

This article was downloaded by:

On: 25 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

Smoke and Toxic Gas Production from Burning Polymers

W. D. Woolley^a

^a Fire Research Station, England

To cite this Article Woolley, W. D.(1982) 'Smoke and Toxic Gas Production from Burning Polymers', Journal of Macromolecular Science, Part A, 17: 1, 1 – 33

To link to this Article: DOI: 10.1080/00222338208056462

URL: <http://dx.doi.org/10.1080/00222338208056462>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Smoke and Toxic Gas Production from Burning Polymers

W. D. WOOLLEY

Fire Research Station
Borehamwood, Herts, England

ABSTRACT

This paper describes current studies at the Fire Research Station on the role of smoke and toxic gases in causing injury and death in fires involving polymeric materials used within the structure and contents of buildings. The work involves obscurational studies of smoke, chemical analysis of decomposition and combustion products, pathological studies and, where appropriate, bioassay procedures. Basic details of these studies are presented together with a summary of the work carried out, and conclusions reached, following the fire at the Woolworth's store, Manchester, on 8 May 1979, in which 10 persons lost their lives. This event focused attention in the United Kingdom on the rapid release of smoke and toxic gases from burning furniture and furnishings.

INTRODUCTION

In recent years the effects of smoke and toxic gases have been singled out as being one of the most important causes of injury and death in fires [1]. As a result, an increasing amount of attention is now being directed on an international front to studies of the combustion products of polymers, particularly those of synthetic origin.

In the United Kingdom (U.K.), approximately 900 persons lose their lives each year in fires and about 6000 are injured. Over one-half of these fatalities are attributed to the combined effects of smoke and gases: statistical fire information indicates that this proportion has risen by a factor of about 3 over the past two decades [1].

The function of the Fire Research Station (FRS) is to carry out research to mitigate the loss of life and property which occur each year in fires. The laboratories have extensive facilities for large-scale tests. For a number of years FRS has been involved in general studies of combustion products. Much of the early work was associated with polymeric materials involved in the structure of buildings [2, 3] but in recent years the station has recognized that it is often the burning of the contents of buildings [4-8] which creates the primary hazard to life. Current work carried out both at the Fire Research Station, and extramurally, includes:

1. Studies of the smoke produced during the burning of both natural and synthetic polymers, as wall linings [9] and complete items of furniture [5, 6], to assess the likely obscurational effects which may be encountered under different usages. This will provide guidance for the selection of combinations of material as well as aiding the development of standard test methods for smoke production.
2. Analytical methods [7, 8, 10] to elucidate the complex chemistry of polymer degradation and to gain an insight into the "cocktail" of different chemical species which can be formed during the decomposition and burning of polymers. This work uses a gas chromatograph-mass spectrometer-data handling system and is being applied to both carefully controlled laboratory studies and experimental fires. Of particular interest is the comparison of chromatographic "fingerprints" of experimental fire atmospheres [8] with those from the combustion toxicity tests currently being proposed in Germany (DIN 53 436) and in the U.S.A.
3. Detailed pathological studies [11] at the Department of Forensic Medicine and Science at the University of Glasgow to measure the amounts of toxic species (including alcohol and drugs) in the blood and tissues of fire victims. This is in order to understand the role of toxic species in causing death and to give an insight into those species which may have impaired the ability of building occupants to escape.
4. Bioassay experiments at the Huntingdon Research Centre to assess the incapacitating effects of sublethal concentrations of combustion products. This is providing valuable information on physiological and behavioral effects which impair escape.

This paper describes details of these programs. However, although fire atmospheres may be directly responsible for many fatalities, a study of this complex subject does not necessarily indicate the most effective ways of mitigating the results. Parallel work is therefore

being carried out on related problems, such as the ignition and burning characteristics of materials and composite items [5, 6], domestic fires where fatalities have been involved [12], and detection [13] and extinction of fires from polymeric materials, so that overall guidelines can be established for minimizing the fire hazards and ensuring the safety of occupants in buildings.

This overall work shows that, in comparison with natural materials, synthetic materials tend to be easily ignited and, when burning, produce intense fires accompanied by the formation of copious amounts of smoke and toxic gases [5, 6]. The work also indicates that where life loss occurs from combustion products, the most direct mitigating action often lies with improved resistance to ignition and reduced rate of burning, thus providing more time for escape and/or rescue.

To illustrate this, some brief details are given of a fire which occurred in the Woolworth's Departmental Store in Manchester on 8 May 1979 in which 10 persons lost their lives. This fire, which occurred in the furniture department, focused attention in the U.K. on the rapid burning characteristic of modern foam-filled furniture and the hazards of rapid production and spread of smoke and gases. To understand the fire development, a fire test was carried out in a reconstruction of the stack of mixed furniture where the fire was first seen. Some of the more important observations and measurements recorded during this test are described.

It must be emphasized that combustion toxicology is a subject of enormous complexity. It includes a consideration of all aspects of the physiological interactions from sublethal effects, where escape may be impaired following a long exposure to low concentrations of smoke and gases, to the acute effects, where sudden exposure to hot toxic gases and smoke (usually with reduced oxygen concentration) may bring about unconsciousness and death within minutes. Also relevant are possible long-term effects and, to those involved with fire fighting, the cumulative effects.

MODES OF COMBUSTION

A study of typical fires can be very helpful in understanding the ways life can be placed in jeopardy from combustion products.

With building contents (beds, upholstery, and so on) there are two quite distinct modes of combustion which occur following contact with an ignition source. These are from smouldering and flaming sources. Sources such as cigarettes can promote smouldering whereas, e.g., a match can promote flaming combustion. With domestic fires (where the majority of life loss occurs), typical ignition sources, such as smokers' materials (matches and cigarettes), electrical appliances, and space heaters, when combined with deliberate ignitions, represent over 90% of the causes of furniture and bedding fires; these claim the lives of nearly one-half of all domestic victims [14].

Smouldering is a self-propagating combustion, usually at a low temperature, which can continue for long periods of time. It can be initiated in both natural materials (cotton, kapok) and natural-synthetic combinations (cotton-polyurethane foam). Smouldering produces very complex decomposition products [8] which are present in the atmosphere as particulate matter, droplets, and gases. The products are usually relatively cool and therefore spread very slowly from the room of origin without marked layering. In this way a person in a chair or bed which is smouldering may be subjected to low concentrations of decomposition products at breathable temperatures over a long period of time, and may become physiologically incapacitated prior to being aware of the problem.

With items of furniture and upholstery, transition from smouldering to flaming can occur after a protracted period. In our experience this transition usually requires a smouldering period in excess of half an hour; with a polyurethane mattress and cotton bedclothes we have observed a transition after 4 h 20 min [13]. An important point is that the smouldering preheats large surfaces of the bed and when flaming occurs the growth of the flaming fire can be very rapid.

It is also relevant to note that the smoke released during smouldering is flammable and when confined may lead, under very critical conditions, to an explosion [15].

The growth of a flaming fire, occurring either directly or following a period of smouldering, depends upon the available ventilation. The oxygen in a typical domestic room (without additional ventilation) is sufficient to burn only part of an upholstered chair or bed; burning may persist until reduced to local smouldering, or the flames may go out. Under vitiated burning conditions there is an immediate hazard to life within the room of origin. Where flaming occurs with an ample supply of oxygen (e.g., open doorway to the room), the development of fire can be very rapid, resulting in flashover. Under these conditions the hazard from smoke and toxic gases may still exist even when the gases are diluted and cooled to breathable temperatures outside the room of origin.

OBSCURATIONAL EFFECTS

Much of our work on the obscurational effects of smoke has been carried out in collaboration with the Property Services Agency of the Department of the Environment [5, 6], which is one of the largest purchasers of furniture and furnishings in the United Kingdom. It has taken a leading role in the development of fire performance specifications for contract purchases following research at the Fire Research Station under both laboratory and full-scale (simulated environmental) tests.

The full-scale tests utilize a special room corridor as shown diagrammatically in Fig. 1. It consists of a compartment 3.0 m × 3.0 m × 2.4 m high which communicates via a vent opening to a corridor

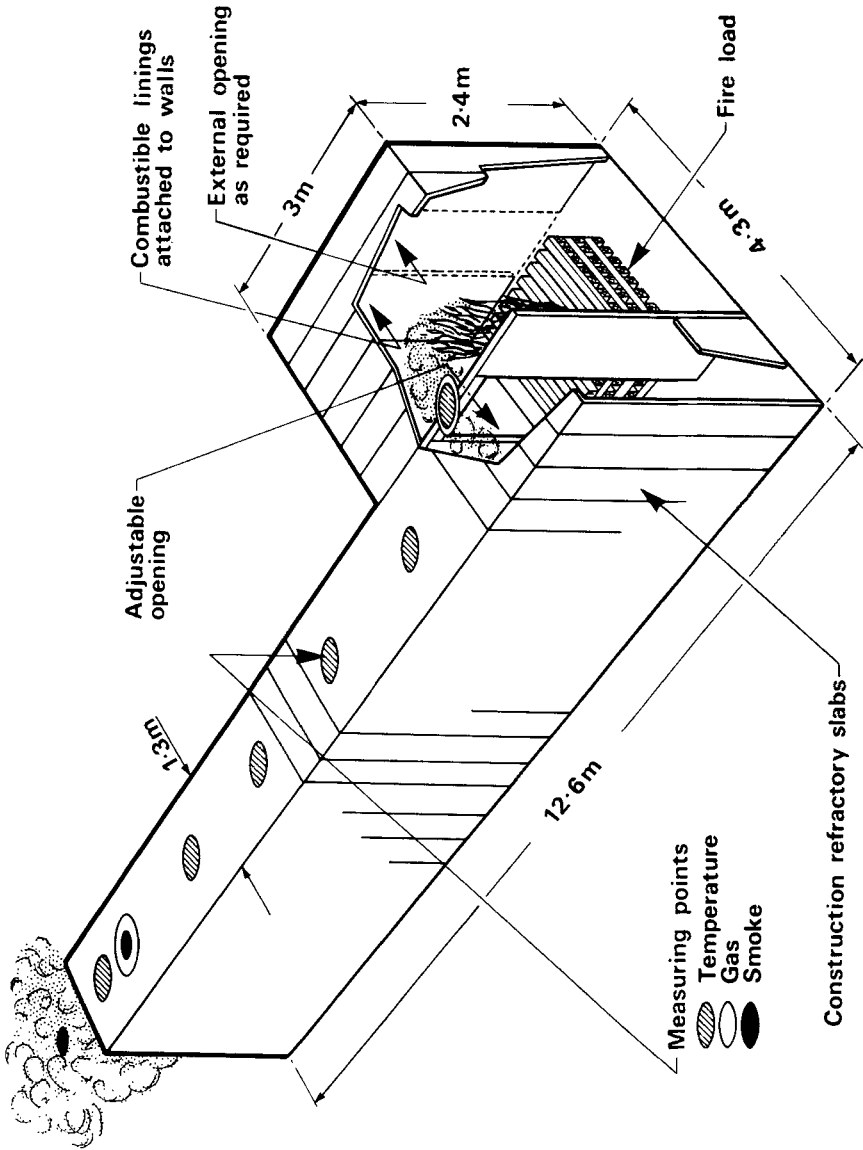


FIG. 1. The compartment-corridor for fire tests.

12.6 m long, 1.17 m wide, and 2.4 m high. It is constructed of reinforced aerated concrete panels (150 mm thick) supported by an external steel frame. The rig is fully instrumented [16] for measurement of temperatures, air velocities, and certain toxic gases (CO, CO₂); all measurements are recorded on special data logging equipment for automatic processing and replay with a small computer. The rig has been designed to operate primarily under "dynamic" conditions; adequate ventilation is available through the open corridor and doorway to the fire compartment, and the majority of fires involving single items of furniture and bedding develop without serious oxygen vitiation.

This dynamic mode of operation also allows smoke release to be studied as a continuous record during the fire. The smoke issuing from the open end of the corridor is monitored optically using a quartz-halogen light source (on the ceiling of the rig) providing a beam of light onto a selenium sulfide photocell at floor level. The degree of attenuation of the light beam relates to the opacity of the smoke and is reported as optical density per meter path length (OD/m). However, in many fires visibility through the smoke at any time may be less important than the rate of production of smoke; it is the rate term which governs the total volume of smoke in the building, and hence the contamination of areas remote to the fires, which places life in jeopardy.

Assuming that the optical density of smoke is directly proportional to the number of particles per unit volume, the total smoke emitted (P) over a time t_1 to t_2 can be given by

$$P = \int_{t_1}^{t_2} S(\text{OD/m})A \, dt$$

where S is the exit velocity of the smoke and A is the cross-sectional area of the smoke plume. The exit smoke velocity is calculated from air velocity measurements and fire gas temperatures and assumes that the mass velocity of air entering and fire gases emerging from the corridor are the same. The units of smoke are recorded as cubic meters related to an optical density per meter of unity [i.e., m³(OD/m)1]; OD/m of unity of smoke relates approximately to a visibility of 1.3 m. Rasbash [17] in recent work has defined a new unit of "obscura" where 1 ob = 1 db light attenuation per meter (i.e., OD/m of 0.1) which enables similar amounts of smoke to be described [i.e., obm³ as opposed to m³(OD/m)1 for the FRS work] but the factor of 10 difference in these units must be recognized.

As an example, Fig. 2 shows the smoke generated during the burning of a single domestic chair made of PVC-cotton cover over flexible polyurethane foam upholstery with a rigid polyurethane and GRP frame. This chair produced the largest amount of smoke which we have recorded for a single item of upholstered furniture. The figure shows the rate of smoke production in m³/min versus the time using

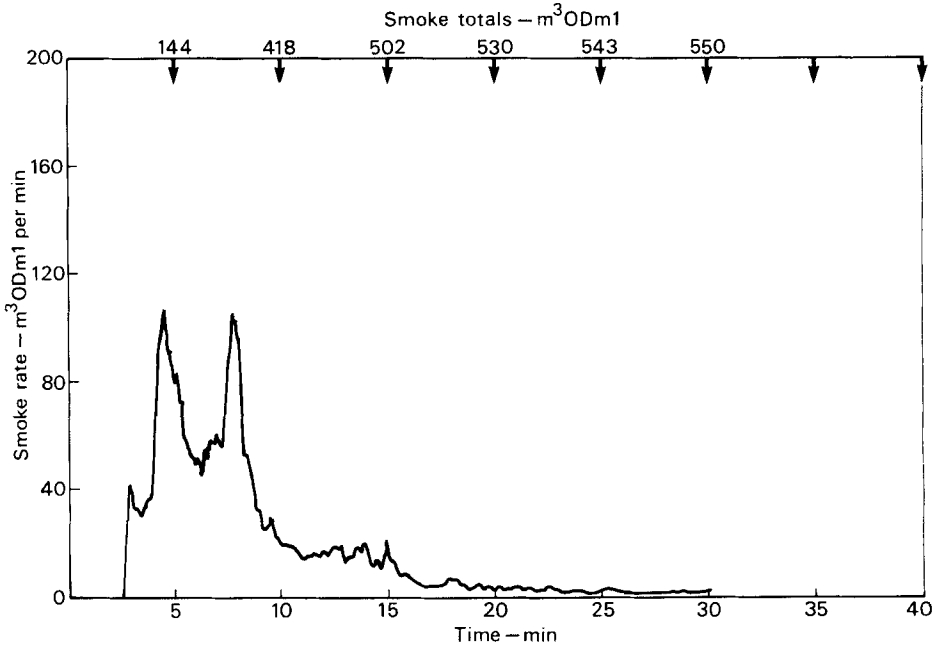
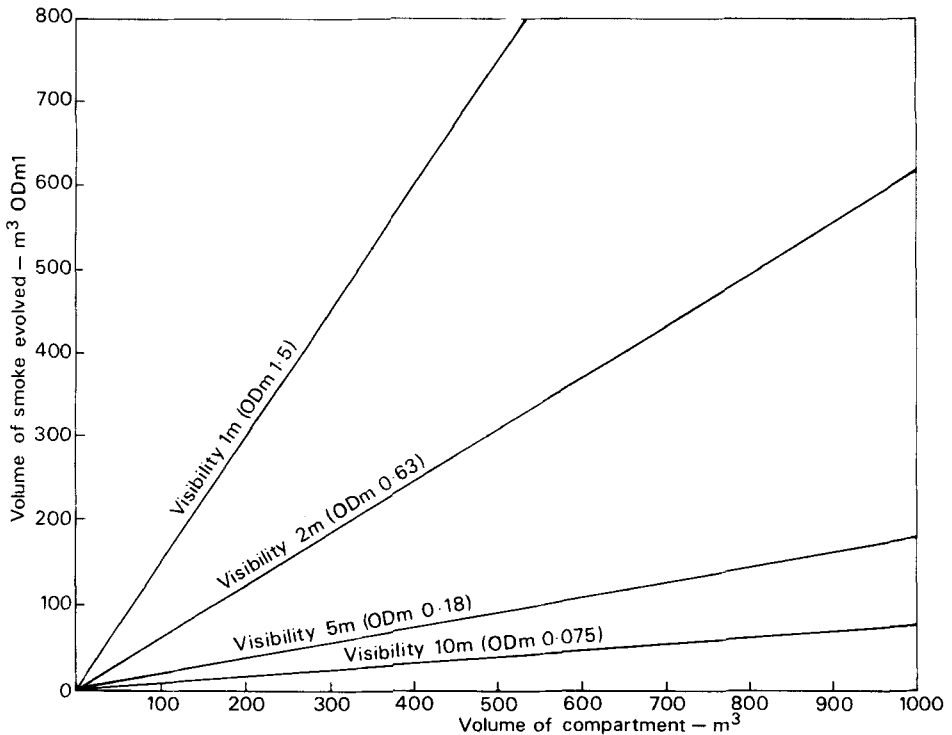


FIG. 2. Smoke production from a domestic chair.

a moving six point averaging method to smooth the curve. Also given is the volume of smoke at 5 min intervals after ignition. In order to relate these to possible room/building contamination, the visibility nomograms of Fig. 3 can be used; this relates the volume of smoke evolved and the volume of the compartment to achieve visibilities of 1, 2, 5, and 10 m. This method of calculating possible contamination of building areas with smoke makes a number of assumptions but can be very valuable in predicting the approximate visibilities to be expected. The domestic chair provides sufficient smoke to contaminate the entire volume of a 300 m³ domestic house to a calculated visibility of about 1 m in 10 min (418 m³ of OD/m³) from the known time of ignition. This illustrates the serious contamination which can occur during fires involving modern materials.

Figure 4 shows the smoke produced [6] from a series of mock-up chairs (metal frame and cushions) upholstered with various fabrics over standard polyurethane (PU) foam or a butadiene-styrene (BS) latex rubber foam. This work was part of an assessment of the ignition and burning characteristics of 17 fabrics (with interlinings) over five different types of foam for contract and domestic considerations. Figure 4 shows the great differences with different material combinations and particularly the larger amounts of smoke produced from BS latex rubber in comparison with PU foam, and the significant



Fi

FIG. 3. Relationship between volume of smoke and volume of compartment for certain visibilities.

contribution from PVC covers. It also gives the calculated visibilities in 100 m^3 (approximately the floor area of a house) or 300 m^3 (total house volume) and shows that even a common PVC-PU foam combination in a single chair can reduce (theoretically) the visibility in a house to 2 m in about 10 min.

More recently we have been involved with a study of the smoke released during tests with wall linings in a fire compartment as an appraisal of the National Bureau of Standards Smoke Box at the request of the British Standards Institution. Selected wall linings [9] have been subjected to round robin evaluation in the NBS Box and the materials burnt as linings to the walls of the test rig. These full scale tests used a wooden crib (140 kg) to give an increasing radiation level on the walls such that in a single crib test (i.e., no wall linings) the 2.5 W/cm^2 would be approached within about 5 min. The details of the wall linings and round robin results are summarized in Table 1 with the smoke results plotted in Fig. 5. From this figure

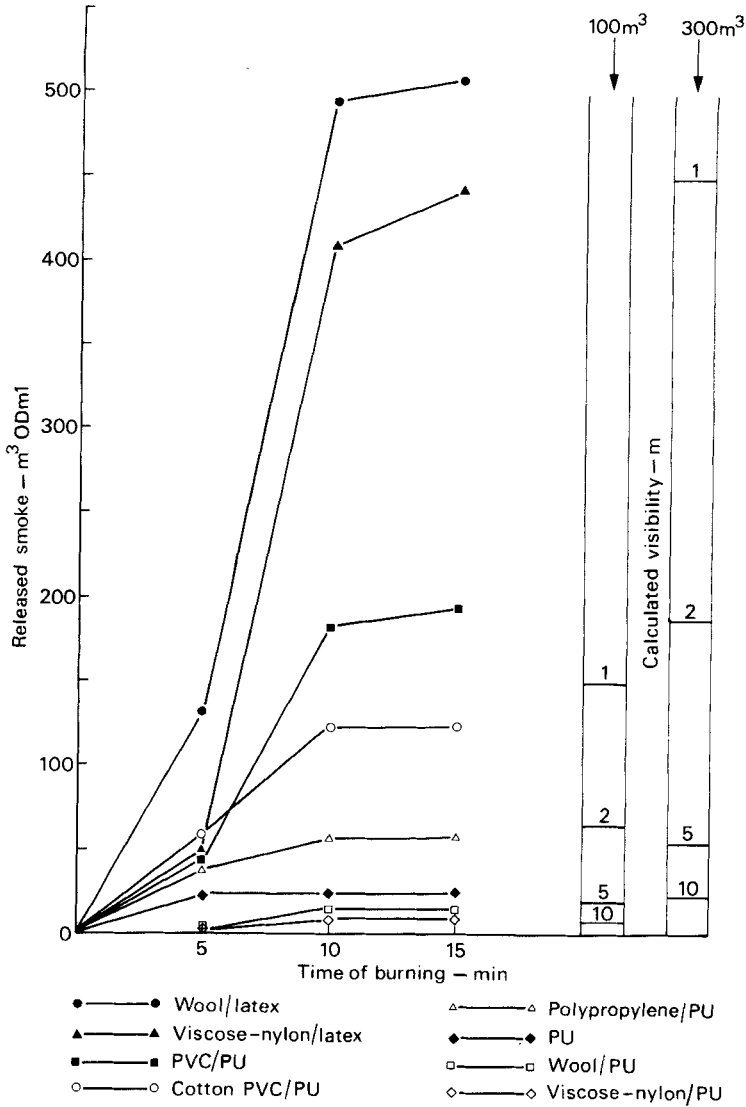


FIG. 4. Smoke produced from polyurethane and latex rubber chairs (mock-up) and calculated room visibilities.

TABLE 1. Smoke Produced during Full-Scale Tests and Round Robin with NBS Box

Material	Fire tests					Round robin		
	Quantity to line wall ^a (kg)	Thickness (mm)	Density (kg/m ³)	Angled jets	Horizontal jets	Dm mean values		
						Smouldering		
Chipboard	360	18	800	390	334	572		
Fiber insulating board	81	14	240	77	58	106		
Hardboard	85	3	900	79	77	597		
Polystyrene	12	25	20	222	32	12		
Plasterboard	283	13	950	88	52	82		
GRP	142	4	1420	651	616	377		

^a.25 m².

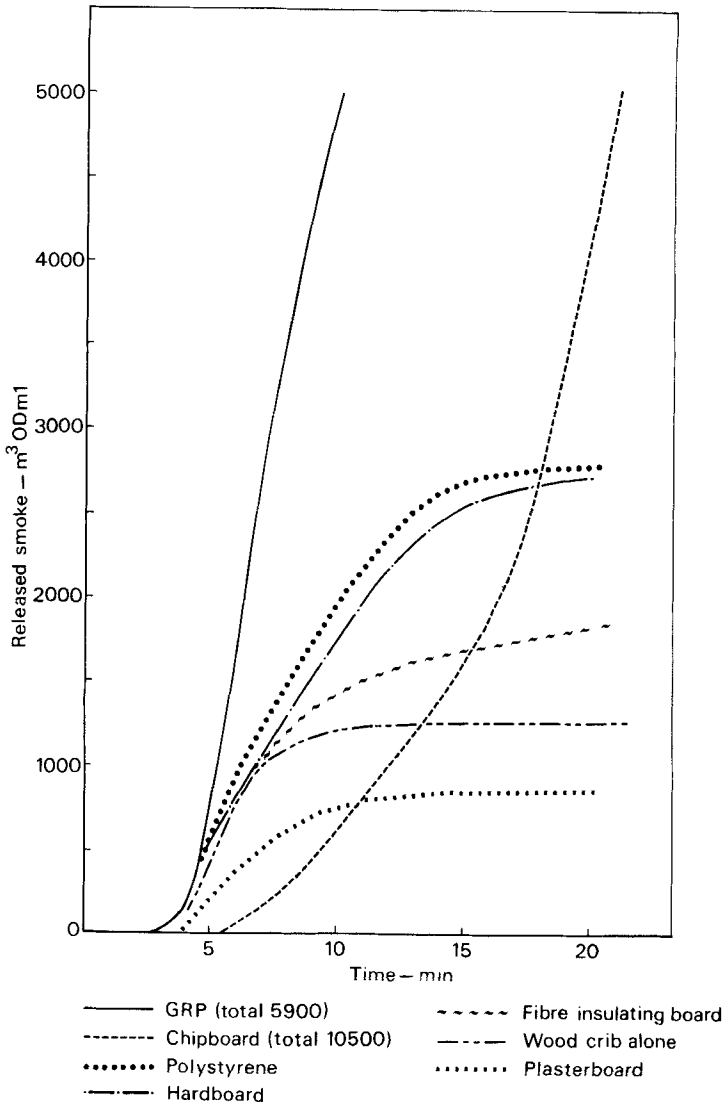


FIG. 5. Smoke production from various wall linings with a 140-kg wooden crib.

a number of general points emerge but conclusions must be taken with some degree of reservation since they relate to a single test only. These are:

1. The smoke from the crib fire alone (140 kg wood), equivalent to the load of a lightly furnished room, was sufficient to produce serious obscuration problems in the compartment and adjacent areas. Volumes of 500 and 1000 m³ could have been contaminated to a calculated visibility of 1.3 m (OD/m of 1) in about 5 and 7 min, respectively.
2. Substantial increases in smoke production were observed with polystyrene (12 kg) and hardboard (85 kg) and, to some extent, fiber insulating board (81 kg) after about 6 min, but the behavior up to this time was similar to that of the wooden crib alone. The results for polystyrene reflect the greater smoke producing potential of this material from the much lower total weight used, in comparison with the hardboard and fiber insulating board.
3. GRP showed a very rapid production of smoke sufficient to obscure 2000 m³ to a calculated visibility of 1.3 m in about 6 min and 5000 m³ in 10 min.
4. Plasterboard released markedly less smoke. The reason for this is not understood but may be associated with the alteration of the thermal characteristics of the rig.
5. With chipboard there was a slower fire development but the 360 kg of lining produced a large fire which ultimately evolved the largest amount of smoke (10,500 m³) observed in any test.

CHEMICAL - ANALYTICAL APPROACHES (LABORATORY STUDIES)

During fire initiation, polymeric materials are subjected to thermal decomposition, and fragmentation of the polymer chains takes place to produce volatile species. If a sufficient concentration of flammable species is attained, a flame may stabilize with feedback of heat to the polymer to continue and accelerate the process. These products may be consumed by the flame to generate combustion products, such as carbon monoxide, carbon dioxide, and water, or may be released unchanged. The materials released in fires are therefore a complex mixture of decomposition and combustion products, with the balance depending upon the general fire conditions.

In our laboratory studies we have attempted to analyze the complex products released during the thermal decomposition of common polymeric materials using a gas chromatograph-mass spectrometer-data handling system [7, 8]. In this work, small samples (usually 10 mg) are decomposed in a tube furnace in a flow of air or nitrogen and the products collected in a refrigerated collection trap coupled on-line to the gas chromatograph for analysis. The mass spectrometer

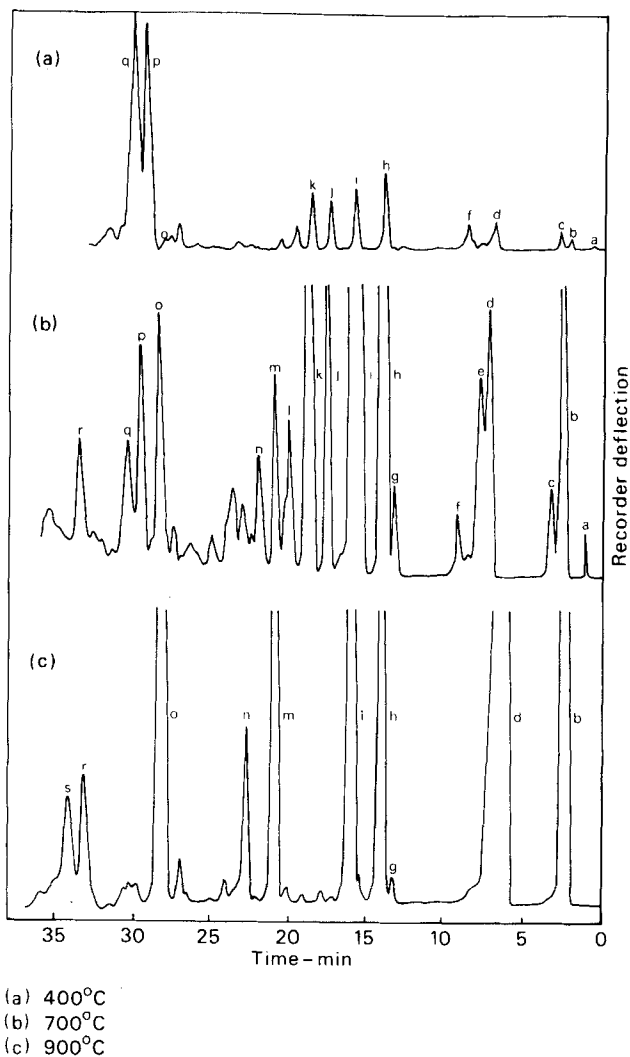


FIG. 6. Chromatograms of the decomposition products of polyacrylonitrile at various temperatures.

is a commercially available, double focusing type unit and is coupled to a data handling system with disk storage and visual display for the processing of data. Figure 6 shows the chromatograms (all recorded on the same scale for direct comparison purposes) of the products of polyacrylonitrile at 400, 700, and 900°C, with the chemical identifications given in Table 2.

TABLE 2. Peak Identifications for the Chromatograms of Polyacrylonitrile Given in Fig. 6.

Peak letter	Mass spectrometric identification
a	Methane
b	Acetylene/ethylene
c	Ethane
d	Hydrogen cyanide
e	Propene
f	Propane
g	1,3- Butadiene
h	Acetonitrile
i	Acrylonitrile
j	Ethyl nitrile
k	Vinyl acetonitrile
l	Crotonitrile
m	Benzene
n	Pyridine
o	Benzonitrile
p	Dicyanobutene
q	Adiponitrile
r	Dicyanobenzene
s	Naphthalene

Work with a range of polymeric materials [18-20] has led us to a basic model to describe decompositions and is illustrated in Fig. 7. In the low temperature region (up to about 400°C) polymers decompose to give a range of complex products. In the medium temperature range (400-700°C) there is a greater complexity of products which may include hydrocarbons, oxygenated species (e.g., aldehydes), nitriles, and so on. This is also the temperature range where oxidation-sensitive polymers, such as polypropylene, can give rise to oxygen-containing organics. Typical products of this kind from polypropylene include formaldehyde, acetaldehyde, acetone, crotonaldehyde, and phenol. It is also in this medium temperature range where complex organic species may arise, as in the case of a

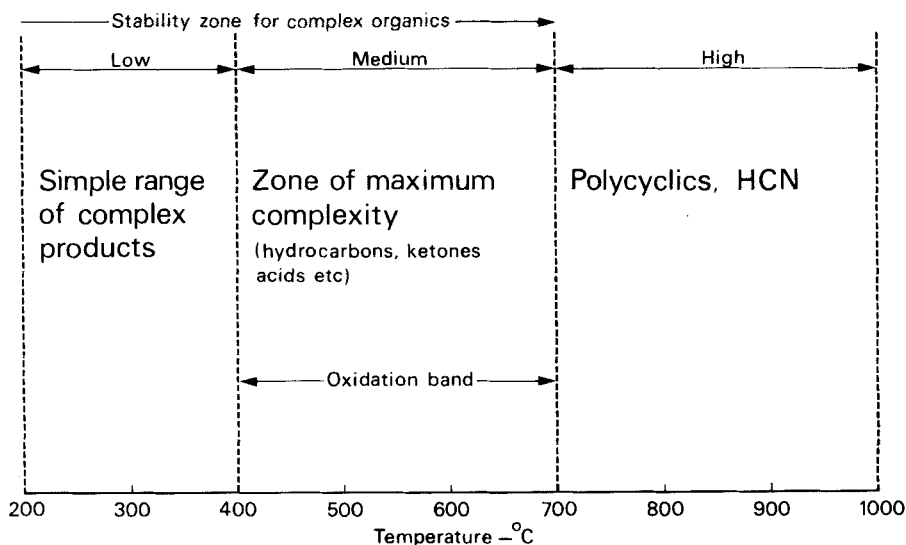


FIG. 7. Important temperature zones during polymer decompositions.

bicyclic phosphorus ester (termed TMPP or BPE), which was observed with certain types of polyurethane foam [21] made with trimethylol propane-based polyols which are no longer available commercially. At high temperatures (in excess of about 700°C) complex organic and organometallic compounds are unstable and decompose. Chromatographic patterns of products simplify in this region and airborne degradations give rise to a series of thermally stable products, such as hydrogen cyanide and low molecular weight nitriles (from nitrogen-containing products); polycyclic hydrocarbons will arise by complex ring cyclization processes. An example of the many polycyclic hydrocarbons generated during the decomposition of a butadiene styrene latex rubber foam at 700°C is given in Fig. 8.

CHEMICAL-ANALYTICAL STUDIES (FIRES)

Experimental fires, both small and large scale, are being used to study the release of unburnt decomposition products so as to indicate the likely contribution of these products to the overall toxicity compared with the carbon monoxide yields [8]. Of particular importance is the "fingerprint" approach, where a chromatographic record of the fire atmosphere can be obtained for direct comparison purposes, particularly with laboratory-generated atmospheres. The fingerprints are usually obtained using an evacuated glass vessel

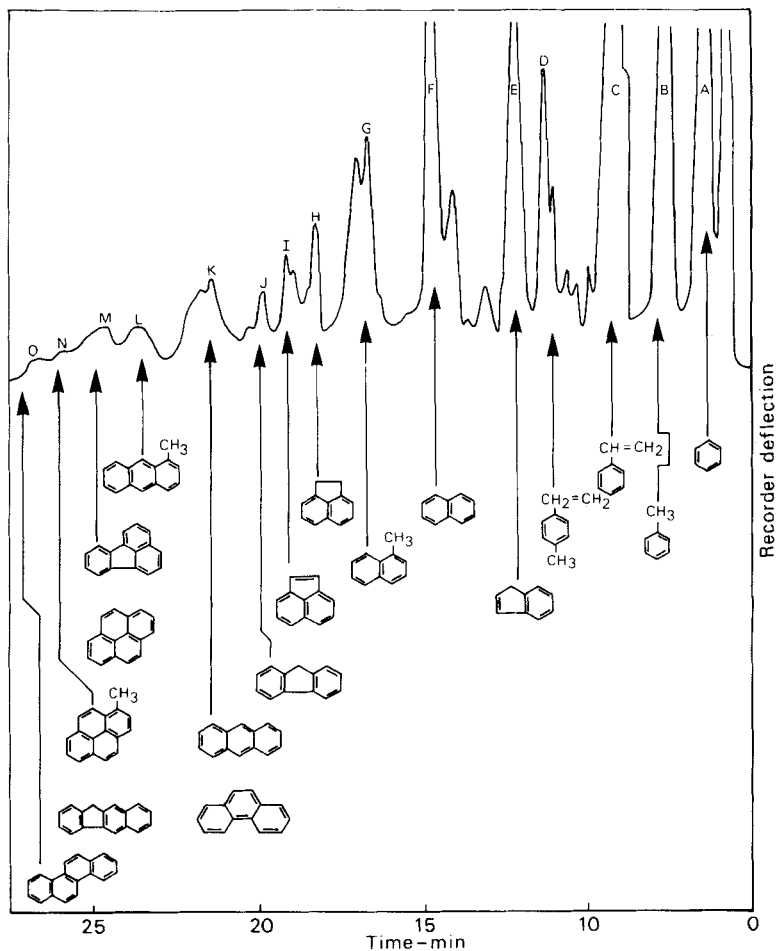


FIG. 8. Polycyclic aromatic hydrocarbons from BS latex rubber foam at 700°C.

which is opened in the fire atmosphere and which has been designed to couple directly to the gas chromatograph-mass spectrometer. The results of this work were presented at a recent U.K. conference [8]. As an example, Fig. 9 shows a fingerprint pattern (identifications in Table 3) of the products during the burning of 5 kg of polypropylene in a room (27 m³) with a closed door. The concentrations of carbon monoxide, carbon dioxide, and oxygen are also recorded, and the sample for fingerprinting was taken at the times marked.

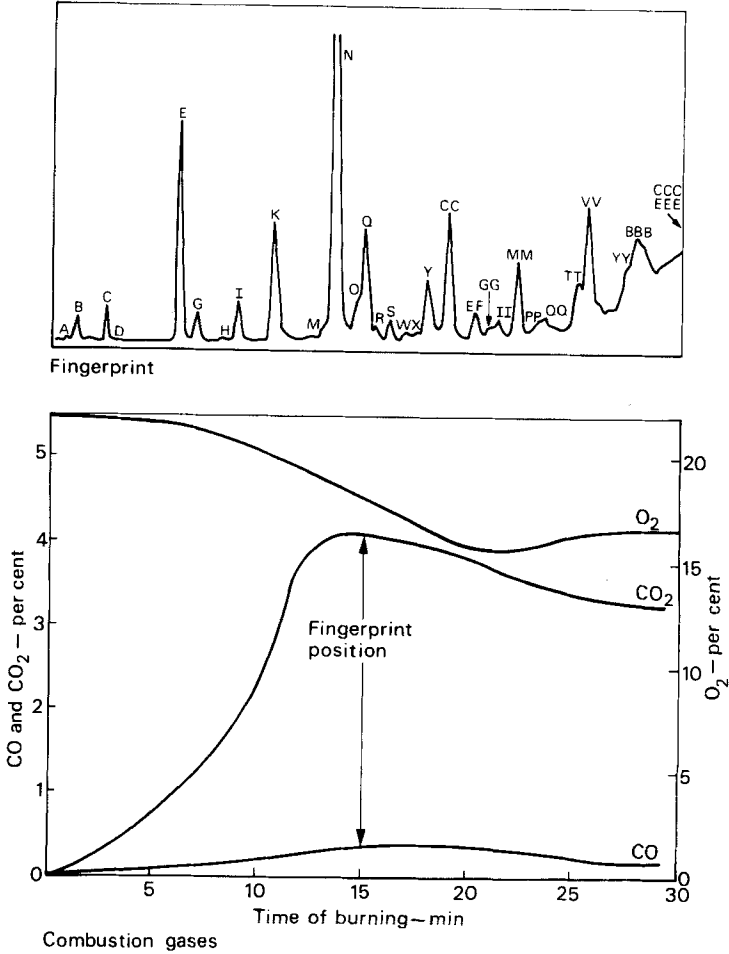


FIG. 9. Yields of combustion gases and chromatographic fingerprint of polypropylene in room burn.

TABLE 3. Identifications of Polypropylene Fingerprint

Peak letter	Mass spectrometric identification	Approximate yield (ppm)
A	Methane	0.2
B	Acetylene	1.4
C	Ethylene	1.8
D	Ethane	
E	Propene	10.7
F	Cyclopropane	
G	Propyne	1.8
H	Formaldehyde	0.2
I	Acetaldehyde	4.6
K	Butene/methyl propene	7.3
M	Butane	0.2
N	Acetone	78.8
O	Pentene/methyl butene	
Q	Cyclopentadiene	5.1
R	Cyclopentene/pentadiene	0.1
S	Crotonaldehyde	1.1
W	Methyl pentene	0.2
X	Hexene	0.1
Y	Cyclohexane	1.9
CC	Benzene	3.6
EF	Pentanone	1.6
GG	Methyl hexyne	0.2
II	Heptyne	0.4
MM	Toluene	2.1
PP	Methyl heptene/octene	0.3
QQ	Octane	0.4
TT	Xylene	1.6
VV	Methyl octene/nonene	3.3

(continued)

TABLE 3 (continued)

Peak letter	Mass spectrometric identification	Approximate yield (ppm)
YY	Propyl benzene	0.1
BBB	Methyl ethyl benzene	6.1
CCC	Indene	
EEE	Ethyl styrene	

FIRE FATALITY STUDIES

Methods of Approach

Pathological studies [11] of fire victims in the Strathclyde region of Scotland are carried out by Professor W. A. Harland at the Department of Forensic Medicine and Science of the University of Glasgow, under a contract from the Fire Research Station.

The pathologist's task is to establish the cause of death, taking into account all contributory causes whether arising from the effects of the fire (burn injuries and soot deposition or other damage to the respiratory system) or from preexisting disease processes. The latter is particularly important where the heart, lungs, or other vital organs are involved, since their condition may impair the ability of the individual to survive a fire.

Chemical analyses are carried out on blood and other tissue samples to detect and measure toxic species, such as carbon monoxide and cyanide arising from the inhalation of fire gases, and also drugs or alcohol. Certain heavy metals (including antimony, zinc, chromium, and lead) are monitored in the soot and mucus taken from the respiratory tracts. These materials may arise from the volatilization of metals or organometallic compounds used as flame retardants or for other purposes, and their effects are as yet uncertain. Computer programs are being developed to aid the storage and statistical comparisons of the pathological and toxicological results of these studies.

Results

From July 1976 to April 1978, 110 fire deaths, comprising 84% of all fire deaths in the region, were studied. The following basic conclusions emerged:

1. The majority of the fire deaths (83%) occurred in dwellings and 2.8% in each of industrial premises, lodging houses, and motor cars. Multiple death fires were encountered in dwellings (total of 16 deaths) and in industrial premises (2 deaths), lodging houses (3 deaths), and motor car fires (2 deaths).
2. The age and sex distribution of the fire fatalities is given in Table 4 for a total of 93 victims. This shows the additional vulnerability of the very young and old in fires and is in broad agreement with national statistics.
3. Burns, either before or after death, were present in 87% of cases and 67% had "fatal" burns (defined as burns covering more than 35% of the body surface). Nonfatal burns were present in 20% of cases and the remaining 13% had no burn injuries. The majority of fire fatalities (88%) had respiratory tract injuries and 90% suffered from soot deposition in air passageways. Many of the victims had evidence of preexisting disease of the heart (25%) or the liver (31%).
4. Carbon monoxide was present in fatal levels [greater than 50% carboxyhemoglobin (COHb)] in one-half of all cases. The frequency distribution is given in Fig. 10 and shows two groups with mean COHb levels of 69 and 18%. The reason for this grouping is not understood but may reflect a demarcation between fires of different types, since the group below the threshold in COHb show a much greater degree of burn injuries than those in the upper COHb group (Fig. 11).

TABLE 4. Age and Sex Distribution of Fire Victims in Strathclyde Region of Scotland 1976-78

Age group	No. males	No. females	% of fatalities	% distribution of the total Scottish population
0-9	11	8	20.4	15.8
10-19	4	1	5.4	17.8
20-29	0	2	2.2	13.8
30-39	3	1	4.3	11.6
40-49	6	3	9.7	11.5
50-59	7	4	11.8	11.5
60-69	14	5	20.4	10.2
70-79	6	6	12.9	6.0
80-	3	9	12.9	1.9

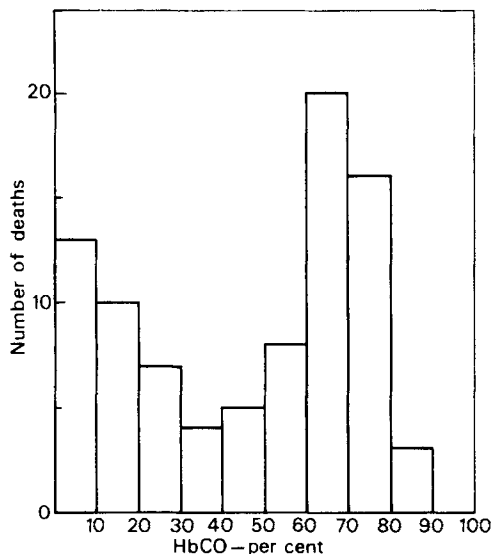


FIG. 10. Frequency distribution of carboxyhemoglobin levels (% COHb) in fire deaths (total = 89).

- For the analysis of cyanide in blood, a great deal of background work has been necessary to develop techniques which enable reliable results to be obtained, since without special precautions cyanide may arise from biological degradations in blood after death. This material cannot then be distinguished from cyanide produced in the fire atmosphere by the decomposition of nitrogen-containing polymers. In spite of these difficulties, reliable measurements of cyanide levels in blood of fire fatalities have been obtained, and the work has been extended to include non-fatal casualties, fire-fighting personnel, and controls, both smokers and nonsmokers.

Cyanide is a normal constituent of blood, present at low concentration (0-20 $\mu\text{mol/L}$). The range of cyanide observed in fire fatalities varies from zero to 130 $\mu\text{mol/L}$ with a mean level of about 30 $\mu\text{mol/L}$. Levels in excess of 100 $\mu\text{mol/L}$ (5% of all cases) can be regarded as potentially dangerous, although a high cyanide level was usually accompanied by high carbon monoxide levels. Analysis carried out at the Forensic Medicine Department showed that, in addition to carbon monoxide, the victims of the recent Taunton rail disaster had significantly elevated levels of cyanide in the blood.

- Alcohol was found in the blood of many of the fire victims and 59% of adults were intoxicated (as based on the maximum permissible

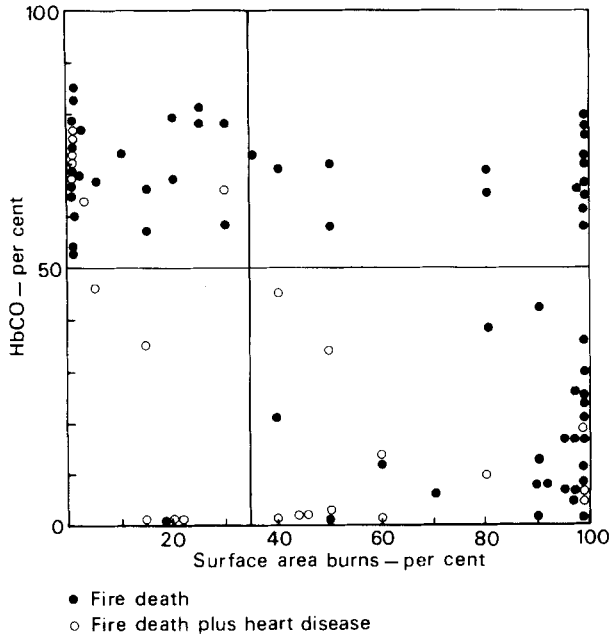


FIG. 11. Scatter diagram showing the incidence of burn injuries and levels of COHb in fire deaths. Cursor lines are set at the fatal threshold for burns (35% surface area burns) and for COHb (5%) (total = 79).

alcohol level in the United Kingdom for drivers of 80 mg/100 mL blood or 107 mg/100 mL urine). The average level was 276 mg/100 mL which is high enough to produce intoxication to the point of incapacitation except in habitual heavy drinkers. Only 5% of cases were found to involve drugs other than alcohol.

7. Heavy metal analyses showed relatively high levels of antimony (4 to 26 ppm) in the soot from the tracheas of victims of a fire in industrial premises (upholstery and clothing) but the significance of this is uncertain. Elevated levels of zinc were common but no correlations with the materials present in the fire have been attempted to date.

BIOASSAY STUDIES

In our bioassay studies, an animal model has been developed, in collaboration with Dr David Purser of the Huntingdon Research Centre, to study the incapacitative effects of low concentrations of specific fire

gases and polymer decomposition products. The particular aims of the work are to detect physiological and behavioral effects likely to impair the escape capability of human fire victims.

In the study separate experiments are done whereby laboratory animals are exposed to atmospheres ranging from very low concentration up to concentrations where physiological effects are detected. These levels are below those at which gross effects could be observed. For this purpose a number of physiological functions are monitored and the measurements are basically of two types:

- (a) Measurement of vital signs; respiration, ECG, and blood gas measurements
- (b) Neurological function; EEG, cortical-evoked responses, and peripheral nerve conduction velocities

The model has been used to assess the incapacitative effects of hypoxia and hypercapnia and of carbon monoxide and hydrogen cyanide; this has provided baseline data on which work on the decomposition products of polyacrylonitrile, rigid and flexible polyurethane foam, wood, polypropylene, and polystyrene can be based.

The results of this work, which are to be published in the near future, have shown that the toxic products fall into two categories:

1. Products which intoxicate basically by effects on the nervous and cardiovascular systems
2. Irritant products which can incapacitate

Among the decomposition products of the materials studied only two compounds, CO and HCN, were found to produce significant degrees of intoxication, and the intoxicating effects of any particular test atmosphere depended upon which of these gases was present in its most nearly toxic concentration.

The occurrence and degree of acute irritant effects and later lung reactions could not be predicted from a chemical analysis of decomposition products, although atmospheres produced under oxidative decomposition conditions were generally more irritant than atmospheres produced from the same materials under pyrolytic conditions. It is likely that a wide range of decomposition products could have serious irritant effects, which could only be categorized by the use of animal exposures.

Another important feature of smoke atmospheres is that both the chemical composition and the toxicity varied greatly with different decomposition conditions, the main factors determining atmosphere composition being the furnace temperature, the degree of oxygen availability to the heated sample, and whether or not the sample was flaming.

THE MANCHESTER WOOLWORTH'S STORE FIRE

General Considerations of the Fire

On 8 May 1979 a fire occurred in the furniture department of the Woolworth's store in Piccadilly, Manchester. There were many hundreds of people in the store at the time of the fire, most of whom escaped or were rescued, but 10 people lost their lives.

The fire was first seen in a stack of stored furniture within the main furniture display area on the second floor adjacent to the restaurant. The majority of persons on the second floor were in the restaurant at the time of the fire and eyewitnesses reported very rapid growth of fire and large amounts of thick, choking smoke. There were four independent means of escape (escalator and three staircases). Nine victims were found very close to an escape route but had not been able to use it.

A series of preliminary ignition and fire tests were carried out on single items of furniture supplied by F. W. Woolworth and Company Limited identical to those present in the stack of furniture at the time of the fire. The furniture consisted of bedding materials (mattresses and a divan base), soft furniture upholstered with polypropylene fabric over polyurethane foam (convertible settees, rocking chairs, fireside chairs, settees), panel furniture (dressing and wardrobe units), together with additional items such as kitchen chairs and coffee tables. All items were stored with the packaging materials and protective bags supplied by the manufacturers.

Tests showed that the soft furnishings were relatively easy to ignite and the panel furniture much more difficult. The mattresses, divan, and all upholstered furniture ignited with a match with or without their packaging materials. When burning, the items upholstered with polypropylene fabric over polyurethane foam showed very rapid fire development. In one test with a two-seat settee in a room under adequate ventilation (open doorway), the room temperature at the ceiling level reached 960°C at 2.75 min after ignition from a match with a rise in temperature from 100 to 900°C in less than 0.5 min.

The mattresses were the only items which smouldered during tests with lighted cigarettes. One of the mattresses spontaneously ignited to flames after 3 h and 10 min of smouldering but a considerable amount of smoke and irritants were produced before ignition occurred. In contrast to the soft furnishings, the wardrobe and dressing units required a flame approximating to that produced by the burning of two sheets of newspaper for ignition.

These fire tests with single items of soft furniture indicated that rapid fire development might occur. Where items of furniture are stacked one above the other, heat transfer between items becomes much greater and fire development may be more rapid than can be predicted from tests with single items. The FRS agreed to carry out a full-scale fire test to study the development of a fire in a stack of furniture representing, as nearly as possible, the type of furniture

and stacking arrangement as was present in the area where the Woolworth's fire was first reported.

The test was carried out using an instrumented test rig with a ceiling area of 5×12 m above the furniture (3 m high), with walls on three sides to give an open-ended rig. This configuration provided a means of studying the movement of smoke and flame beneath the ceiling; air flow to the fire and discharge of smoke and hot gases was limited to a single opening to assist measurements.

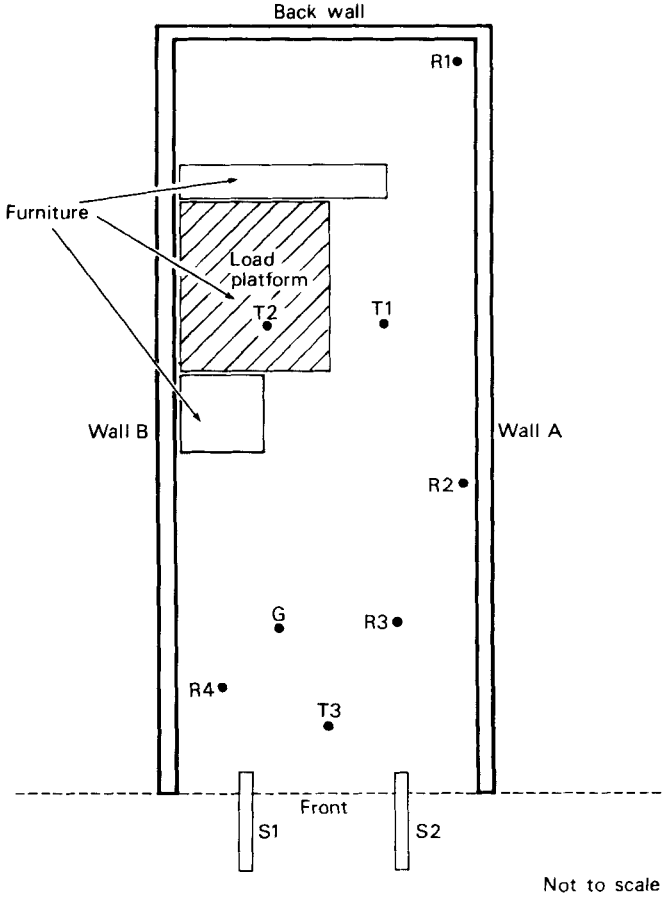
The rig is shown diagrammatically in Fig. 12 with the main furniture stack positioned on the load platform along Wall B. T1, T2, and T3 are stacks of thermocouples fitted to the ceiling to monitor the temperatures inside the rig. R1 to R4 inclusive are radiometers positioned about 0.5 m above the floor and directed toward the furniture stack. G is a gas analysis point for continuous monitoring of oxygen, carbon monoxide, and carbon dioxide at a point 230 mm below the ceiling. For smoke measurements, two quartz-iodide lamps (S1 and S2), collimated to give parallel beams of light, were fitted to the top of the rig, with the light directed through smoke emerging from the rig, onto a photocell at floor level in front of the rig. Two anemometers were positioned directly beneath the light beams to measure the flow of air into the rig during the early stages of the fire.

The arrangement of furniture in the stack is shown in Fig. 13. All the materials supplied were tested as received together with the appropriate packaging materials. The stack of furniture was ignited with a match, to represent a common source of flame, at the point shown in Fig. 13.

RESULTS AND CONCLUSIONS

The temperatures near the ceiling, the smoke density, and the weight of fuel on the load platform are recorded in Figs. 14, 15, and 16, respectively. From a consideration of these results, and basic observations during the tests, the following conclusions have emerged:

1. After ignition by a match, the fire developed rapidly over the packaging materials, soft furnishings, and bedding, and after 30 s the flames had reached the top of the stack of furniture.
2. Flames were impinging on the ceiling 40 s after ignition and at 50 s the soft furnishings were burning fiercely, but there was little evidence of smoke beneath the ceiling.
3. At 1 min after ignition the flames were spreading under the ceiling with a temperature of 1000°C at the ceiling level above the furniture. Black smoke was forming a distinct layer under the ceiling.
4. At 1 min 25 s the majority of the upper part of the furniture stack was ablaze and smoke formed a 1.5-m layer beneath the ceiling. The fire was noisy because of delamination and involvement of the panel furniture.



- R - Radiometers
- T - Thermocouples
- G - Gas analysis tube
- S - Smoke measuring instruments (and anemometers)

FIG. 12. Plan of test rig.

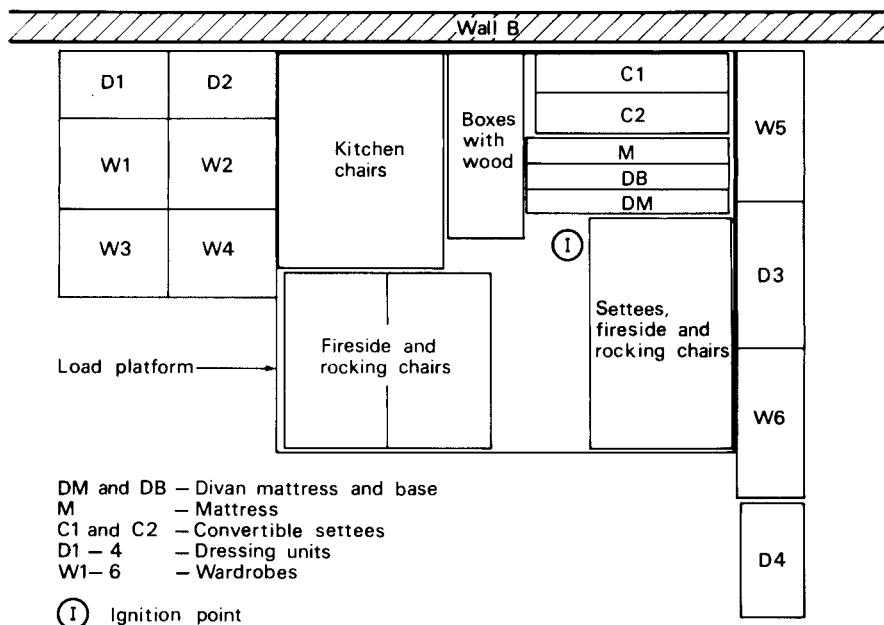


FIG. 13. Layout of furniture.

5. Flames began to emerge from the open end of the rig at 1 min 40 s after ignition, and the temperature of the gases near the exit at ceiling level was in excess of 800°C.
6. At 2 min after ignition the fire had reached maximum severity as indicated by the temperature recordings. Smoke was issuing from the open end of the rig at a calculated rate of about 1700 m³/min at 800°C with a visibility of less than 0.6 m. The radiation level from the fire was sufficient to cause the probable ignition of wooden furniture if stored in the front area of the rig. The combustion gases were very hot, contained high concentrations of carbon monoxide (in excess of 5%) and low concentrations of oxygen (about 6%). Direct contact with these gases would cause very severe injury and probably be fatal in a short exposure in terms of both toxicity and high temperatures.
7. At 2 min 30 s after ignition, weight loss measurements of the furniture on the load platform indicated a calculated heat output of about 23 MW. A severe condition, with flames emerging steadily from the open end of the rig, persisted for several minutes with damage to the lining materials in the rig: the test was terminated after about 9 min.
8. The overall study has shown that rapid fire development can occur

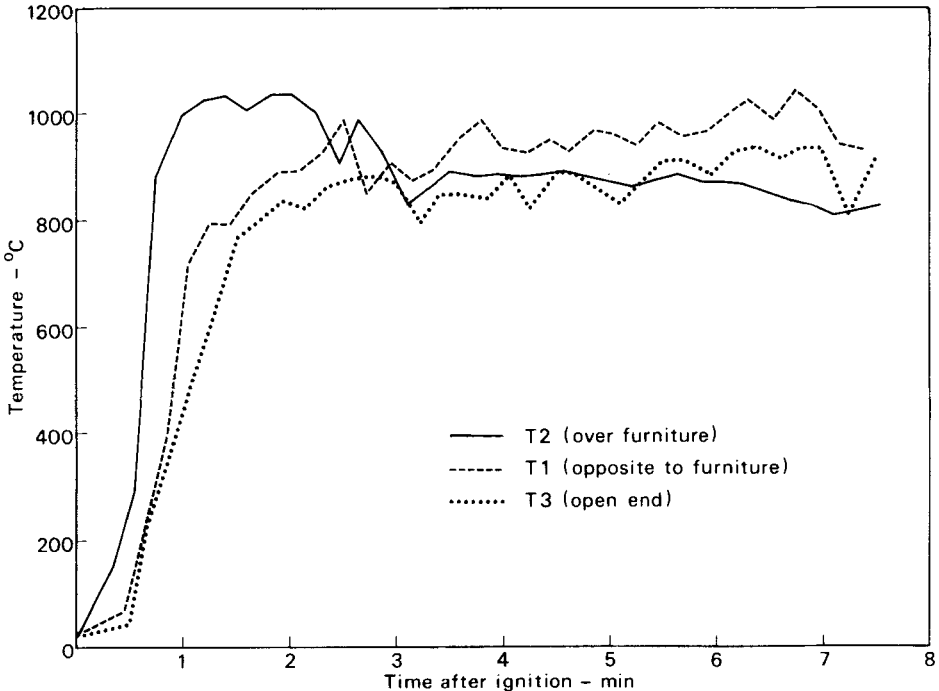


FIG. 14. Temperatures recorded beneath ceiling.

with furniture upholstered with polypropylene fabric over polyurethane foam. In the stack of furniture where there was effective heat transfer, the build up of the fire became very rapid indeed. Immediate evacuation of persons in the vicinity of a fire of this kind is necessary, because of the rapid spread of smoke and toxic gases.

In preliminary experiments the burning of a two-seat settee made from polypropylene fabric over polyurethane foam gave a temperature of 960°C at ceiling level in a small domestic room within 2 min 45 s of ignition from a match. The potential of these items in causing injury and death in domestic dwellings cannot be overlooked.

Application of Results to the Woolworth's Store Fire

In the Woolworth's store the development of fire in a floor area of 1300 m^2 would depend upon many local factors, particularly the ventilation to the fire. With adequate ventilation the fire may have

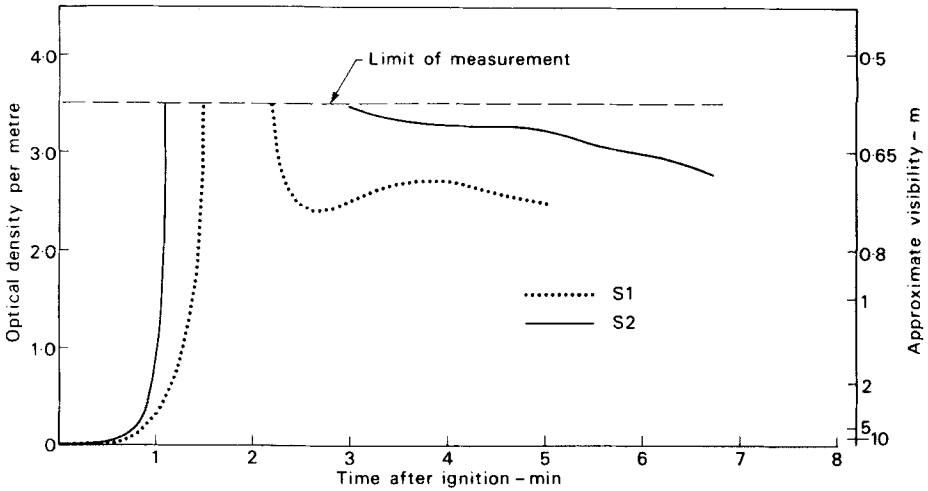


FIG. 15. Optical density and visibility of smoke emerging from rig.

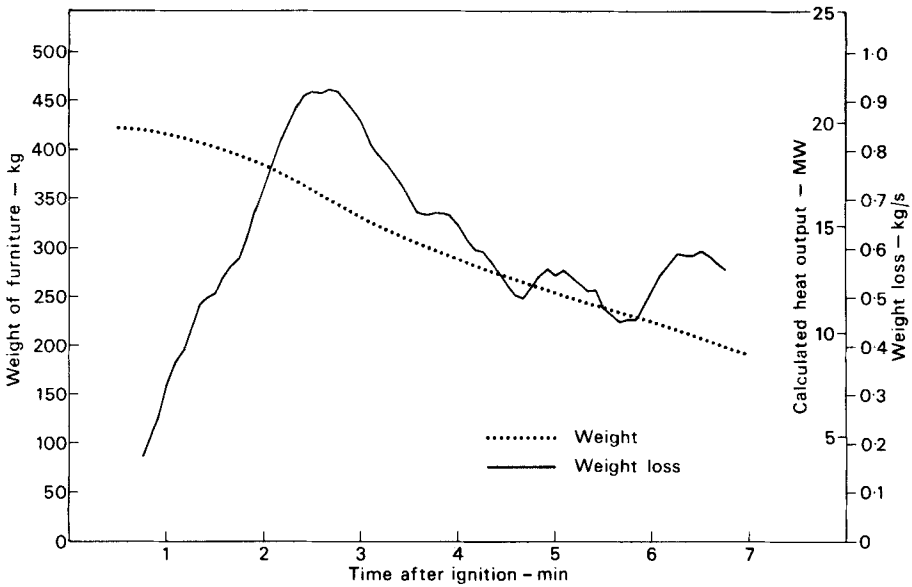


FIG. 16. Weight and rate of weight loss of furniture on load platform.

developed very rapidly. If detected when flames were visible above the furniture stack and touching the ceiling (about 1 min after ignition), first aid fire fighting may have presented insuperable problems unless carried out by a trained and experienced fire fighter. This arises because of the rapid development of fire, the difficulty in locating the seat of the fire, and the heat and smoke in the atmosphere.

The smoke and hot vitiated combustion gases would have spread out as a layer under the ceiling, and after 2 min the downward radiation may have been sufficient to have ignited adjacent furniture, giving rise to greater fire development.

Even with the fire limited to a furniture area of about 3×3 m, the fire experiment indicated that a discharge of about $1700 \text{ m}^3/\text{min}$ (at 800°) of very dense, toxic, and vitiated smoke may have been present 2 min after ignition. Within a further minute this smoke and hot toxic gases are likely to have formed a layer under the ceiling over the majority of the departmental floor, with mixing with air and cooling bringing the smoke down to floor level at the boundary walls.

This wall effect and the possible obscuration of exit routes, together with the acceleration of the fire and the production of smoke and gases (sufficient to cause injury and death in a very short time following exposure), may have made escape from the floor area very uncertain after 2 min from detection (3 min from ignition).

SUMMARY AND CONCLUSIONS

The research currently in progress at the Fire Research Station into the problems of smoke and toxic gases released during the burning of polymers has been outlined. The important findings can be summarized as:

1. GC/MS analysis shows the enormous chemical complexity of products which can be generated during the decomposition and burning of even "simple" polymers. The work gives a good indication of the types and yields of products formed under different combustion conditions but illustrates the great care which needs to be taken in the extrapolation of analytical results to toxicological significance.
2. Bioassay work can overcome some of the analytical limitations in the understanding of the incapacitative and injurious effects of combustion products. However, care needs to be taken in the interpretation of results. The nature of this work often dictates that a simple fire model is used for the generation of combustion products, and systems such as the German [22] DIN 53 436 and the American Potts' Pot [23] are under consideration as International Standards. Little work has been carried out to date to verify whether the products generated by these tests are representative of those formed at various stages of fires. In addition,

it does not always follow that the results with animals are directly applicable to man.

3. The work on the obscurational effects of smoke produced during fires shows the great potential of many modern material composites in restricting visibility. Even a single item of modern upholstery (chair) is capable of reducing the visibility in an entire domestic house to a very low distance in a short period of time. The problems of smoke obscuration in preventing escape, thereby confining building occupants in a dangerous (toxic) environment, have been highlighted in a number of recent fires (including the Woolworth's fire).
4. The fire fatality study has been effective in providing, for the first time in the United Kingdom, full details of the pathology and toxicology of fire fatalities in a large area of the country. It has shown that carbon monoxide is almost certainly the cause of death in 50% of cases but when other causes, such as burns and heart disease are eliminated, a significant proportion remains unexplained. Future work is expected to produce evidence for the presence of other toxic agents still needing identification.

The presence of alcohol in the blood of victims is significant and may indicate that many of the fire victims are severely incapacitated even before the fire effects become important. There is no evidence from this study that carbon monoxide and alcohol are synergistic in the toxicological sense. The additional incapacitative effects of the fire atmosphere in reducing escape ability are not clear from this work and need further investigation.

5. The Woolworth's store fire focused attention in the U.K. on the problems of smoke and gases in fires, and there were some calls for polyurethane foam to be banned because of combustion toxicity. However, the subsequent "reconstruction" of the fire in a simulated furniture stack showed that the soft furnishings upholstered with polypropylene fabric over polyurethane foam resulted in a very rapid development of fire and therefore a very rapid development and spread of smoke and toxic gases. The work has indicated, once again, that the most effective means of mitigating the effects of fire atmospheres is the improvement of ignitability and the reduction of the rate of fire growth by careful material selection or other appropriate means.

The results of this research emphasize the need for a wide viewpoint in minimizing the overall hazard to life from the burning of polymers in buildings. The fire atmosphere is only one part of the hazard and must be integrated with other considerations such as ignitability and flame spread if mitigating action is to be effective.

ACKNOWLEDGMENTS

The author wishes to acknowledge the help of Professor W. A. Harland and Dr R. A. Anderson (University of Glasgow) in the Fire

Fatality Study and Dr D. A. Purser (Huntingdon Research Centre) for the development of the bioassay model. Thanks are also due to Mr P. J. Fardell and Mr S. A. Ames of the Fire Research Station for various aspects of the work reported here. The paper forms part of the work of the Fire Research Station, Building Research Establishment, Department of the Environment, United Kingdom. It is contributed by permission of the Director, Building Research Establishment.

REFERENCES

- [1] P. C. Bowes, Ann. Occup. Hyg., **17**, 143 (1974).
- [2] G. W. V. Stark, Toxic Gases from PVC in Fires in the FRS Full-Scale Test Rig (Fire Research Note 1030), Fire Research Station, Borehamwood, 1975.
- [3] G. W. V. Stark, Smoke and Toxic Gases from Burning Building Materials. 1. A Test Rig for Large-Scale Fires (Fire Research Note 1015), Fire Research Station, Borehamwood, 1974.
- [4] G. W. V. Stark, P. Field, and A. L. Pitt, The Hazard from Fires of Small Loads of Flexible Polyurethane Foam (Fire Research Note 1017), Fire Research Station, Borehamwood, 1974.
- [5] W. D. Woolley, S. A. Ames, A. L. Pitt, and J. V. Murrell, Fire Mater., **1**(2), 63 (1976).
- [6] W. D. Woolley, S. A. Ames, A. L. Pitt, and K. Buckland, Fire Saf. J., **2**, 39 (1979-80).
- [7] W. D. Woolley and P. J. Fardell, J. Fire Res., **1**, 11 (1977).
- [8] W. D. Woolley, S. A. Ames, and P. J. Fardell, Fire Mater., **3**(2), 110 (1979).
- [9] W. D. Woolley, M. M. Raftery, S. A. Ames, and J. V. Murrell, Fire Saf. J., **2**, 61 (1979-80).
- [10] W. D. Woolley, Plast. Polym., **41**(156), 280 (1973).
- [11] R. A. Anderson, I. Thomson, and W. A. Harland, Fire Mater., **3**(2), 91 (1979).
- [12] A. Silcock, D. Robinson, and N. P. Savage, Fires in Dwellings—An Investigation of Actual Fires. Parts II and III (CP 80/78), Building Research Establishment, Borehamwood, 1978.
- [13] R. H. Kennedy, K. W. P. Riley, and S. P. Rogers, A Study of the Operation and Effectiveness of Fire Detectors Installed in the Bedrooms and Corridors of Residential Institutions (CP 26/78), Building Research Establishment, Borehamwood, 1978.
- [14] S. E. Chandler, Some Trends in Furniture Fires in Domestic Premises (CP 66/76), Building Research Establishment, Borehamwood, 1976.
- [15] W. D. Woolley and S. A. Ames, The Explosion Risk of Stored Foamed Rubber (CP 36/75), Building Research Establishment, Borehamwood, 1975.
- [16] S. A. Ames, Automated Fire Test System (Information paper IP 23/79), Building Research Establishment, Borehamwood, 1979.

- [17] D. J. Rasbash and B. T. Pratt, Fire Saf. J., 2, 23 (1979-80).
- [18] W. D. Woolley, P. J. Fardell, and I. G. Buckland, The Thermal Decomposition Products of Rigid Polyurethane Foams under Laboratory Conditions (Fire Research Note 1039), Fire Research Station, Borehamwood, 1975.
- [19] W. D. Woolley, Br. Polym. J., 3(4), 186 (1971).
- [20] W. D. Woolley, Ibid., 4(1), 27 (1972).
- [21] W. D. Woolley and P. J. Fardell, Formation of a Highly Toxic Organophosphorus Product (TMPP) during the Decomposition of Certain Polyurethane Foams under Laboratory Conditions (Fire Research Note 1060), Fire Research Station, Borehamwood, 1976.
- [22] G. Kimmerle, J. Combust. Toxicol., 1, 4 (February 1974).
- [23] W. J. Potts and T. S. Lederer, Ibid., 4, 114 (May 1974).