam and solid particles of smoke in a helium atmosphere. These degradation products were separated by the Porapak Q column using the same temperature programming as for the previous gaseous products.

Infrared Analysis

For this work infrared absorption spectra were recorded by a spectrophotometer with a spectral range of 250-4000 cm^{-1} . For gaseous samples a 1 m gas cell was used. For solid samples either the potassium bromide (KBr) pellet technique or the liquid phase technique in carbon tetrachloride (0.07 mm cell) was used. The KBr technique provides a convenient method of sample preparation; especially for samples not soluble in the usual spectroscopic solvents. A 1% mixture of sample in KBr is finely ground and pressed under vacuum and high pressure into a clear disc or pellet 1 cm in diameter by approximately 1 mm thick. The carbon tetrachloride or solution method involves a dilute solution of the sample placed in a cell with NaCl windows and in this case an optical path length of 0.07 mm. This method has the disadvantage that solvent absorption may interfere with sample absorption.

EXPERIMENTAL RESULTS

Considerable emphasis was placed on analysis of pyrolysis gases leading up to the onset of a flash fire. Identification of the gas or gases responsible could be important in suggesting ways of reducing this hazard. Thermal decomposition of polyurethanes in air produces a complex mixture of gases and smoke. This report describes the analysis of components with molecular weight 50 or less evolved during the initial stages of decomposition.

Combustible Gas Analysis

Total combustible gas release as a function of temperature was obtained in a special apparatus designed for the purpose [6].¹ A sample of foam was heated in nitrogen at a constant rate and the gases swept through a combustible gas analyzer. The resulting curve shows the total combustible gas release as a function of temperature (Figure 4). Fine thermocouple wire is employed with some care being given to maintaining thermal contact with the sample so that the temperatures will reflect actual decomposition points. Small amounts of combustible gas are released at 290 °C (554 °F) and 320 °C (608 °F) with most decomposition occurring at 410 °C (770 °F). The heating was not continued above 500 °C (932 °F).

Gas Analysis

The gaseous pyrolysis products evolved by heating flexible polyurethane foam samples in air, were analyzed before and after flashover phenomenon by gas chromatography and infrared spectroscopy. Typical chromatograms of pyrolysis mixture before flashover are shown in Figures 5 and 6. Figure 5 contains in effect two chromatograms, the upper curve monitored with the flame ionization detector (FID) and the lower curve with the thermal conductivity detector (TC). The temperature scale represents the column temperature program and the times are elution or retention times. Both detectors are required because of their differing responses to the various components. The numbers are attenuation factors

¹ Analysis performed by R. J. McCarter, Fire Technology Division, National Bureau of Standards.

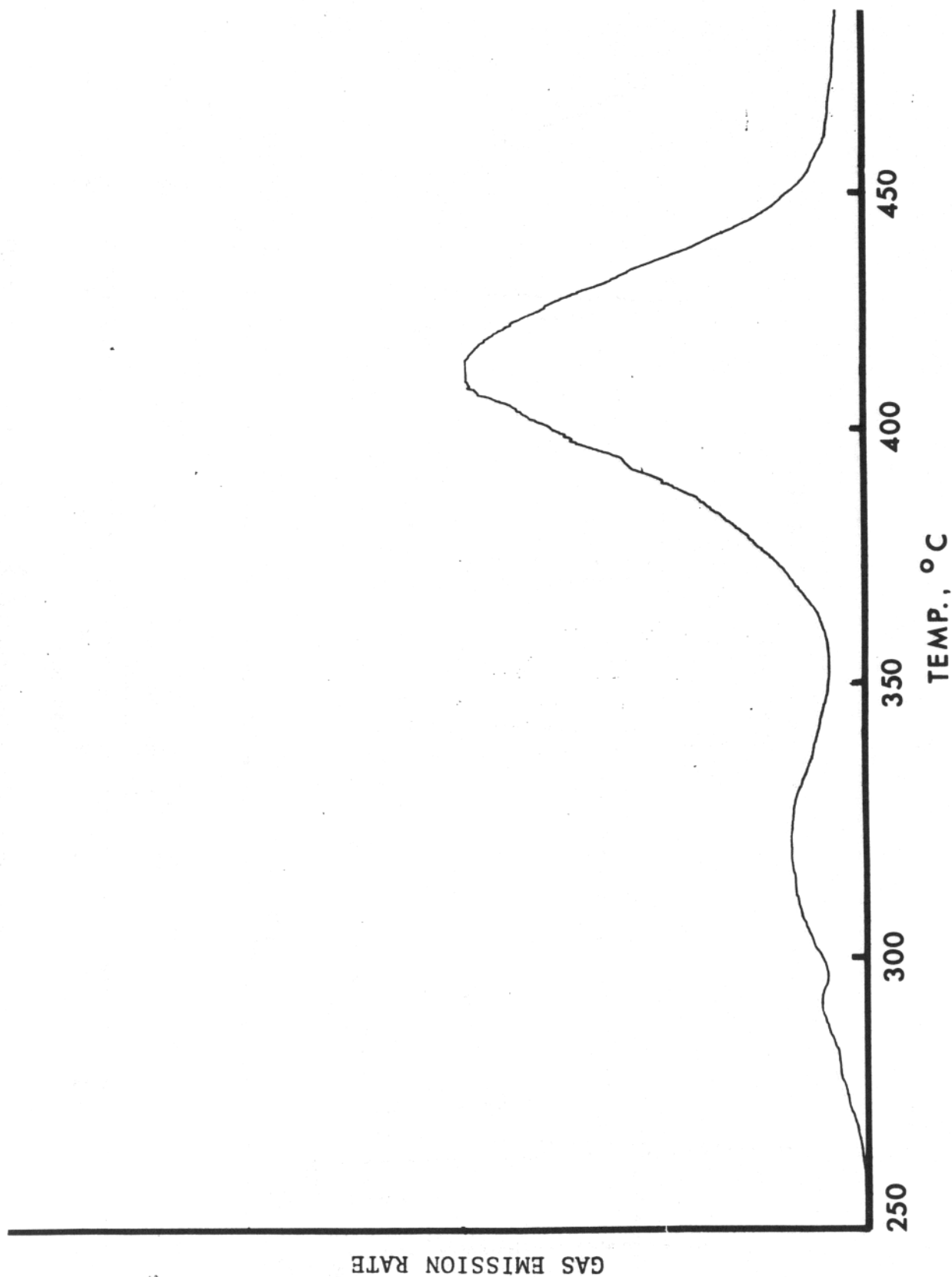


Figure 4 - Total combustible gases evolved from polyurethane foam heated in nitrogen as a function of temperature.

Attenuation factors used for reducing the output signal are listed next to each peak (for example - to obtain the absolute signal response value for peak A the peak height must be multiplied by 32×10^2 or 3200).

- A - Methane
- B - Ethylene/Acetylene
- C - Ethane
- D - Propylene
- E - Unidentified
- F - Acetone

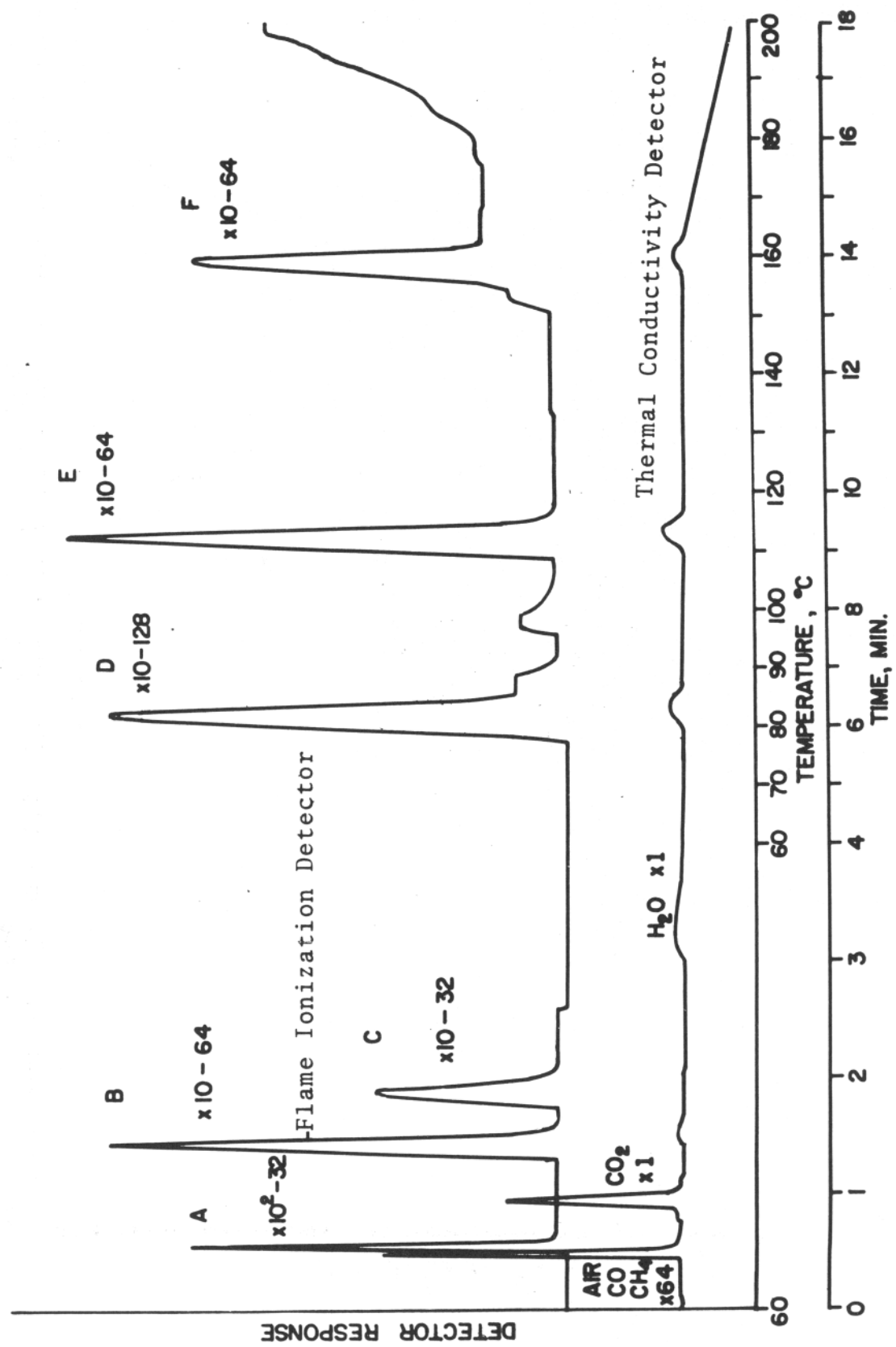


Figure 5 - Chromatograms of flexible foam decomposition products in air before onset of flash fire.

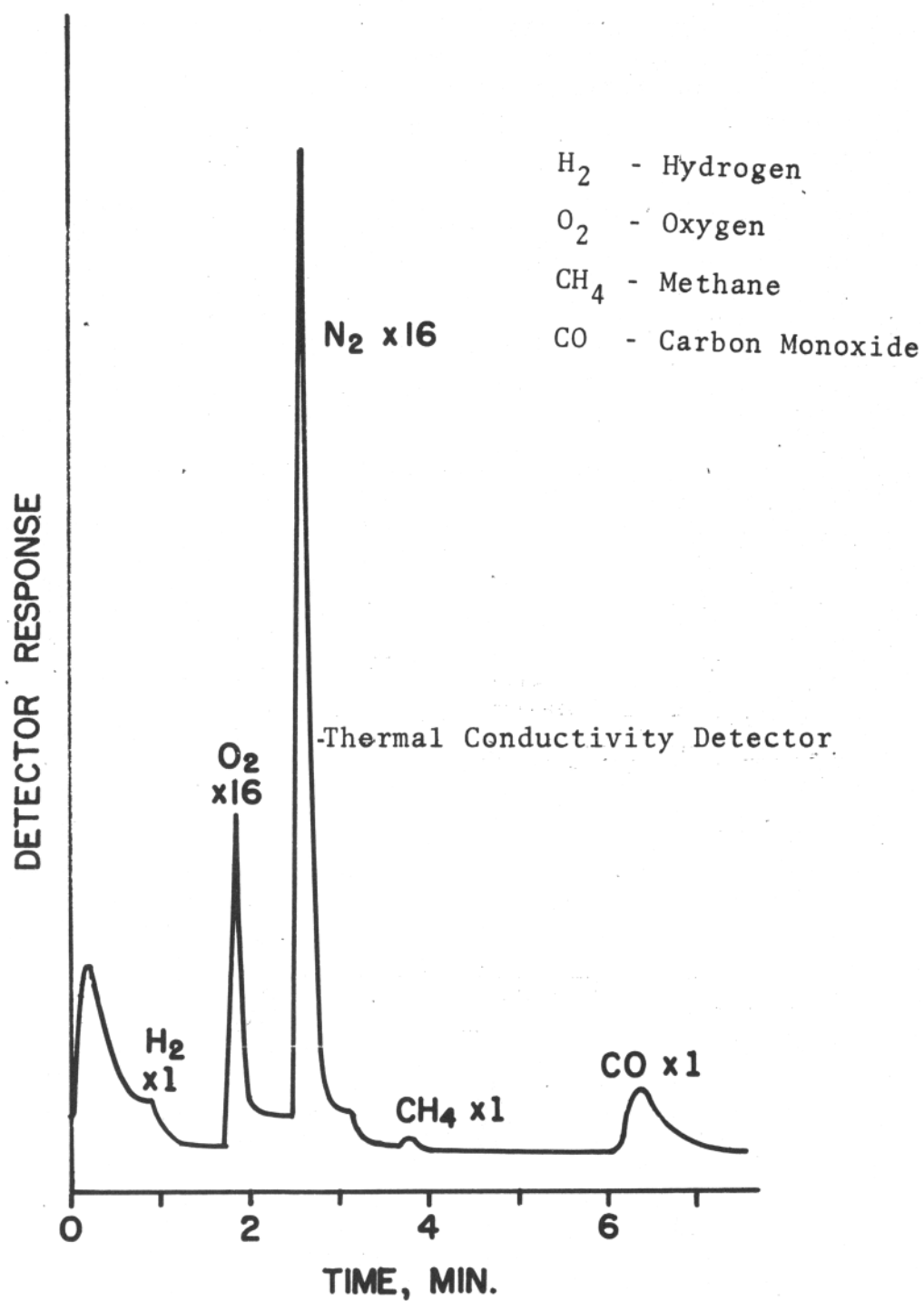


Figure 6 - Chromatogram of same mixture as Figure 5, but with "air" peak resolved only.

by which each peak area must be multiplied to intercompare amounts of each component. However, the two separate curves may not be intercompared because of the vastly differing response factors of the two detectors to the same compound.

The chromatograms obtained of gaseous mixtures before and after flashover were found to be similar when intercompared. The differences are probably obscured by the continuous generation of pyrolysis products replacing those depleted during combustion. The experimental system at the present does not permit isolation of the pyrolysis compartment from the main chamber. Refinement of this design will be considered in the future.

For qualitative identification of permanent gases and major low molecular weight decomposition products a comparison of the retention data of the pyrolysis mixture was made with those of known compounds. Nine major products were detected and eight were identified as carbon monoxide, carbon dioxide, water, methane, ethylene and/or acetylene, ethane, propylene, and acetone. Of the numerous minor peaks hydrogen, propane and methanol were identified.

Infrared spectra provide a convenient method of urethane identification and have been extensively studied [7].

Characteristic absorptions for urethanes are observed at 6.5 μm (Amide II - NH deformation), 5.8 μm (Amide I - C=O stretch), and 3.0 μm (NH stretch). Polyether type urethanes (-C-O-C-) absorbing at 9.0 μm may be distinguished from polyester types (-C-O-C-) absorbing at 8.0 μm [8].

0

Positive identification of the organic components in a complex unknown gaseous mixture, however, cannot be made from gas chromatographic retention data alone. Infrared spectroscopy was used as the only ancillary technique available for further confirmation. Infrared spectra of pyrolysis mixtures before and after flashover were obtained. Identification of minor components was not possible because of their low concentrations in the sample which is predominantly air.

Quantitative estimates of the pyrolysis products were made by determination of the recorded peak areas on gas chromatograms and by comparing peak heights of respective compounds.

The accuracy and reproducibility of the sampling system was tested by flushing a mixture of 6.1% methane and 93.9% air through the flashover chamber and analyzing gas samples by the chromatographic technique. The peak areas of the molecular sieve chromatograms were evaluated by means of a disc integrator. The area normalization method using thermal conductivity detector response factors for O_2 , N_2 , and CH_4 was used to yield true weight areas [9]. The average methane content of these determinations was $6.0\% \pm 0.3$.

Table I lists the weight percentage composition of the polyurethane pyrolysis products resolved by means of a molecular sieve column estimated by the normalization method above. Figures in parentheses are the concentrations estimated by the absolute calibration method. Pure gases were sampled at known pressures and the recorder response per torr of pressure was determined. These results, however, are somewhat scattered because of the wide range of extrapolations from the calibration standards and the uncertainty of the detector sensitivity from day to day.

The absolute calibration method includes detector sensitivity, which will vary for different compounds, and relates the experimentally obtained peak area of the chromatogram to the measured pressure of a given component. The absolute calibration method was used to check the normalization method. To facilitate analysis the normalization method, where the air peak including CH_4 is taken as 100%, and the concentrations of other minor organic components were ignored, was employed. Within experimental error the two sets of data appear to agree.

The quantities of other organic compounds resolved by the Porapak Q column and detected by the flame ionization detector which do not respond to air or water were estimated by normalizing the peak heights to that of methane. The results are listed in Table II. At the bottom of Table II are listed the estimated ratios of carbon dioxide to air and the presence of water as detected by the thermal conductivity detector. The Porapak Q column did not resolve methane from air as monitored by the thermal conductivity detector and the concentrations of other organic components were near or below the limit of sensitivity of the thermal conductivity detector.

Tables I and II reveal that none of the lower molecular weight combustibles are present in concentrations approaching their lower limits of flammability in air listed in Table III. The lower limit of flammability is defined as the critical concentration of a combustible gas in a mixture below which no ignition occurs. The values in

WEIGHT PERCENT COMPOSITION OF
POLYURETHANE PYROLYSIS PRODUCTS IN AIR

	Sample				
	11A	11B (a)	12 (b)	13	15 (c)
Hydrogen (H ₂)	---	trace	trace	trace	-----
Methane (CH ₄)	0.1 (d) (0.15) (e)	0.2 (0.14)	0.1 (0.13)	0.2 (0.45)	0.1 (0.16)
Carbon Monoxide (CO)	0.1 (0.15)	0.5 (0.6)	-----	1.0 (1.2)	1.8 (1.7)
Oxygen Plus Argon (O ₂ + Ar)	22.6 (19.0)	21.7 (19.6)	23.2 (19.5)	19.1 (19.0)	19.2 (18.7)
Nitrogen (N ₂) (f)	77.2 (68.8)	77.6 (73.6)	76.6 (68.0)	79.6 (82.7)	78.8 (79.3)

(a) after flashover, all other runs before flashover

(b) duPont sample, all other runs FAA sample (unretarded)

(c) electrical furnace heat, all other runs external burner

(d) percentage composition calculated by the normalization method

(e) figures in parentheses are estimated by the calibration method

(f) composition of air (weight percent): N₂ 75.5, O₂ 23.15, Ar 1.29, CO₂ 0.05

TABLE II
POLYURETHANE PYROLYSIS PRODUCTS
(Peak Identification Based on Retention Times)

Peak	Sample				
	11A	11B (a)	12 (b)	13	15 (c)
A. Methane (CH_4)	1	1	1	1	1
B. Ethylene, Acetylene ($\text{H}_2\text{C}=\text{CH}_2$, $\text{HC}\equiv\text{CH}$)	0.16	0.31	0.07	0.25	0.2
C. Ethane ($\text{H}_3\text{C}-\text{CH}_3$)	0.06	0.04	0.03	0.03	0.05
D. Propylene ($\text{H}_3\text{C}-\text{CH}=\text{CH}_2$)	0.60	0.25	0.36	0.45	0.49
E. Unidentified	0.43	0.13	0.66	0.42	0.26
F. Acetone ($\text{H}_3\text{C}-\text{CO}-\text{CH}_3$)	0.28	0.10	0.46	0.23	0.16
Carbon Dioxide (CO_2)/air (d)	0.008	----	----	0.005	0.009
Water (H_2O) (e)	+	+	+	+	+

a, b, c - See Table I
d, e - thermal conductivity detector

TABLE III
LOWER LIMITS OF FLAMMABILITY
OF PYROLYSIS PRODUCTS IN AIR¹

gas	² L ₂₅
Hydrogen (H ₂)	4.0
Carbon monoxide (CO)	12.5
Methanol (CH ₃ OH)	6.7
Methane (CH ₄)	5.0
Ethane (H ₃ C-CH ₃)	3.0
Ethylene (H ₂ C=CH ₂)	2.7
Acetylene (HC≡CH)	2.5
Acetone (H ₃ C-CO-CH ₃)	2.6
Propylene (H ₃ C-CH=CH ₂)	2.4
Propane (H ₃ C-CH ₂ -CH ₃)	2.1

¹Reference 4

²Volume percent at 25 °C and atmospheric pressure

Table III, designated L_{25} , refer to the combustible mixtures in air at atmospheric pressure and 25 °C (77 °F) [4]. Relatively small experimental variations of temperature and pressure and the type of ignition source have been included when the concentrations of combustibles are compared to their lower limits of flammability. For sample 13, for example, we have in volume percent listing L_{25} first and weight percent found second: H_2 (4.0, trace), CH_4 (5.0, 0.2%), CO (12.5, 1.0%), and hydrocarbons of Table II in much lower concentrations. The concentrations reported in Table II are relative to CH_4 taken as one (1) so that for sample 13 propylene is 0.45 of 0.1 or 0.05%, for example. The weight percentages of O_2 include 1.3% argon which is not resolved from the O_2 value by the molecular sieve column. The nitrogen-oxygen ratios may also be effected by varying amounts of nitrogen released by the sample. Using Chateliers law for sample 13 we may estimate the lower limit of flammability L_{25} for the mixture considering only the major components, CO and CH_4 , present in the ratio of about 4 to 1. We obtain:

$$L_{25}(\text{Mixture}) = \frac{100}{\frac{n(\text{CO})}{L_{25}(\text{CO})} + \frac{n(\text{CH}_4)}{L_{25}(\text{CH}_4)}} = \frac{100}{\frac{80}{12.5} + \frac{20}{5}} = 9.6$$

9.6% for L_{25} for the mixture.

Analysis of Smoke

As the heating of the urethane sample progresses with the evolution of the gases listed in Tables I and II a dark brown or orange smoke is evolved before flashover. Its possible importance in flash fires, suggested by the fact that flash fires in the cell do not occur in its absence, dictated additional tests.

During the experiments of determining the appropriate weight of a polyurethane foam sample that causes flashover in the 1 liter chamber without additional air intake, it was observed that in case the high voltage spark was placed above the sample compartment, no flashover occurred until the heavy orange smoke reached the ignition source. Also, no flashover occurred when a filter of glass wool was placed between the sample compartment and main chamber for trapping out most of the solid particles.

The technique selected for characterization of the condensed smoke particles involved flash pyrolysis of the

sample in a stream of helium by a heated electric filament. This pyrolysis unit is an integral part of the gas chromatographic equipment and the record of resulting volatile fragments is commonly called a pyrogram.

Pyrolysis-gas chromatography has been used to identify urethane foams with pyrolysis in a quartz tube in the 650-1000 °C (1202-1832 °F) temperature range [10]. Product identification required both infrared spectroscopy and mass spectrometry. The main pyrolysis products from polyether foams at 650 °C (1202 °F) would appear to be aliphatic ketones, ethers, or esters while at 850 °C (1562 °F) the primary products are aromatic ring compounds.

In an attempt to elucidate the structure of the orange smoke and to determine its contribution to the flashover phenomenon, the condensed material was collected from the walls of the flashover chamber, and samples of the smoke and its acetone extract were subjected to pyrolysis-gas chromatography in a helium atmosphere at 1000 °C (1832 °F). Pyrograms of the orange smoke and its acetone extract are illustrated in Figures 7 and 8, respectively. A comparative pyrogram of unretarded polyurethane foam is in Figure 9.

The pyrograms were obtained using 0.9 mg (approx. 3×10^{-5} ounce) of sample indicating the sensitivity of the flame ionization detector. The pyrograms are generally comparable in terms of major identified components with the typical chromatogram obtained for the pyrolysis gas-air mixture, Figure 5. However, it should be noted that for the pyrograms pyrolysis was in a helium atmosphere in a relatively small volume, thereby greatly improving the accuracy and detectability of low concentration components.

A major problem in gas analysis in the flash cell results from the low total concentration of products in air. In both cases, however, identification of additional components in the complex gas mixture will require a mass spectrometer. Quantitative accuracy has been limited by the necessity of using peak heights rather than areas due to lack of a good integrator. In the case of the FID the digital integrator has not performed well. Cell design changes would also improve analytical accuracy and this would include sealed end windows and redesigning of sampling ports. The orange smoke and its acetone extract were also analyzed by infrared spectroscopy. Figures 10 and 11 show the infrared spectra of the two samples at 1% in KBr discs. A more detailed infrared spectrum of the acetone extract of the orange smoke was obtained as its solution in carbon tetrachloride in Figure 12.

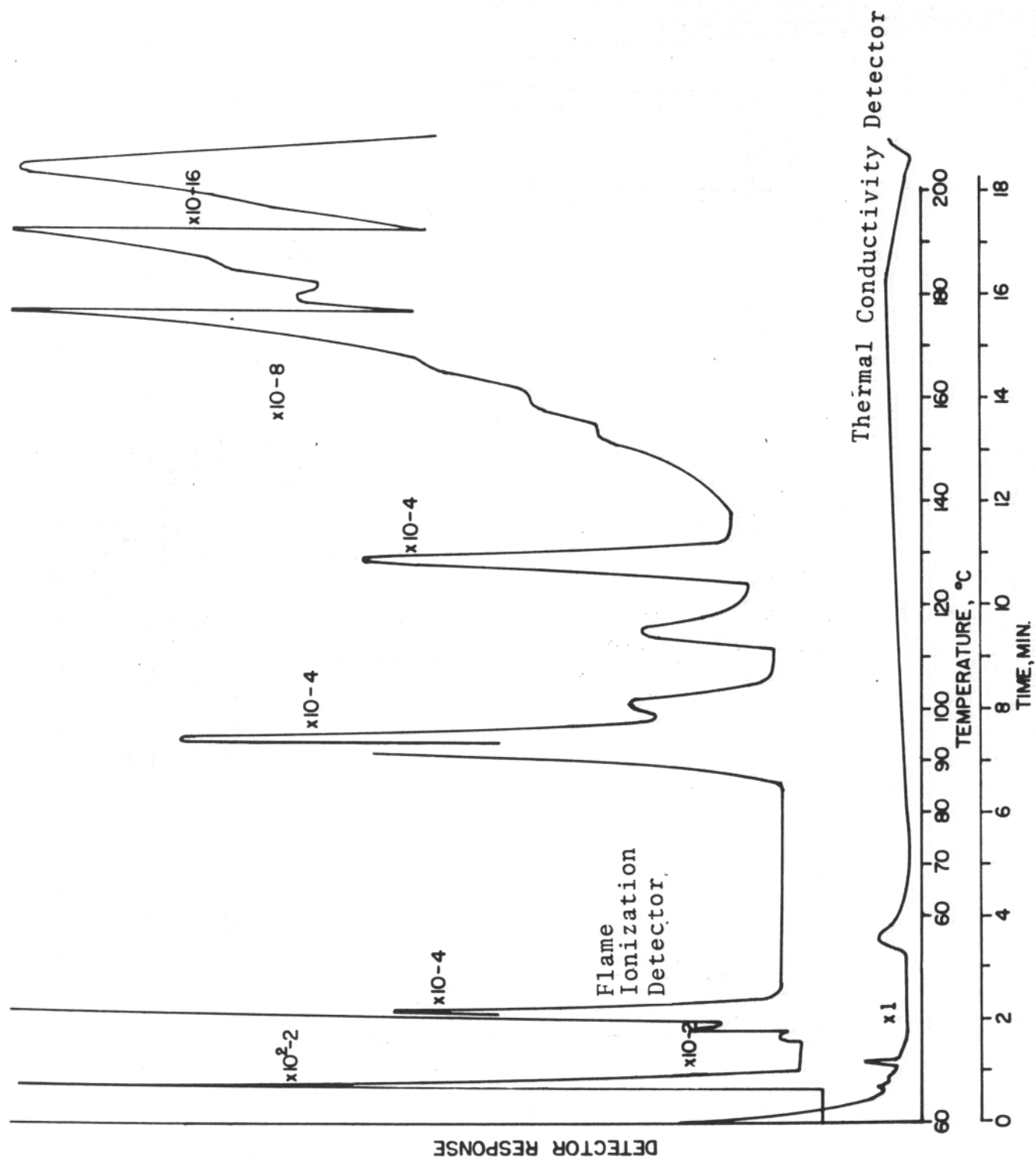


Figure 7 - Pyrogram of orange smoke deposit from flexible urethane.

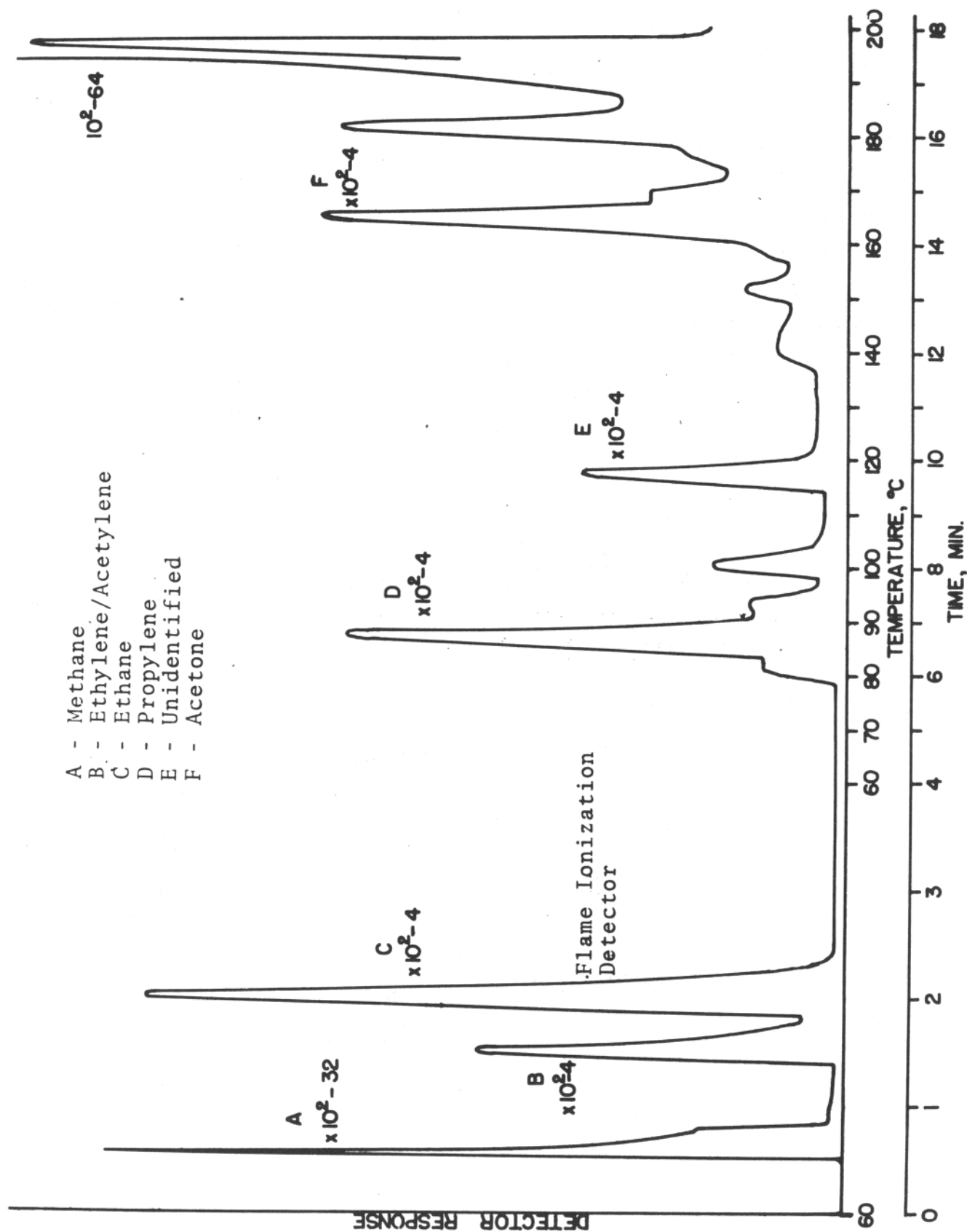


Figure 8 - Pyrogram of acetone extract of orange smoke deposit.

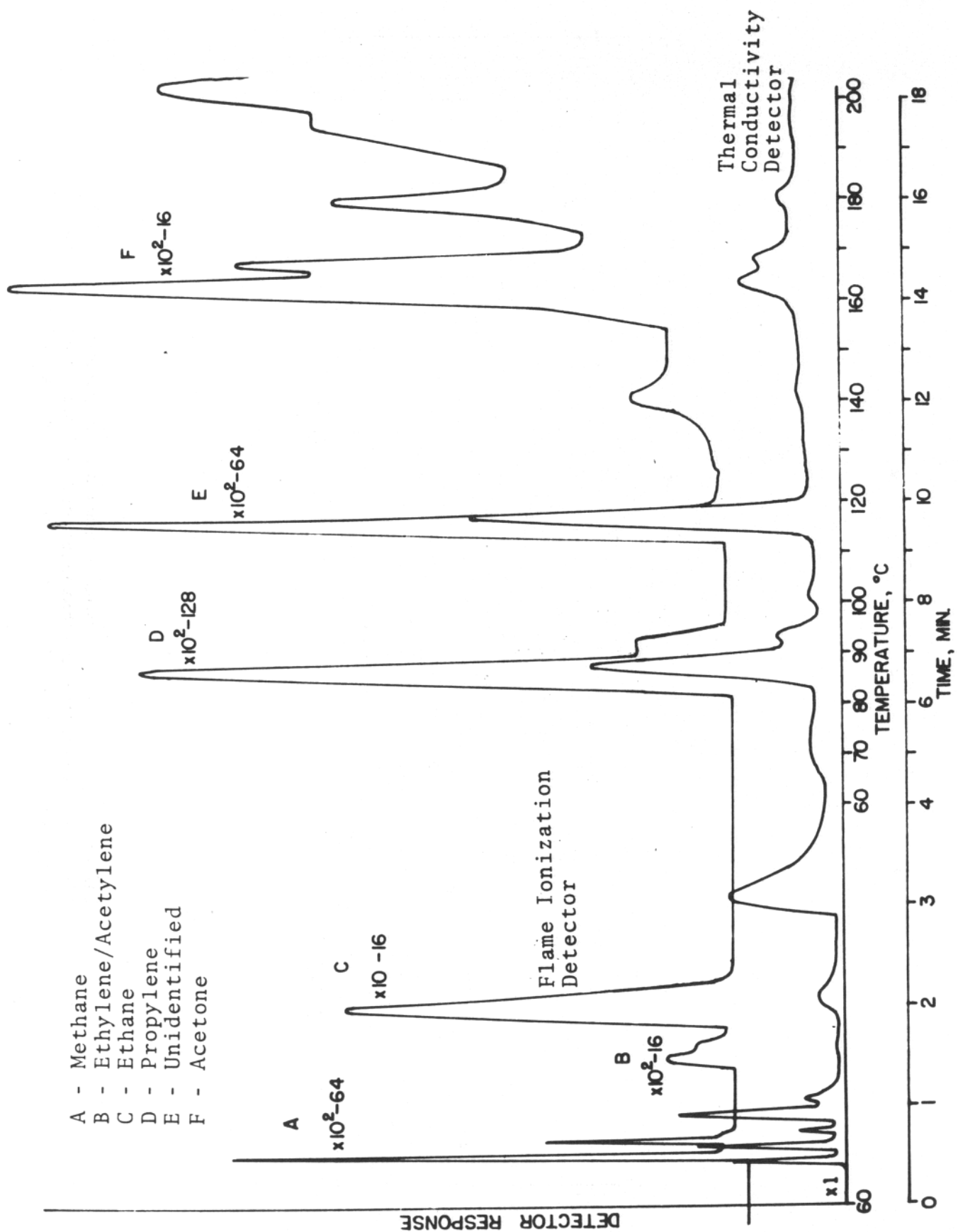


Figure 9 - Pyrogram of original unretarded urethane foam.

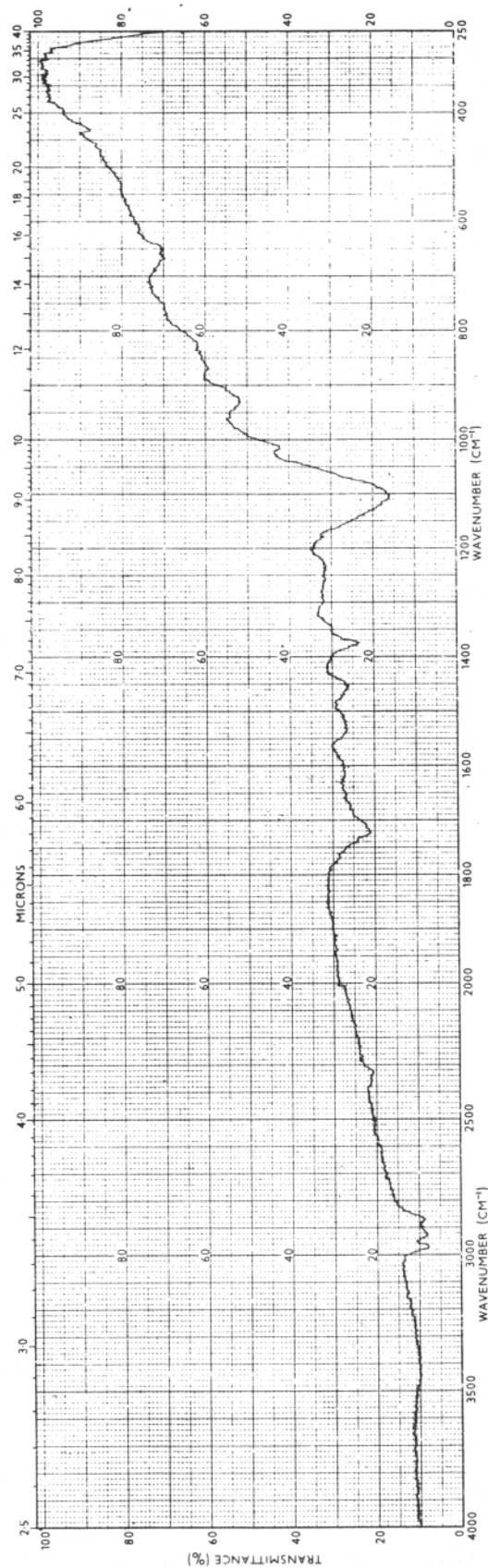


Figure 10 - Infrared spectrogram of smoke condensate in potassium bromide.
 (Strong 9 μm absorption characteristic of polyether type urethane).

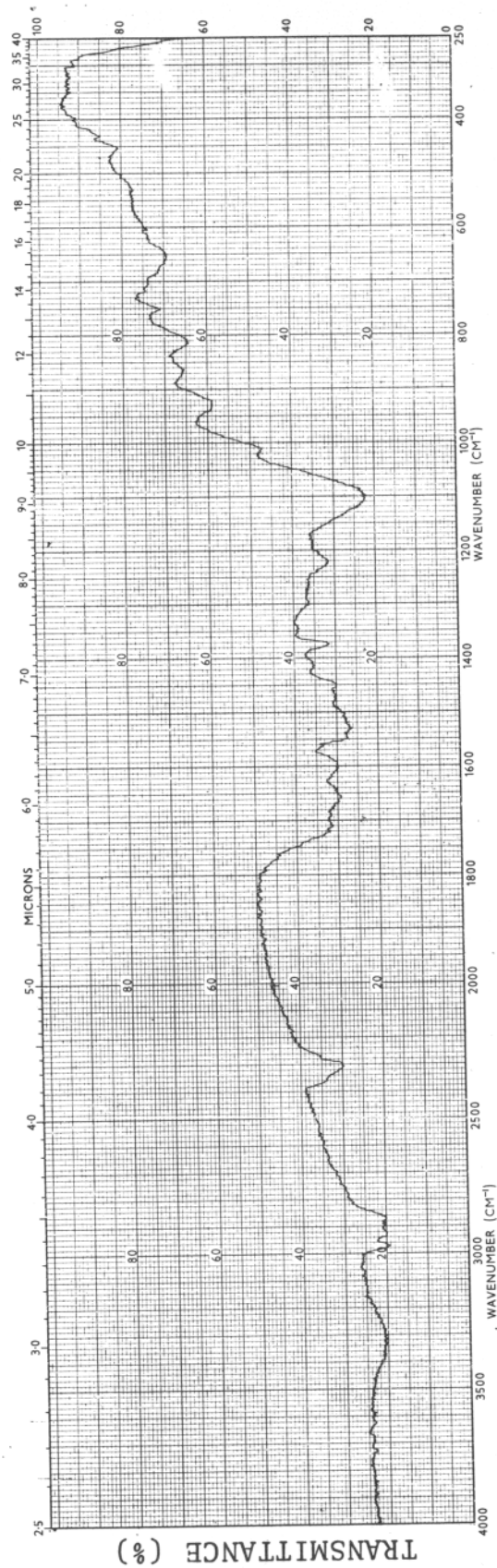


Figure 11 - Infrared spectrogram of acetone extract of smoke condensate in potassium bromide. (Strong 9 μ m absorption characteristic of polyether type urethane).

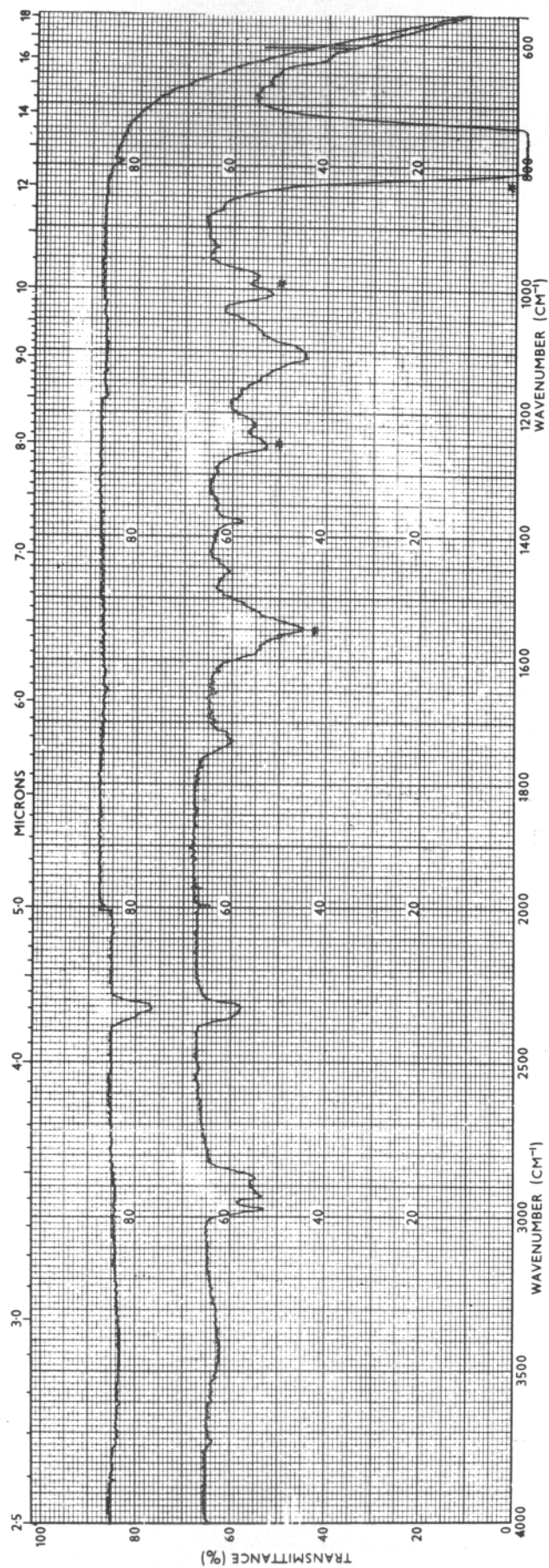


Figure 12 - Infrared spectrogram of acetone extract of smoke condensate in carbon tetrachloride. (*solvent absorption).

The large amount of scatter indicated by the low I background in the short wavelength region of the spectrum appears to be typical of these materials and prevents higher concentrations of sample from being used in the potassium bromide (KBr). The spectrum in carbon tetrachloride (CCl₄) solution does not show improved resolution, Figure 12, where the upper curve is a very thin capillary film. The curves suggest that the bulk of the smoke is the isocyanate portion of the polyurethane, the polyol fraction being lost in the low temperature ranges. This should be confirmed by further analysis since some polyol appears to remain (Figures 10, 11 and 12).

A sample of orange smoke was subjected to microanalysis to compare its elemental composition with that of the original polyurethane foam. The results are listed in Table IV. The elemental analysis indicates decreases in the carbon and hydrogen contents as expected from the formation and release of primarily hydrocarbons in the low temperature range. The increase in nitrogen reflects the fact that the nitrogenous compounds are released in the higher temperature range.

The smoke appears to be particulate, coated with a tar-like material which precludes redispersal of the material in air. The elemental analysis does confirm, however, the gas chromatographic analysis that the initial low temperature pyrolysis results in hydrocarbons (C and H compounds only) of low molecular weight plus the smoke. Other investigators have noted that finely divided particulates, such as coal dust in methane-air mixtures will significantly decrease the lower flammability limit. [12,13] Polyurethane dusts were assigned a high "explosibility" index by the authors. Additional experimental work is required to determine the concentrations of particulates in the urethane smoke and an estimate of its contribution to lowering the flammability limit of the mixture.

Intercomparison of Materials - Flash Fire Potential

A number of polymers were compared in the flash fire cell to determine the magnitude of the differences, if any, obtainable with the present cell configuration. Weighed samples of the materials were heated using identical rates and timing the onset of smoke development and flash fire. These tests were conducted with the cell in a vertical position with the ignition source near the bottom. The results are presented in Table V where the times listed are average values of two or more experiments. In each case except for the latex, which showed spontaneous ignition, the high voltage ignition source was turned on at the beginning of heating. This was also done for the latex but spontaneous ignition occurred near the sample surface.

TABLE IV

ELEMENTAL ANALYSIS OF THE ORANGE SMOKE
AND POLYURETHANE FOAM (a)

Sample	C%	H%	N%	O% ^(b)
orange smoke	60.2	7.5	9.4	22.9
polyurethane foam	63.0	8.9	5.6	22.5

(a) maximum limits of uncertainty are $\pm 0.3\%$

(b) oxygen percentage obtained by difference

TABLE V
INTERCOMPARISON OF MATERIALS - FLASH FIRE POTENTIAL

Material (a)	Time	
	Visual Appearance (b) of Smoke	Flashover (c) (upward propagation)
Latex Foam (d)	40 sec	1 min 15 sec
Polyurethane Foam	50 sec	1 min 50 sec
Polyethylene	50 sec	3 min 30 sec
Acrylic Resin	3 min 20 sec	4 min
PVC (e)	55 sec	none
Cellulose [f]	1 min 50 sec	none

(a) 0.3 g samples

(b) The variation in time of appearance of smoke did not exceed ± 5 seconds except for acrylic resin where the range of variation was ± 10 seconds.

(c) Time of occurrence of flashover phenomenon varied within ± 10 seconds for all samples except polyethylene where the variation was within $\pm 1/2$ minute.

(d) Spontaneous ignition of gases at the heat source in approximately 50 seconds.

(e) Gases burn in the vicinity of spark.

(f) No flashover even with 1 g sample.

The ranking of materials in Table V is as expected with the latex and urethanes developing a flash fire most readily.

SUMMARY OF RESULTS

Gas Analysis and Smoke Characterization

Previous studies of urethane decomposition have emphasized high temperature inert atmosphere decomposition of the polymer. The low temperature decomposition products have been determined including hydrogen, carbon monoxide, and hydrocarbons through propylene. Additional work, particularly mass spectrometric, is required to establish the role of the smoke in the flash fire. We have been unable to produce the flash fire with the smoke filtered out. Propylene, with a lower flammability limit of about 2.8% has not been eliminated as a possible contributor. Methane, hydrogen, and carbon monoxide have been eliminated due to their very low concentrations. A third possible factor in the flash fire are the higher molecular weight hydrocarbons. Evidence to date suggests the smoke produced is, in some circumstances, essential to produce flashover. Additional experimentation is required to better define the role of smoke in the flash fire.

Development of Flash Fire Cell

The laboratory model has performed well although optimized only in terms of cell orientation. The lower flammability limit varies with the orientation of the cell in the gravitational field [11] with the lowest values obtained with a vertical tube and the ignition source near the bottom.

CONCLUSIONS

Based upon the laboratory tests described above it may be concluded that:

1. A laboratory scale model can provide a small scale system with appropriate instrumentation for obtaining precise gas analysis data ultimately leading to an understanding of flash fires.

2. A laboratory model can be used to intercompare flash fire potential of polymers.

3. Of the limited number of materials tested to evaluate the model, polyurethane and latex foams would appear to develop a flash fire most readily.

APPENDIX
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