NATIONAL BUREAU OF STANDARDS REPORT

10 807

TOXIC ATMOSPHERES ASSOCIATED WITH REAL FIRE SITUATIONS

Sponsored by

Fire Services Section

of

Office of Fire Programs

NBS

U.S. DEPARTMENT OF COMMERCE

NATIONAL BUREAU OF STANDARDS

NATIONAL BUREAU OF STANDARDS

The National Bureau of Standards[1] was established by an act of Congress March 3, 1901. The Bureau's overall goal is to strengthen and advance the Nation's science and technology and facilitate their effective application for public benefit. To this end, the Bureau conducts research and provides: (1) a basis for the Nation's physical measurement system, (2) scientific and technological services for industry and government, (3) a technical basis for equity in trade, and (4) technical services to promote public safety. The Bureau consists of the Institute for Basic Standards, the Institute for Materials Research, the Institute for Applied Technology, the Center for Computer Sciences and Technology, and the Office for Information Programs.

THE INSTITUTE FOR BASIC STANDARDS provides the central basis within the United States of a complete and consistent system of physical measurement; coordinates that system with measurement systems of other nations; and furnishes essential services leading to accurate and uniform physical measurements throughout the Nation's scientific community, industry, and commerce. The Institute consists of a Center for Radiation Research, an Office of Measurement Services and the following divisions:

> Applied Mathematics—Electricity—Heat—Mechanics—Optical Physics—Linac Radiation[2]—Nuclear Radiation[2]—Applied Radiation[2]—Quantum Electronics[3]—Electromagnetics[3]—Time and Frequency[3]—Laboratory Astrophysics[3]—Cryogenics[3].

THE INSTITUTE FOR MATERIALS RESEARCH conducts materials research leading to improved methods of measurement, standards, and data on the properties of well-characterized materials needed by industry, commerce, educational institutions, and Government; provides advisory and research services to other Government agencies; and develops, produces, and distributes standard reference materials. The Institute consists of the Office of Standard Reference Materials and the following divisions:

> Analytical Chemistry—Polymers—Metallurgy—Inorganic Materials—Reactor Radiation—Physical Chemistry.

THE INSTITUTE FOR APPLIED TECHNOLOGY provides technical services to promote the use of available technology and to facilitate technological innovation in industry and Government; cooperates with public and private organizations leading to the development of technological standards (including mandatory safety standards), codes and methods of test; and provides technical advice and services to Government agencies upon request. The Institute also monitors NBS engineering standards activities and provides liaison between NBS and national and international engineering standards bodies. The Institute consists of a Center for Building Technology and the following divisions and offices:

> Engineering Standards Services—Weights and Measures—Invention and Innovation—Product Evaluation Technology—Electronic Technology—Technical Analysis—Measurement Engineering—Fire Technology—Housing Technology[4]—Federal Building Technology[4]—Building Standards and Codes Services[4]—Building Environment[4]—Structures, Materials and Life Safety[4]—Technical Evaluation and Application[4].

THE CENTER FOR COMPUTER SCIENCES AND TECHNOLOGY conducts research and provides technical services designed to aid Government agencies in improving cost effectiveness in the conduct of their programs through the selection, acquisition, and effective utilization of automatic data processing equipment; and serves as the principal focus within the executive branch for the development of Federal standards for automatic data processing equipment, techniques, and computer languages. The Center consists of the following offices and divisions:

> Information Processing Standards—Computer Information—Computer Services—Systems Development—Information Processing Technology.

THE OFFICE FOR INFORMATION PROGRAMS promotes optimum dissemination and accessibility of scientific information generated within NBS and other agencies of the Federal Government; promotes the development of the National Standard Reference Data System and a system of information analysis centers dealing with the broader aspects of the National Measurement System; provides appropriate services to ensure that the NBS staff has optimum accessibility to the scientific information of the world, and directs the public information activities of the Bureau. The Office consists of the following organizational units:

> Office of Standard Reference Data—Office of Technical Information and Publications—Library—Office of International Relations.

---

[1] Headquarters and Laboratories at Gaithersburg, Maryland, unless otherwise noted; mailing address Washington, D.C. 20234.

[2] Part of the Center for Radiation Research.

[3] Located at Boulder, Colorado 80302.

[4] Part of the Center for Building Technology.

NATIONAL BUREAU OF STANDARDS REPORT

NBS PROJECT		NBS REPORT
4001130	February 16, 1972	10 807

TOXIC ATMOSPHERES ASSOCIATED WITH REAL FIRE SITUATIONS

by
Julian M. Ives
Ernest E. Hughes
John K. Taylor

Division of Analytical Chemistry

Sponsored by
Fire Services Section
of
Office of Fire Programs

NBS

U.S. DEPARTMENT OF COMMERCE

NATIONAL BUREAU OF STANDARDS

SUMMARY

This report summarizes the results of a survey, sponsored by the Fire Research and Safety Office of NBS, to ascertain the nature of toxic atmospheres associated with real fire situations. The study involved a review of the literature, both scientific and popular, and discussions with knowledgeable people in the field. While the available information is less quantitative than desirable, definite conclusions may be drawn from it.

Statistics from American and British surveys show that toxic gases are an important cause of casualties in fires. A wide variety of toxic substances are produced in burning structures at levels that can be extremely hazardous. While indivdual gases can often reach dangerous levels, combinations can occur which are more toxic than the sum of the individual toxicities and this may be the real hazard of a fire situation. The dangers related to smoke and to oxygen deficiency are very real and always require protective measures.

Because it is not possible to predict the levels of hazardous gases that may be encountered in any fire occurrence, firemen are well advised to consider each situation as potentially hazardous.

Table of Contents

List of Figures

List of Tables

List of Tables (Con't.)

Table Page

1. INTRODUCTION

The inability of the human body to adapt to gross changes in its environment is emphatically demonstrated by the narrow range of permissible changes in composition of the air necessary for respiration and more emphatically demonstrated by the extremely low tolerance to a variety of foreign substances in this same air. Fortunately, most of us have some control over the quality of the air we breathe and only in the most extraordinary circumstances do we exceed the normal adjustive capacity of the respiratory system. The firefighter, however, must of necessity enter into situations which tax or even exceed this adaptive capacity. Furthermore, the atmosphere which he must breathe is neither of known composition nor is the toxicology of the possible constituents well understood. An added uncertainty and one of possible fatal consequence is the effect of combinations of toxic agents.

This report is intended not to solve these problems but rather to elucidate them in terms of current knowledge derived from studies reported in the literature and from other pertinent sources.

It is apparent at this point that little real knowledge exists which would allow an instantaneous assessment of the conditions of an atmosphere within a fire situation. Nor does it seem likely that a situation will soon exist where an on-the-spot assessment can be made which will reveal the presence of all possible toxic substances or of substances which could combine to form a toxic atmosphere.

Combustion itself is a little understood process and as the materials inventory of structures likely to be involved in fires increases in kind, the end products of combustion become an even more confusing mass of potentially dangerous substances. Were structures and furnishings to be fabricated solely from natural products, then perhaps definitive limits could be derived which would allow a formal assessment of a fire situation. However, the ever increasing use of new and different synthetic materials both in construction and in manufactured goods continually expands the dimension of the problem.

Perhaps then, this report will serve its most useful function in pointing out not what is known, but rather the vast areas where current knowledge is substantially lacking.

2. STATISTICS ON CASUALTIES

Comprehensive figures on U. S. fire casualties specifically due to toxic gases are not available. Surveys about casualties of fire fighters by the IAFF (International Association of Fire Fighters) and the IAFC (International Association of Fire Chiefs) indicate that toxic gases may be an important cause of injuries to fire fighters, but the magnitude of the problem, as presented in these surveys is quite uncertain due to the manner in which the statistics were gathered. For example, the IAFF survey [1] of casualties for 1968 indicates toxic gases accounted for 25 percent of fire fighter injuries, and 22 percent of lost-time accidents. In the IAFF survey [2] for 1969, the latest year available, these percentages were 9 and 11 percent, respectively. The reason for the large decrease from 1968 to 1969 is not clear. A change in the reporting form may be responsible. The results of the survey are dependent on response to questionnaires sent out by the IAFF. An example of the continuing IAFC survey [3] indicates that among firemen, there is a high rate of casualties due to smoke inhalation. The sampling methods used in this survey do not appear sufficiently valid, however, to provide a good value for numbers of casualties due to toxic gases.

The United Kingdom fire statistics [4-7] gathered and treated in a statistically valid manner, provide a good picture of the toxic gas problem there. Table 1, which was compiled from the latest available statistics (1968), and statistics from the previous years, shows toxic gas data gathered in the United Kingdom survey. Whether these statistics can be considered to be representative of the hazards in this country is conjectural, due to possible differences in fire fighting methods and construction materials.

Several U. S. surveys of smaller than national scale indicate that toxic gases are a large contributor to fire department casualties. An unpublished report by H. P. Utech [8]

Table 1. Casualty data related to toxic gases from surveys in the United Kingdom.

	Fatalities from gas or smoke	total fatalities	Non-fatal casualities from gas or smoke	Total non-fatal casualities
<u>1968</u>				
Fire Brigade	0	5	56	373
Others	477	860	512	4239
<u>1967</u>				
Fire Brigade	1	3	72	404
Others	382	776	401	4248
<u>1966</u>				
Fire Brigade	3	3	45	404
Others	373	777	372	4028
<u>1965</u>				
Fire Brigade	0	0	21	364
Others	271	702	401	4037

of the Fire Services Section at NBS, based on a Bureau of Labor Statistics survey of injuries incurred by fire fighters during 1964, shows the significant relation of inhalation of toxic materials to casualties. Contact with caustic, toxic, and noxious substances accounted for 17.8 percent of all fire scene injuries and are ranked as the most frequent cause of injury. Blows from falling or flying objects ranked second as a cause of injury (15.0 percent). Of the injuries caused by toxic substances, 81 percent were received when the substance was inhaled, which makes inhalation of toxic substances, by itself, second as a cause of injuries to fire fighters. Another statistically valid, unpublished report by H. P. Utech [9], on injuries to fire fighters in the District of Columbia showed, over the period serveyed, that the number of injuries to the respiratory system was the largest (538 incidents), with sprains and strains being second (324 incidents). An annual report of the Contra Costa County Fire Department in California [10] included an analysis of personnel injuries for the years 1966 and 1967. In 1966, three of 137 injuries were due to toxic gases (smoke inhalation) and in 1967, 30 of 158 injuries were from toxic gases. The sample size here was too small to give a valid indication of the general magnitude of the toxic gas problem.

A survey on single fatality fires in the U. S. (3,145, covering the period from February 1966 to June 1968) indicates the lethal nature of smoke and toxic gases to individuals involved in fires [11]. In the non-clothing fires (2,620), toxic gases and smoke caused the most deaths (1,378) with burns causing the next highest number of fatalities (1,168).

A survey of hospital fires over a recent 20 year period showed that, of a total of 189 fatalities, 119 were caused by smoke and toxic gases, 50 were caused by burns, and the rest were due to anesthesia explosions and falls or falling objects [12].

Numerous individual fires also point up the hazards of toxic gases to the individual. A prime example is the Cleveland Clinic Fire of 1929 where 123 died from exposure to the combustion products of nitrocellulose film, which contained high concentrations of NO_2, HCN, and CO [13].

Unfortunately, this brief description summarizes essentially all of the available statistical information on the hazards to fire fighters associated with toxic gases. It does not appear at this time that any more information will be available in the future unless an increased effort is made to more thoroughly collect and analyze fire casualty data.

3. REVIEW OF EXPERIMENTAL STUDIES

Many types of fire tests have been performed to characterize the atmospheres produced during combustion of various materials and structures. These tests may be divided into four categories as follows: 1. Thermal decomposition of materials in relatively small flasks or reaction chambers in an air or nitrogen atmosphere. 2. Burning materials or combustible articles in air in larger, room sized chambers. 3. Burning of full sized structures. 4. Sampling of gases at actual fires. The discussion below gives the results of some of the more important experiments.

Olsen *et al.* [14] in 1933 thermally decomposed newspapers, rubber insulation, woolen material, and silk in atmospheres of both nitrogen and excess air either in small flasks or in a silica tube. The atmospheres produced were analyzed for such gases as CO_2, CO, O_2, NH_3, HCN, H_2S, and SO_2. Table 2, taken from this work, gives the results of burning wool in a silica tube.

Table 2. Gases produced by burning wool according to Olsen [14].

	Concentration in Mole Percent			
	A %	B %	C %	D %
Carbon dioxide	4.6	9.2	6.2	9.2
Carbon monoxide	0.5	4.4	5.0	2.5
Oxygen	14.2	6.6	10.8	7.2
Unsatd. hydrocarbons	0.0	0.4	0.6	0.4
Satd. hydrocarbons	0.2	0.4	0.4	2.8
Hydrogen sulfide	0.02	0.40	0.17	0.41
Sulfur dioxide	0.03	0.12	0.10	0.12
Methane	0.0	0.0	0.6	0.6
Ammonia	1.25	3.70	1.68	2.59
Hydrogen	0.2	0.4	0.2	0.6
Hydrocyanic acid	1.26	1.75	2.52	2.37
Nitrogen	77.72	72.63	71.73	71.21

Olsen, *et al.* used an 1104 cu. ft. room for burning tests on wood and gasoline. These materials were burned in air and the gases produced were analyzed at various sampling levels with the results shown in Table 3.

Some more recent work has been performed by Gross *et al.* [15] on the smoke and gases produced by burning 141 different aircraft interior materials. These materials included a large variety of synthetics such as polyvinyl chlorides, polymethylmethacrylate, polyvinyl acetate, and natural products (wool, cotton) likely to be found in any structure which might be involved in a fire. A 3 x 3 in. sample of each material was thermally irradiated in an 18 cu. ft. chamber such that both smoldering and flaming conditions were observed. Gas analysis of the atmospheres resulting from the tests were made with commercial colorimetric detector tubes. These tubes were used to determine CO, HCN, HCl, HF, SO_2, $NO+NO_2$, NH_3, Cl_2, and $COCl_2$. The results of these experiments are described in the sections on individual gases.

Gaskill [16] has recently conducted some fire tests on urethanes and polycarbonates. The test materials were decomposed in an 18 cu. ft. chamber which was equipped with devices for varying the ventilation rate and for producing either flaming or smoldering thermal decomposition. Tables 4 and 5 give the results of the analyses of the atmospheres produced by the decomposition of the test materials.

The ASTM E84 Flame Spread Tunnel Furnace has been used to conduct combustion tests on various building materials and furnishings [17]. This furnace is 25 ft. long, 12 ft. high and 17 in. wide and has provisions for varying the air flow through the tunnel. Table 6 shows the results of the analysis of the combustion products of 15 tests performed under varying conditions. Where there is a blank in a particular column in Table 6 no determination was performed.

		Concentration in Mole Percent					
Material	Height Above Floor in Meters	CO_2	CO	O_2	Unsat'd Hydrocarbons	Sat'd Hydrocarbons	C_2H_5COOH
Wood	0.3	5.7	2.7	9.0	1.4	0.4	0.24
Excelsior	0.9	6.0	3.4	9.6	0.4	0.4	0.55
Wood	1.5	6.2	6.2	9.8	0.4	0.3	0.15
Excelsior	1.5	7.6	1.9	9.1	0.1	0.1	1.01
Gasoline	0.3	3.0	0.6	18.6	0.0	0.0	—
Gasoline	0.9	3.2	0.0	16.0	0.0	0.2	—
Gasoline	1.5	3.8	0.0	16.0	0.2	0.0	—
Gasoline	0.3	0.8	1.0	16.0	0.2	0.3	—
Gasoline	0.9	0.9	1.0	17.1	0.0	0.1	—
Gasoline	1.5	0.7	2.0	16.1	0.0	0.1	—

Table 3. Analyses by Olsen of combustion products of wood and gasoline [14].

		Urethane elastomers				Polycarbonate		
		Polyether		Polyester		Self-extinquishing		Self-extinguishing
Ventilation	Exposure time (min)	CO (ppm)	HCN (ppm)	CO (ppm)	HCN (ppm)	CO (ppm)	HCl (ppm)	CO (ppm)
No ventilation	2	—	—	450	20	∿750	∿22	—
	5	300	15	900	45	—	—	400
	10	1000	25	1500	75	—	—	1500
3 changes/hr	2	—	—	180	10	500	∿ 6	—
	5	500	15	600	25	—	—	∿750
	10	500	25	1000	35	1300	20	1500
6 changes/hr	2	—	—	200	10	∿800	3-24	—
	5	200	10	800	25	—	—	500
	10	300	20	1000	40	1000	24	1500
12 changes/hr	2	—	—	150	10	—	—	—
	5	250	25	350	15	500	20	—
	10	150	10	450	15	—	—	—
20 changes/hr	2	—	—	400	10	∿300	∿16	—
	5	200	5	500	18	—	—	150
	10	100	5	—	—	—	—	250

Table 4. Products from flaming polycarbonates and urethanes according to Gaskill [16].

				Nonflaming				Flaming			
				$\%O_2$	Max ppm of:			$\%O_2$	Max ppm of:		
Foam type	Density (lb/ft^3)	Blowing agent	Ventilation (changes/hr)	(min)	CO	HCN	HCl	(min)	CO	HCN	HCl
PAPI-ether (rigid, fire-retardant)	2	CO_2	0	—	—	—	—	20.0	275	7	—
			3	—	—	—	—	—	250	—	—
			6	—	—	—	—	20.2	250	10	—
			12	—	—	—	—	20.0	150	4	—
			20	—	—	—	—	20.7	50	2	—
PAPI-ether (rigid, fire-retardant)	2	Fluorocarbon	0	20.9	—	—	—	19.5	700	32	120
			3	20.4	—	—	—	19.1	500	20	90
			6	20.9	—	—	—	19.8	400	16	110
			12	20.9	—	—	—	19.5	300	18	110
			20	—	—	—	—	20.0	250	15	80
PAPI-ester (rigid, high-temperature)	4	CO_2	0	20.9	—	30	—	19.0	2000	100	—
			3	20.9	—	20	—	20.0	1000	200	—
			6	20.9	—	—	—	19.7	1300	60	—
			12	20.9	—	5	—	20.0	700	50	—
			20	20.9	—	4	—	20.8	1200	15	—
TDI-ester (fire-retardant)	25	CO_2	0	20.9	70	—	—	19.2	800	25	—
			3	—	—	—	—	19.0	—	75	—
			6	—	—	—	—	20.1	—	60	—
			12	—	—	—	—	20.0	500	75	—
			20	—	—	—	—	20.2	500	50	—
TDI-ether (non-fire-retardant)	13	CO_2	0	—	—	—	—	16.0	400	10	—
			3	—	—	—	—	17.0	250	—	—
			6	—	—	—	—	16.2	400	7	—
			12	—	—	—	—	18.0	220	5	—
			20	—	—	—	—	18.8	170	—	—
TDI-ester (fire-retardant)	2.5	CO_2	0	—	—	—	—	20.0	125	—	20
			6	—	—	—	—	20.5	90	—	25
			12	—	—	—	—	20.3	—	—	—
TDI-ether (fire-retardant)	1.8	CO_2	0	20.8	—	—	—	20.4	580	—	—
			3	—	—	—	—	20.0	550	—	—
			6	20.8	—	—	—	20.0	500	—	—
			12	20.8	—	—	—	20.0	490	—	—
			20	20.8	—	—	—	—	—	—	—
MDI-sucrose (rigid, fire-retardant)	2	Fluorocarbon	0	—	—	—	—	20.2	950	100	—

Table 5. Products from flaming and nonflaming urethane foams according to Gaskill [16].

Concentration in Parts Per Million

Material	CO	CO_2	O_2	HCN	H_2S	Acetic Acid	SO_2	NO_2	$COCl_2$	Cl	Br	NH_3	HCl	ClO_2
Acrylic Carpet 4/3	1,100	33,300	150,000	100			0	1		0	0		0	16
Wool Carpet 4/3	19,000	180,000	50,000	10,250			0	0		0	0		0	16
Wool 4/17	30,000	150,000	100,000	7,500	4		20	10				Trace	Trace	Trace
Red Oak 4/17	13,600	93,000	100,000	35	0		50	10				0	0	4
D-Fir 5/2	9,400	56,000	110,000	30	0		25	Trace	4	0	0	0	0	0.2
Red Oak 5/2	11,000	100,000	100,000	55	10		50	Trace	0.5	0	0	0	0	0
D-Fir 5/29 (A)		9,000		1	0	10	5	0	0	0	0	0		
D-Fir 5/28				0.5	0	10	4.0	Trace	0					
D-Fir 6/5 (A)	1,850	20,000		5	0	0	1.5	0	0	0	0	0	0	
D-Fir 6/6		12,000		2	0	10	6	0	0	0	0	0	0	
PVC 6/16	1,500												100	
Polyester 6/17 (A)	1,025			18	0	0	0	0	0	0	0	0	0	Trace
Acrilan 6/18 (A)	1,300	15,000		65	0	0	0	0.3	0	0	5	0	2	0
Wool 6/19	1,100			80	0	0	10	0.2	0	0	0	0	0	0
Tile 6/20 (A)	900	10,000		10	0	50	15	0	0	0	0	0	0	0

Table 6. Analysis of combustion products from materials burned in the ASTM E-84 Tunnel Furnace [17].

The Forest Products Laboratory [18] performed several fire tests in an 8' x 12' x 8' room equipped with draft ports for varying the ventilation. 375 pounds of mock-up furnishings, chairs, tables, *etc.* were ignited for each test. In addition to other variables, various gas concentrations were measured at different stages of the fires. Results of one such test are shown in Table 7.

Hafer and Yuill [19,20] conducted a series of burning tests on bedding and upholstery materials. These tests consisted of igniting the test material with a small source in a 12' x 14' x 8' room with two doors and two windows and monitoring, among other variables, O_2, CO, and CO_2 in all tests. In five tests, other noxious gases were determined as shown in Table 8.

Gas concentrations have been measured during several full scale fire tests of dwellings. As far as is known, the first full scale tests where gases were monitored were conducted in Britain in 1949 [21]. Two houses lined with fiber insulating board were allowed to burn after igniting wood shavings in the living room. One house had an additional lining of 3/8" plaster board over the fiber board. Measurements were made of CO, O_2, CO_2, and H_2 as a function of time in both houses in a bedroom with a closed and an open door. Figures 1 and 2 show the results of these experiments.

Oxygen and carbon monoxide concentrations were measured in six two-story dwelling burns in Canada [22]. Fires were started on the first floor and gases were monitored in open and closed bedrooms on the second story. Three buildings had combustible wall linings and three had non-combustible wall linings. Results of the tests are given in the sections on oxygen and carbon monoxide.

In fire tests of interior wall assemblies at Southwest Research Institute, CO, CO_2, and O_2 were monitored at various heights and locations in two test structures [23]. The test structures were wood frame buildings with three rooms (a bed-

		Concentration in Mole Percent					
Sample No.	Time	Carbon dioxide	Oxygen	Carbon monoxide	Unsaturated hydrocarbons	Saturated hydrocarbons (calculated as methane)	Hydrogen
	Min.	Percent	Percent	Percent	Percent	Percent	Percent
1	0.1	0	20.8	0	—	—	—
2	3.0	1.5	20.0	0	—	—	—
3	6.0	2.6	17.8	0	—	—	—
4	6.8	13.6	3.3	2.6	—	—	—
5	7.4	18.4	.8	5.8	—	—	—
6	7.9	17.2	2.1	4.5	—	—	—
7	8.6	16.9	.9	5.7	1.0	1.3	6.6
8	9.2	18.1	1.0	10.0	—	—	—
9	9.7	10.4	2.3	13.8	1.6	1.2	6.0
10	10.1	15.2	1.7	12.8	1.8	1.5	5.6
11	10.5	11.7	6.9	3.4	—	—	—
12	11.2	2.4	17.8	.7	—	—	—

Table 7. Composition of gas samples as a function of time, Forest Products Laboratories [18].

	Concentration in Parts Per Millon				
	Test 1	Test 4	Test 7	Test 8	Test 21
Hydrogen Cyanide (HCN)	5	5	2	2	0.05
Hydrogen Chloride (HCl)	1	0	2	500	0
Hydrogen Sulphide (H_2S)	50	10	8	25	10
Sulphur Dioxide (SO_2)	100	70	50	90	30
Oxides of Nitrogen (NO_2)	0.5	0.4	3	—	0
Phosgene ($COCl_2$)	1	1	1	0.5	0
Bromine (Br_2)	0	5	41	5	0
Chlorine (Cl_2)	0	0.5	6	1	0
Chlorine Dioxide (ClO_2)	0	0	10	16	0
Ammonia (NH_3)	50	0	0	0	30
Acetic Acid	0	200	0	0	0

Test 1: Innerspring mattress with rayon ticking, cotton muslin sheets.

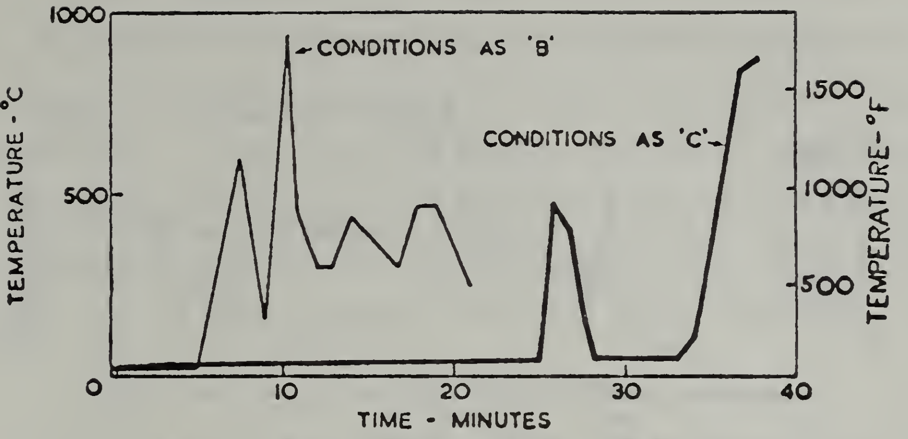
Test 4: Innerspring mattress with rayon ticking, cotton percale sheets.

Test 7: Polyurethane mattress, cotton muslin sheets.

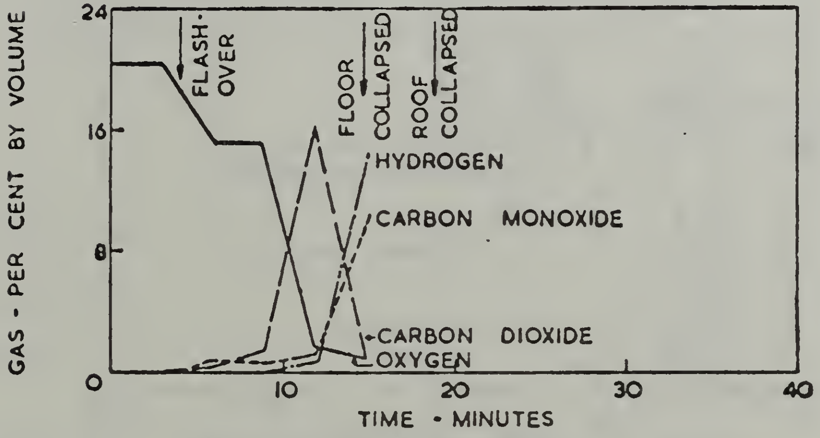
Test 8: Latex rubber mattress, cotton muslin sheets.

Test 21: Innerspring mattress with rayon ticking, feather pillow, cotton muslin sheets.

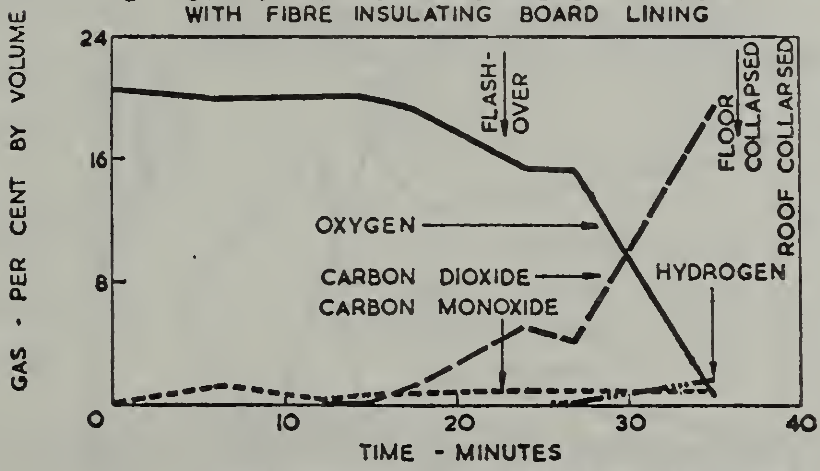
Table 8. Analysis of gases from bedding and upholstery fire tests [19,20].



A - AIR TEMPERATURE AT CEILING LEVEL

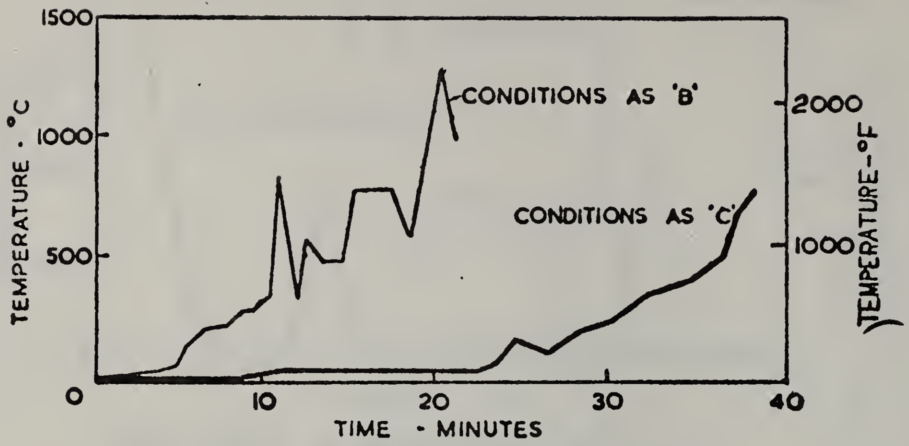


B - COMPOSITION OF ATMOSPHERE IN ROOM WITH FIBRE INSULATING BOARD LINING

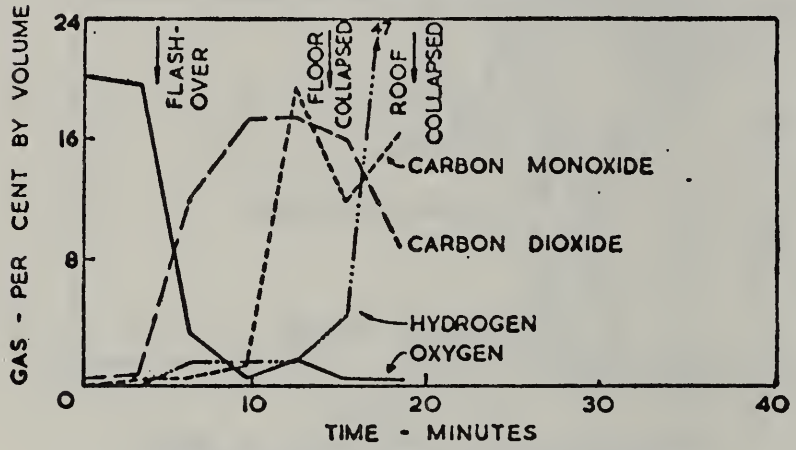


C - COMPOSITION OF ATMOSPHERE IN ROOM WITH FIBRE INSULATING BOARD LINING COVERED WITH PLASTERBOARD

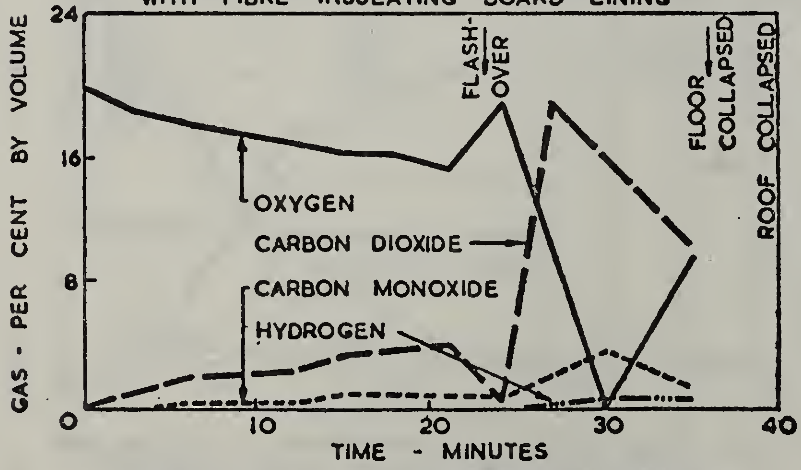
Figure 1. Atmospheric record in bedrooms with closed doors in full scale fire tests performed in Britain [21].



A - AIR TEMPERATURE AT CEILING LEVEL



B - COMPOSITION OF ATMOSPHERE IN ROOM WITH FIBRE INSULATING BOARD LINING



C - COMPOSITION OF ATMOSPHERE IN ROOM WITH FIBRE INSULATING BOARD LINING COVERED WITH PLASTERBOARD

Figure 2. Atmospheric record in bedrooms with open doors in full scale fire tests performed in Britain [21].

room, living room, and dining room) containing furniture, beds, rugs, and draperies. One structure, test 1, had hard wood panelling only, the other, test 2, had wood panelling over gypsum wall board. The investigator selected gas concentrations and a temperature generally considered fatal for more than a few seconds exposure and measured the time after ignition required to attain these values. The limiting conditions

Table 9. Time of initial occurrence of some hazardous condition in fire test of interior wall assemblies [23].

	Height (Feet)	Times of Initial Occurrence Test 1 (min:sec.)	Test 2
T-300 °F			
Living room	5	5:50	6:22
	1	14:50	8:58
Dining room	5	6:42	8:04
	1	14:54	17:50
Bedroom	5	26:24	28:03
	3	28:36	27:32
CO-1 per cent			
Living room	5	13:20	7:20
	1	14:10	8:20
Dining room	5	14:20	8:30
	1	14:40	9:20
Bedroom	5	24:32	25:30
	3	25:30	26:00
CO_2-12 per cent			
Living room	5	14:30	9:30
	1	12:30	10:30
Dining room	5	11:40	11:00
	1	12:40	14:30
Bedroom	5	—*	26:40
	3	—	27:30
O_2-7 per cent			
Living room	5	15:00	10:08
	1	19:44	16:40
Dining room	5	15:00	15:45
	1	17:00	22:30
Bedroom	5	26:30	26:40
	3	27:30	27:15
Flashover			
Dining room		24:23	23:30
Bedroom door burned through		26:34	25:30

*Dash indicates that those levels or conditions were not reached.

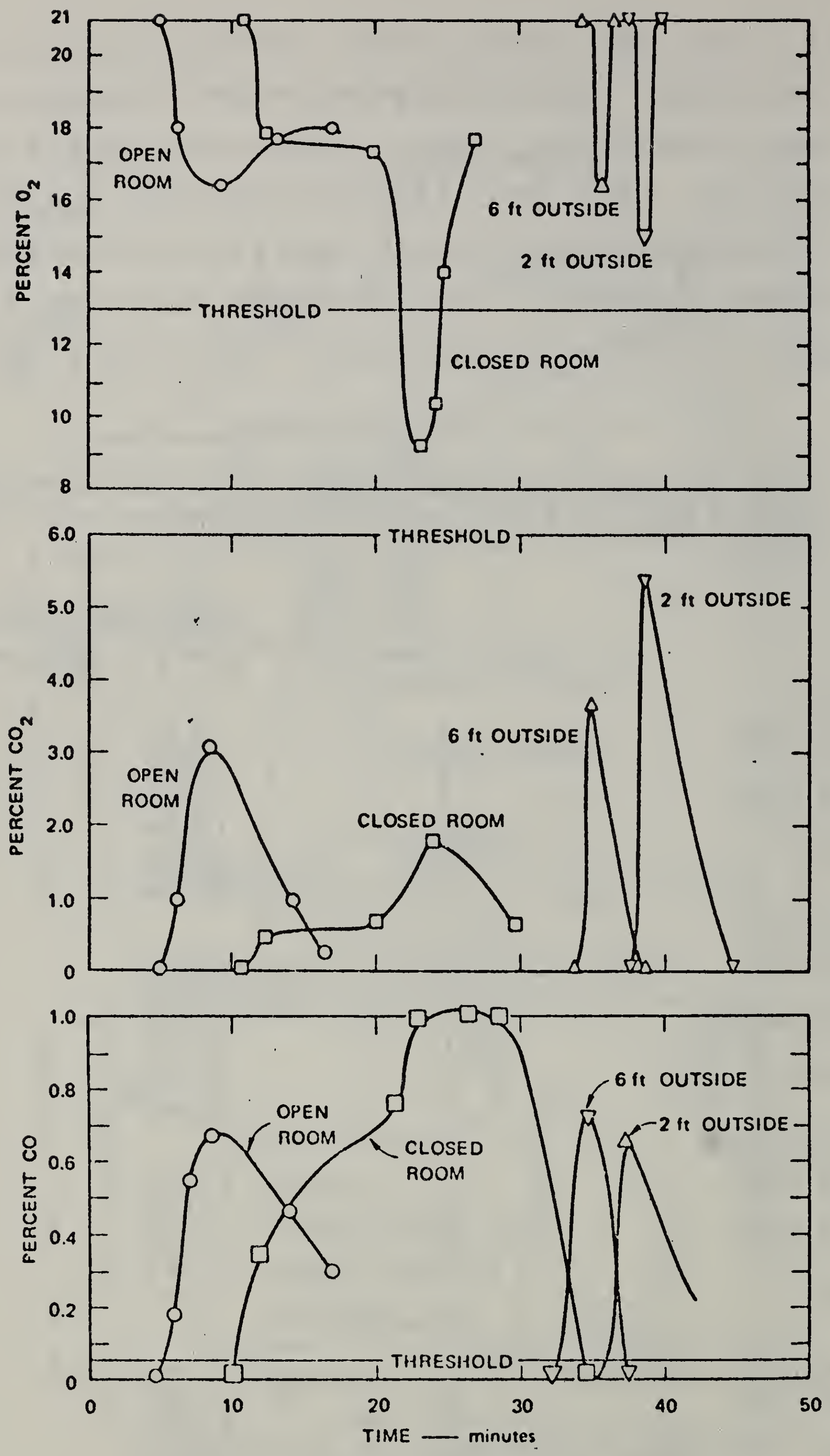


Figure 3. Gas concentrations measured during Stanford Research Institute Fire Test of November 30, 1969 [24].

were as follows: temperature 300 °F; CO - 1.0 percent; CO_2 - 12.0 percent; and O_2 - 7.0 percent. Table 9 shows the results of these experiments.

Stanford Research Institute has recently performed some well instrumented full scale burns on four army barracks and three horse barns [24]. Measurements were made of CO, CO_2, and O_2 at various locations inside and outside all barracks. Figure 3 shows the results of one of these tests. "Threshold" levels noted in Figure 3 indicate what the authors consider to be concentrations for O_2, CO_2, and CO, which can be survived for one hour. These concentrations are 6, 13 and 0.05 percent, respectively.

Few measurements of toxic gases have been made in actual fire situations, the only available measurements being those obtained on carbon monoxide in Project Monoxide [25] and reported on in Section 4A of this paper.

4. SPECIFIC TOXICANTS PRODUCED IN FIRES

A. Carbon Monoxide

Fires, almost without exception involve the rapid oxidation of organic materials. These materials are composed chiefly of carbon, hydrogen, and oxygen with usually lesser amounts of other elements. Combustion in the "ideal" sense results in production of the highest oxidized form of the elements present in the burning material. The real situation, however, is quite different and intermediate states of oxidation occur and, in some cases, compounds are formed in which an element other than oxygen is substituted. The most important substance, from the standpoint of toxicology, which represents an intermediate stage of oxidation, is carbon monoxide. Carbon monoxide is an almost universal product of combustion and in any situation in which heat, flame, and smoke are produced then carbon monoxide is sure to be produced.

More data is available concerning carbon monoxide than on any other toxic gas. This no doubt is due to the extent to which it exists in fire situations as well as in other processes involving combustion.

Carbon monoxide is a colorless, odorless gas which, when respired, acts as a chemical asphyxiant. It combines with the hemoglobin of the blood to form carboxyhemoglobin which will not combine with, and thus not transport oxygen to the body tissues. When there is inadequate oxygen in the lungs and blood, a condition known as hypoxia results, the effects of which are somewhat dependent upon the physical characteristics of the individual. In addition to the displacement of oxygen from hemoglobin, CO may also cause a decrease in oxygen delivery rate to the tissues by oxyhemoglobin [26] and will hinder removal of CO_2 from the blood stream by the lungs [27].

The principle mode of entry of CO into the body is through the respiratory system and no observations of adsorption of CO through the skin of humans have been reported. Rabbits exposed to a gas containing 7 percent CO over a large area of exposed skin died after 10 - 31 hours [28]. A similar but unlikely situation could occur in the case of a human protected by a self-contained breathing apparatus but with large areas of skin exposed.

The response of an average individual to specific levels of carbon monoxide in air will vary somewhat depending on two principal factors. These are the length of exposure and the rate of breathing. The rate of breathing depends on the activity in which the individual is engaged. Obviously, one engaged in strenuous physical activity will breathe faster than one at rest and a consequence will be a greater uptake of carbon monoxide. Other factors more specifically related to the individual such as age, health, smoking habits, and previous exposure to carbon monoxide all have some bearing on the total effect of any specific concentration of carbon monoxide. Thus, while it is difficult to define exactly the physiological response to a concentration of carbon monoxide, it is possible to describe within limits the symptoms associated with certain levels. The 1970 threshold limit value (TLV) for CO adopted by the American Conference of Governmental Industrial Hygienists is 50 ppm [29]. This is the time weighted concentration which may be tolerated by nearly all humans for an 8 hour day and 40 hour week without adverse effect. Table 10, showing the effects of carbon monoxide at various levels, is based on a number of studies, some of which were derived from clinical data and some of which are based on less exact information [30-32].

Table 11 from the work of Schulte [30], summarizes in more detail the expected physiological effects of various carboxyhemoglobin levels (COHb).

Table 10. Physiological effect of carbon monoxide as a function of concentration.

Carbon Monoxide Concentration (ppm)	Maximum Exposure	Approx. COHb Level attained and symptoms
50	8 hours	10% no effect
200	2 hours	20% slight effect
1,000	1 hour	40% severe effect
10,000	1 minute	20% fatal

Table 11. Signs and symptoms at various concentrations of carboxyhemoglobin (COHb)

Percent COHb	Signs and Symptoms
0-10	No signs or symptoms
10-20	Tightness across forehead, possible slight headache, dilation of the cutaneous blood vessels
20-30	Headache and throbbing in the temples
30-40	Severe headache, weakness, dizziness, dimness of vision, nausea, vomiting and collapse
40-50	Same as above, greater possibility of collapse, Syncope and increased pulse and respiratory rates
50-60	Syncope, increased respiratory and pulse rates, coma, intermittent convulsions, and Cheyne-Stokes respiration
60-70	Coma, intermittent convulsions, depressed heart action and respiratory rate, and possible death
70-80	Weak pulse, slow respiration leading to death within hours
80-90	Death in less than an hour
90+	Death within a few minutes

A more extensive description of the physiological effects of carbon monoxide has been graphically presented by Forbes *et al.* [31]. Figure 4, from the work of Forbes *et al.*, relates time, activity, and concentration to carboxyhemoglobin level. The data are based on actual observation of seven healthy male laboratory workers, and marked individual differences were noted in the rate of CO uptake. The authors state that certain individuals may vary by as much as ±20 percent from the data shown in the chart. These observations show some conflict with statements of others but in general the information probably represents reliable guidelines for the actual effects of exposure on a working subject, rather than the more academic problem of the medical researcher. Differences in observations probably reflect experimental variabilities, variations in subjects, and in some cases personal interpretation of the data. Schulte [30] for example in a study of 49 subjects observes that 100 ppm of carbon monoxide results in a carboxyhemoglobin level of 20.4 percent. The data of Forbes *et al.* [31] would indicate a maximum of 14 percent carboxyhemoglobin at this concentration of carbon monoxide.

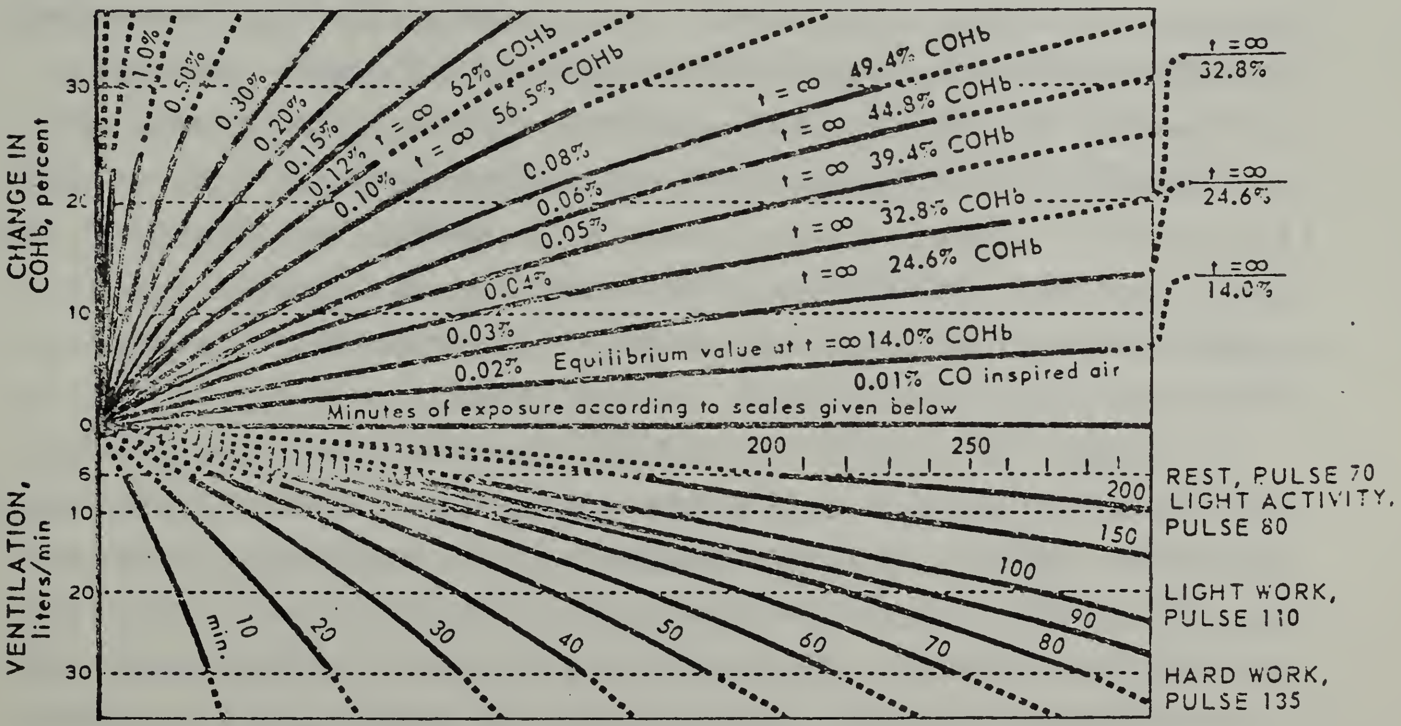


Figure 4. Carboxyhemoglobin level in the blood as a function of carbon monoxide concentration, ventilation rate and activity, from Forbes, *et al.* [31].

A basic difficulty in the use of the estimated carbon monoxide concentration to predict physiological effects is that the individual responds adversely to the carboxyhemoglogin level in his blood and not to the external concentration of carbon monoxide. Carboxyhemoglobin is a very stable compound and is only slowly eliminated by normal respiratory processes. Consequently, an individual previously exposed to high levels of carbon monoxide may a short time later react adversely to lesser and presumably safer concentrations. Henderson and Haggard [32] state that "during the first hour after moderate degrees of gassing, with no treatment other than fresh air, little more than half the carbon monoxide is eliminated."

There is no conclusive evidence that continuous exposure to low concentrations of carbon monoxide produces any adverse physiological effect. In fact, Monaco [33], presents evidence of the acquisition of immunity of sorts after continued exposure to higher than normal carbon monoxide concentrations. There is some controversy as to whether "chronic poisoning" is a result of continued exposure to low concentrations or to intermittent exposures to high concentrations. An evaluation of this aspect of the problem is beyond the scope of this report, or the abilities of the authors, and indeed appears beyond the abilities of the Federal Government to resolve (F. R. Vol. 36, No. 84 Part II, pg. 8186).

A number of studies have been reported concerning minor impairment of certain motor and visual functions of individuals exposed to carbon monoxide concentrations producing carboxyhemoglobin levels in the range from 0 to 10 percent [30,34]. This range is not considered toxicologically significant and is a condition commonly associated with heavy smokers and individuals who are, on a daily basis, exposed to moderate concentrations of carbon monoxide. The nature of the tests and the results indicate that the degree of impairment of any of the functions tested is insignificant in any practical sense.

Carboxyhemoglobin levels of working firemen have been measured in several studies. Tests performed under Project Monoxide [25] showed that there is a definite increase in the carboxyhemoglobin level of firemen when fighting fires. For example, in the course of fighting 31 fires lasting more than five minutes, about two-thirds of the carboxyhemoglobin measurements on a group of firemen were in excess of 10 percent In one case, a level of 44 percent was attained. When not fighting fires, this same group of firemen displayed carboxyhemoglobin levels which were in the normal 0 - 4 percent range. The authors noted that there was a wide range in carboxyhemoglobin levels evident in different individuals at the same fire, and that there was no way of predicting what carboxyhemoglobin level would be reached at what fire. It was found that both filter-type and self-contained breathing apparatus significantly protected fire fighters from high carboxyhemoglobin levels.

A 1967 study involving 45 firemen at 15 fires showed carboxyhemoglobin levels ranging from 2 to 28 percent [35]. Thirty-three measurements gave carboxyhemoglobin levels of 5 percent or higher.

The incomplete or inefficient combustion of any carbonaceous material will result in increased production of carbon monoxide when compared with efficient and complete combustion. Depletion of oxygen in a fire will result in the production of increasing amounts of carbon monoxide as the fire progresses. The concentration of carbon monoxide at any time will likely depend largely on the nature of the fuel and the extent of ventilation. In any case where there is fire, there is very likely to be carbon monoxide. Even in well ventilated fires or in laboratory situations involving adequate air, carbon monoxide is produced in significant concentrations. For example, even with excess oxygen, burning wool produced from 0.5 to 5.0 percent CO (see Table 2). A large number of studies, including real fires, full scale fire tests, and small scale laboratory combustion experiments all confirm that carbon monoxide is produced in some quantity during combustion.

Early laboratory investigations by Olsen *et al.* (see page 6 and Table 2) on the combustion of various common materials in an excess of air indicated that CO could reach concentrations in the 3 - 7 percent range. Pyrolysis of the same materials in a nitrogen atmosphere yielded much higher concentrations of CO, up to 42 percent. Wood and gasoline burned in an 1104 cu. ft. chamber gave the results shown in Table 3.

Table 7 shows the results of one of a series of tests conducted by the Forest Products Laboratory in a room sized chamber (see page 12). As can be seen, the CO concentration remained at lethal levels for at least 8 minutes. One of the conclusions of this series of tests was that CO was produced in toxic concentrations although its concentration varied considerably depending on air supply and the path of the air through the room. The statement is made that "the intense heat would have made the room unbearable by a human occupant before the CO. An upstairs room however, into which fumes from the fire might have been rising, would probably have been made unbearable first by smoke and toxic gases."

Recent work (see page 7) on flaming and smoldering thermal decomposition of 141 aircraft interior materials shows that CO is produced in almost every case. Concentrations of CO as high as 2200 ppm were obtained with 3 x 3 in samples in an 18 cu. ft. test chamber.

Gaskill's work on urethanes and polycarbonates (see page 10 and Tables 4 and 5) shows CO concentrations can reach as high as 0.2 percent. This work also shows CO concentrations to be dependent, in part, on ventilation and generally decrease with increasing ventilation.

Ignition of bedding and upholstery in a room sized chamber (see page 12) produced CO concentrations of at least 0.15 percent except in one test. Concentrations of CO in the 0.5 - 0.6 percent range were reached in 6 tests.

The various building materials and furnishings shown in Table 6 (see also page 10) produced CO in concentrations from 0.09 to 3.0 percent when burned in the ASTM E84 Flame Spread Tunnel Furnace. In another study, untreated Douglas fir was burned in this same tunnel furnace to determine the effects of varying ventilation on combustion products [36]. Carbon monoxide was found to increase from 0.05 percent at 400 feet-per-minute airflow to 1.0 percent at 100 feet-per-minute.

Table 12 is a summary of a large number of tests on a number of materials. The concentrations shown are the measured values of carbon monoxide at some time during the burning. These concentrations do not necessarily represent a maximum but they indicate that at some point in the combustion, CO attained the values shown.

In several of the tests described above, an attempt was made to determine the effect of varying some condition on the concentrations of carbon monoxide that was produced [36,16,14]. These studies, while limited in number, lead to the conclusion that the following can be expected:

Condition	Effect
Increased Air Velocity	Decreased CO
Decreased Ventilation	Increased CO
Low Oxygen Concentration	Increased CO

Full scale tests of burning structures have already been mentioned (see page 14). In the British studies, two houses lined with fiber insulating board were allowed to burn after igniting wood shavings in the living room. One house had an additional lining of 3/8" plaster board over the fiberboard. Figures 1 and 2 show the results obtained when CO was monitored in both houses in two bedrooms, one with a closed and one with an open door. In the house having only the fiber insulating board, flashover occurred rapidly after which CO concentration increased to nearly 20 percent in the closed bedroom and about 10 percent in the open bedroom. In the house with both fiber and plasterboard, flashover was slower to occur. After flashover, CO concentration gradually increased to about 1 percent in the closed bedroom and 4 percent in the open bedroom. It was concluded that the plasterboard retarded the spread of fire "but did not increase substantially the fire resistance of the structure once the fire had become established."

Table 12. Carbon monoxide produced by thermal decomposition of various materials

Material	Observed CO conc. (%)
Acrylic Carpet	0.11
Wool Carpet	1.9
Red Oak	1.36, 1.1
Bedding	0.043 to 0.673
Chairs	0.105 to 0.405
Newspaper	5.8 to 6.8 in excess air 36.5 to 41.5 in nitrogen
Rubber Insulation	3.4 to 7.55 in excess air 8.1 to 17.6 in nitrogen
Silk	3.0 to 4.4 in excess air 11.6 to 20.0 in nitrogen
Douglas Fir	0.94, 0.185
Polyether	0.0 to 0.1
Polyester	0.0 to .15
Polycarbonate	0.0 to 0.13 (self-extinguishing) 0.0 to 0.15 (non-self-extinguishing)
Tile	0.09
PVC	0.15
141 Different aircraft interior materials	>0.0005 to 0.22

In a series of six dwelling burns in Canada (see page 12), test fires were started on the first floor and CO was monitored in two second story bedrooms in each dwelling, one with an open door and one with a closed door. In three of the buildings, which had non-combustible wall linings, an average of 18.6 min. in the closed bedroom and 12.0 min. in the open bedroom elapsed before CO reached a level of 1.28 percent, which level was considered the limit for survival. In the three buildings with combustible linings an average of only 5.6 min in the closed bedroom and 2.9 min in the open bedroom elapsed before 1.28 percent CO was attained.

The Los Angeles Fire Department in 1960 conducted 13 tests of burning materials, for example, sofas, chairs, containers filled with rubbish, in one and two story dwellings [37]. Concentrations of CO and temperatures were monitored in various rooms. The conclusions were that CO concentrations became hazardous before high temperatures in slow burning, smoldering fires, but the opposite ocurred in the fast burning fires.

In well instrumented full scale fire tests of interior wall assemblies at Southwest Research Institute, (see page 12) the time interval between ignition and attainment of a 1 percent CO concentration was measured at various heights and locations in two test structures. Table 9 shows that the above time interval ranged from about 7 to 26 minutes depending on sampling location. It was noted that at one location, a CO concentration of 3.7 percent was reached after about 16 minutes.

In the tests performed by Stanford Research Institute (see page 17), CO concentrations were measured in and outside all barracks and in the center of the street between two horse barns burning simultaneously 40 feet apart. Time versus CO concentration curves were prepared. Figure 3 shows the results from one barracks burn. In some cases, the curves show a sudden appearance or disappearance of CO, usually in the later stages of the fire. It was noted that "while these temporary gusts of noxious gases exceeded thresholds of human tolerance, they do not necessarily pose a serious life hazard because they are so transient". Basement concentration of CO in one barracks burn reached a maximum of 1.5 percent. It was observed that CO consistently attained hazardous levels before O_2 or CO_2 and concluded that CO was the major life hazard due to noxious gases in these tests. The concentration of CO measured in the center of the street between the two burning horse barns never exceeded 0.04 mole percent.

During Project Monoxide [25], six fires were set in common combustible materials in a Quonset hut. These produced CO concentrations which ranged from 200 to 3200 ppm. In the course of Project Monoxide, measurements of carbon monoxide at six actual fires gave CO concentrations from 450 to 6850 ppm. However, it was stated that sampling was a "hit or miss venture".

The foregoing shows that CO can be produced in hazardous concentrations in most fire situations. Due to movement of gas masses during a fire, for example, if ventilation is effected, if a floor suddenly falls, or a door is opened, the nature of the atmosphere surrounding one involved in a fire can change quickly from harmless to lethal or from lethal to harmless. Emphasis must be placed upon the fact that there can be no absolute threshold CO concentrations at which untoward physiological or psychological effects occur or at which death occurs, nor any specific time of exposure. The effect of a given CO level varies with such factors as the individual's tolerance to a particular carboxyhemoglobin level, the individual's general physical condition, age, inhalation rate, physical activity at time of exposure, duration of exposure, and other gases present in the respired air.

Gases produced by fires obviously exist at highest concentrations in enclosed or partially enclosed structures. The 1969 NFPA estimates of fires and fire losses show that, excluding grass, brush, and rubbish fires, the greatest number of fires and the largest monetary losses occur in residential occupancies, both fires and losses being far the highest in one and two family dwellings and apartments [38]. The fire situation where firemen would encounter toxic gases most frequently then, is that in the residential occupancy.

Dangerous CO levels should be suspected with fires or smoldering materials in poorly ventilated, tightly enclosed spaces, though the overall fire situation might not seem hazardous. During or after extinguishment of a fire in a poorly ventilated area, CO concentrations might conceivably rise due to oxygen consumption by smoldering materials. Carbon monoxide concentrations at the 0.1 percent level are perceptible to the individual because headache or dizziness are usually present before incapacitation occurs and hence there may be sufficient warning that the atmosphere is hazardous. There is no sensory warning of CO concentrations of about 1 percent or higher before escape is too late, thus care must be taken to assess the CO hazard of a given fire situation before entering without respiratory protection. Since CO is eliminated slowly from the blood stream, two or three exposures to relatively low CO concentrations can have cumulative effects, as has been pointed out by Thomas [39]. Obviously firemen exposed to CO should not enter into a fire situation until several hours after exposure, or until a carboxyhemoglobin test proves satisfactory.

B. Oxygen Deficiency

Respired oxygen is absorbed by the blood in the lungs, then transported to other parts of the body for use in metabolic processes. Lower than normal oxygen levels in the respired atmosphere cause disruption or cessation of these processes and subsequent deleterious physiological and psychological effects. Severe hypoxia, defined as inadequate oxygen in the lungs and blood, may cause permanent organic damage to the nervous tissue. Table 13 presents the physiological effects expected at reduced atmospheric oxygen levels. These data cannot be considered absolute, and are based on an assessment of various data in the literature surveyed.

Table 13. Physiological effects of reduced oxygen levels

Percent Oxygen in Atmosphere	Symptoms
21	none
17	some impairment of muscular coordination, increase in respiratory rate
12	dizziness, headache, rapid fatigue
9	unconsciousness
6	death within a few minutes due to respiratory failure and concurrent heart failure

A combustible material when heated to a sufficient temperature in air will react with oxygen, causing the oxygen content of the immediate atmosphere to be reduced and forming oxides which are predominately carbon dioxide and carbon monoxide. The decrease in oxygen concentration is dependent upon the material combusted and the physical conditions surrounding the combustion. A few examples of laboratory experiments on the burning of various materials will serve to illustrate the oxygen decrease in an atmosphere due to combustion.

The work of Olsen *et al.* (see page 7 and Table 3) on burning wood and excelsior in air in a 1104 cu ft. room showed oxygen was reduced to about 9 percent. Burning gasoline under the same conditions reduced the oxygen to the 16-18 percent level.

In one of the burning tests conducted by the Forest Products Laboratory (see page 12 and Table 7), the oxygen concentration reached the amazingly low concentration of 0.8 percent and remained below 7 percent for about 4 min. In two other tests, oxygen reached a minimum of about 12 percent.

In some more recent fire tests on bedding and upholstery materials in a 12' x 14' x 8' room (see page 14), Hafer and Yuill found that the minimum oxygen concentration only once fell below the 14 percent level, which level was considered tolerable for two hours exposure. Most minimum oxygen concentrations were in the 17-18 percent range. The amount of material burned in these tests was much less than that in Forest Products Laboratories work (above). Also the ignition source was small, for example, a cigarette, compared to the wood crib used by Forest Products Laboratories, so that less oxygen consumption might be expected.

In the full scale British fire tests described on page 12, Figures 1 and 2 show that oxygen decreased to the 1-2 percent level in all four cases 5-10 minutes after flashover occurred. Generally, in all four tests there was a slow decrease in oxygen to the 16 percent level in the period between ignition and flashover.

Oxygen concentrations were determined during the full scale burns performed in Canada in 1958 (see page 12). The authors considered a 10 percent oxygen concentration as being incompatible with life, and gave average times required to reach this level. In the closed bedrooms, 10 percent oxygen was reached between 13 and 20 minutes after ignition, in the open bedrooms, between 2.5 and 4 minutes after ignition.

The Southwest Research Institute fire tests of interior wall assemblies described on page 12 included oxygen analyses. The author assumed 7 percent oxygen was fatal for more than a few seconds exposure and determined the time of initial occurrence of this level in both tests. These times (see Table 9) ranged from about 10 to 22 min., depending upon location.

Oxygen concentrations as a function of time were measured during each of the four barracks burns in the Stanford Research Institute burns (page 17 and Figure 3). In one open room oxygen decreased to about 3 percent and a measurement 5 minutes later also showed an oxygen concentration of about 3 percent. Oxygen concentration dips of 1-2 minutes duration to about the 10 percent level were observed in two other cases. All other oxygen measurements indicated the decrease in oxygen level by itself would probably not have posed any serious threat to life.

Oxygen depletion is probably not as great a threat to life in fires as is CO. The tests discussed above show, however, that oxygen concentrations can easily decrease to lethal levels in fires. Since oxygen is odorless and colorless, the oxygen level of an atmosphere is not perceptible *per se* by sensory means except that it should be obvious that where smoke or flame are present, oxygen concentrations would probably be lower than normal. An individual exposed to an oxygen deficient atmosphere may show signs of hypoxia but be unaware of his condition due to psychological factors. Hypoxia leads to a loss of insight and irrational behavior. McFarland [40] in describing the reactions of a subject in an experiment where the O_2 concentrations were lowered from normal to about the 7 percent level in one hour states that, "The insidious loss of insight as to the nature and extent of the subject's deterioration was one of the most significant aspects of the experiment." A fireman during the course of an average fire would probably change locations sufficiently often and would not be exposed for a long enough time to be affected by moderate oxygen deficiencies. Concerning oxygen levels, the principal danger to the firemen, with no mask or with a filter mask, would be entrance into an atmosphere containing less than about 6 percent oxygen, which would quickly cause unconsciousness without much prior warning other than obvious evidence of the occurrence of significant combustion.

A certain degree of oxygen deficiency would be expected in any fire situation, since most common non-oxide materials will combine with oxygen if heated. Low oxygen levels should be suspected in conjunction with high CO and CO_2 levels in poorly ventilated fires.

C. Carbon Dioxide

Carbon dioxide is an end product of the complete combustion of carbonaceous materials, thus it must be considered in any fire situation. Normally, air contains about 300 ppm CO_2.

When an atmosphere containing higher than normal CO_2 levels is respired, the CO_2 concentration of the blood increases causing stimulation of the respiratory center of the brain. The TLV (1970) for CO_2 is 0.5 percent [29], which may cause a slight increase in lung ventilation [41]. At a CO_2 level of 5-7 percent in air, humans experience a marked increase in lung ventilation, headache, dizziness, sweating, and mental excitement [17,41]. Concentrations of 10-12 percent CO_2 are fatal within a few minutes due to paralysis of the respiratory center of the brain [23,41]. An obvious corollary to the hyper-ventilation effect of CO_2 is that the intake of other toxic gases, if present, would be increased.

Olsen's results on burning wood in air in a 1104 cu. ft. chamber (see page 7 and Table 3) show CO_2 was present at the 6-8 percent level. Table 3 shows that burning gasoline yielded 0.7 to 3.8 percent CO_2. Table 7 shows the results of a fire test conducted by the Forest Products Laboratory (see Page 12). Here CO_2 remained above 10 percent for 7 minutes and reached a maximum of about 18 percent. In the bedding and upholstery tests (see page 12), CO_2 reached a maximum of 6.75 percent in one mattress test. Three other tests gave maximum CO_2 concentrations of 5.0 to 5.5

percent while in the remainder of the tests, CO_2 was below 5 percent. Table 6, giving results for various materials combusted in the ASTM E-84 Tunnel Furnace, shows CO_2 to be produced in concentrations ranging from 0.9 to 18 percent.

Carbon dioxide has been measured during several full scale burns. Figures 1 and 2 show CO_2 concentrations as a function of time in the British fire tests described on page 14. The maximum CO_2 concentration reached was about 20 percent. In the full scale tests of interior wall finish assemblies (see page 12), the time required, after ignition, to reach 12 percent CO_2 was measured. Table 9 shows that in both living rooms and dining rooms, this ranged from about 9 to 15 minutes. In the bedrooms (with doors shut) a 12 percent CO_2 concentration ocurred in about 27 minutes in one test (after the door burned through) and not at all in the second test, even though the door burned through. During the Stanford Research Institute burns (see page 17 and Figure 3), CO_2 was measured as a function of time. Generally, CO_2 was found to be highest in the basement, reaching about 14 percent for a few minutes in two of the three barracks burns where basement CO_2 concentrations were measured. Maximum CO_2 concentrations in other locations inside and outside the barracks ranged from about 2 to 10 percent. The preceeding data indicate CO_2 in fires can easily reach concentrations which are hazardous.

Higher than normal CO_2 concentrations may be perceptible by their acidic taste. Symptoms such as a marked increase in ventilation rate, dizziness, and headache would warn of the presence of CO_2 at hazardous levels, if the concentration were lower than that which would cause immediate unconsciousness.

Since it is heavier than air, CO_2 might accumulate at the lower levels in a fire involving an enclosed structure. Note that basement CO_2 concentrations were highest in the Stanford Research Institute tests described above. Higher CO_2 concentrations would be associated more with freely burning fires than with smoldering fires. The possibility of abnormally high CO_2 levels should be taken into account in cases where a CO_2 extinguisher or extinguishing system has or is being used. Activation of a CO_2 extinguishing system in an enclosed space might yield a hazardous CO_2 concentration, which could be present for some time after the fire is extinguished. An unpublished report of the Division of Fire Protection of Montgomery Country, Maryland on a non-fire situation in which a fireman and a civilian died emphasizes the hazards of a high CO_2 concentration [42]. The fatalities occurred when the subjects entered a manhole where the atmosphere, analyzed soon after the accident contained 10 to 18 percent O_2 and 13 percent CO_2. The report quoted a toxicologist, who had been consulted in the case as saying that the CO_2 concentration "would cause paralysis of the respiratory center in the brain with two or three breaths even if the oxygen were normal."

D. Hydrogen Chloride

Hydrogen chloride is a colorless gas which, when released to the atmosphere in high concentrations, may form a white mist due to condensation of atmospheric moisture. It is easily detected by its pungent odor and intense irritating action on the eyes and respiratory tract. It may be classified as a primary irritant, that is, it exerts no systemic toxic effect [32]. The principal deleterious effect of a primary irritant gas such as HCl is to cause edema at some level in the respiratory tract. Edema causes obstruction of the respiratory tract, either from blockage by cellular fluids at lower levels or swelling at any level. Hydrogen chloride affects mainly the upper respiratory tract. Obstruction of the respiratory tract obviously decreases the efficiency of respiration and can result in suffocation.

According to Henderson and Haggard [32], 35 ppm HCl in air will cause throat irritation on short exposure, 50 to 100 ppm is the maximum concentration tolerable for one hour, and 1000 to 2000 ppm is dangerous for short exposures.

Hydrogen chloride must be considered in a fire situation because widely used chlorine-containing plastics may be involved. Heating these plastics at temperatures ordinarily found in fires usually produces HCl as one of the major products.

A 1954 study in which chlorinated polymethylmethacrylate, polyvinylchloride, and vinyl and vinylidene co-polymer were heated at various temperatures in a flask in air showed copious quantities of HCl to be liberated, the amounts generally increasing with increasing temperature [43]. The principal decomposition products were HCl, CO, and CO_2. The authors considered that three pounds of any of these plastics heated in an unventilated room of 1,000 cu. ft. could produce a toxic hazard due to the CO and HCl generated, but stated that in a real fire, ventilation would probably prevent such accumulations of the decomposition products.

Underwriters Bulletin No. 53 [44] discusses the results of several unpublished reports on evolution of gases from chlorine-containing polymers. For example, Yarborough and Haskin [45] burned samples of polyvinyl chloride-acetate "Vinylite" sheeting in a flask with the purpose of obtaining the composition of the evolved gases which would be produced under conditions similar to those in a fire in an open room. At low oxygen contents, HCl was the major gaseous product. At the highest oxygen contents used, CO_2, HCl, and CO were major products.

Table 8 which contains data on five tests on bedding and upholstery, (see page 12), indicates HCl was produced in significant amounts in Test 8. The specific source of the HCl in this test is not, however, stated.

In the work on aircraft interior materials (see page 7) HCl, as well as several other gases, was measured. The general conclusion was that HCl was released rapidly during combustion or pyrolysis of polyvinyl chloride, modified acrylics, and retardant-treated materials. Flaming conditions produced higher HCl concentrations, probably due to the higher temperatures involved. The measured HCl concentrations changed rapidly due to the high reactivity and absorptivity of HCl.

In Gaskill's work (see page 7), HCl, in relatively small amounts compared to CO, was found on combustion of several formulations containing fire retardants, as the results in Tables 4 and 5 indicate. The author suspects HCl values may be low due to absorption of HCl on smoke particles. A urethane foam in which a fluorocarbon foaming agent was used produced a significant quantity of HCl, 120 ppm, under certain conditions. It was thought that this HCl was due to decomposition of the foaming agent.

Cornish and Abar [46] have studied the toxicity of the pyrolysis products of polyvinyl chloride polymers and formulations thereof. Four different vinyl chloride polymers and three formulations using three of the polymers were heated in an air stream, the pyrolysis products being directed into an animal chamber. In the case of the four polymers, the major cause of death of the rats used for the experiments was from the effects of CO and little evidence of lung damage was noted. When enough oxygen was added to the stream of pyrolysis products to prevent death from CO, evidence of pulmonary edema, presumably from HCl and other pyrolysis products, was found when the animals were examined. The pyrolysis products of the three polyvinyl chloride formulations, two commonly used in electrical insulation and one used in floor tile, were generally less toxic per gram of material pyrolyzed, probably due to inert additives. The authors state that the toxicological findings in pyrolysis studies will depend greatly on methodology, for example, on the presence of particulates and the type of exposure chamber used.

That HCl can be present in a fire situation is evident from the foregoing discussion. Hydrogen chloride may be produced from vinyl chloride type plastics and formulations and plastics which contain additives such as certain fire retardants and foaming agents.

The use of vinyl chloride has increased markedly over the last ten years, and will probably continue to do so. In 1960, 205 million pounds of polyvinyl chloride and copolymers thereof were consumed [47]. In 1970, 3050 million pounds were consumed [48]. Polyvinyl chloride was the third most used plastic in 1970, after polyethylenes (5805 million pounds) and polystyrenes (3323 million pounds) [48]. The major uses for polyvinyl chloride in 1970, in order of quantity consumed, were as follows: electrical insulation, pipes and conduit, flooring, furniture upholstery, records, and packaging film [48]. Hydrogen chloride may be evolved in any fire involving materials such as these.

If one is knowledgable concerning the odor characteristic of HCl, a fire situation in which this odor is present would not be entered (or would be left), though the atmosphere was physically bearable. Since HCl is adsorbed rather easily by many materials, high concentrations of it would tend to be found near the combustion site, rather than in more remote areas. If the odor of HCl is not recognized, a potential danger exists because HCl can be produced in a fire before dense smoke, as is pointed out in the National Bureau of Standards Technical News Bulletin, November 1969 [49]. This article also states that HCl is produced in potentially hazardous concentrations from polyvinyl chloride wire insulation. In April 1970, an article in Modern Plastics [50] stated that the NBS article greatly exaggerated the threat to life from HCl and said that the tests made in the test chamber did not approximate conditions in a burning building. To refute the NBS article, evidence is given that HCl concentrations in a fire involving polyvinyl chloride depends on ventilation and other factors. The evidence is from fire tests by the British Joint Fire Research Organization, and presumably based on a paper by Stark (51) in which cellulose and PVC materials were burned in an 0.9 cubic meter compartment. The author stated that HCl would contribute little to the hazardous situation due to the concentration of CO already present, if ventilation were poor.

In spite of the article, HCl has, however, since been shown to be hazardous to firemen. A June 1, 1970 fire in a Washington, D. C. office building in an electrical service vault, caused 31 firefighters to be treated for what "appeared to be inhalation of hydrogen chloride" before the fire was extinguished [52]. A testing laboratory later reported that the insulation was polyvinyl chloride and that at 540 °F, HCl, as well as CO and CO_2 were given off with no visible smoke.

In conclusion, HCl generated in fires is probably not a serious threat to life, unless one is unable to move from its area of generation. The sensory warning given and the physically unbearable nature of a lethal concentration fortunately serve to warn of its presence.

E. Hydrogen Cyanide

Hydrogen cyanide (HCN) is a colorless gas and has the faint odor of bitter almonds. When inhaled, it is absorbed by the blood and carried to the tissues, where it deactivates catalysts necessary for natural oxidative processes. Since HCN prevents the use of oxygen by the cells, it may be classified as a chemical asphyxiant. The 1970 TLV for HCN is 10 ppm [29]. An atmosphere containing 200-480 ppm HCN in air is fatal to humans within 30 minutes, 3000 ppm is rapidly fatal [32].

Hydrogen cyanide can be produced in the laboratory during combustion of a variety of materials. Olsen *et al.* (see page 6) in laboratory experiments showed that wool (see Table 2) and silk produced relatively large quantities of HCN, namely, about 1-7 percent by volume of total gas, when heated in air in a silica tube. Moss *et al.* [53] found that melamine and melamine formaldehyde formulations could yield relatively large quantities of HCN when pyrolyzed in a flask, depending on pyrolytic conditions. In an unpublished report by Hobbs and Patten [54] cited in Underwriters Bulletin No. 53 [44], wool, silk, and nylon were shown to produce HCN under both flaming and smoldering conditions when heated in air in a combustion tube. Another unpublished report, by McDermott and Critchfield [55], cited in Underwriters Bulletin 53, gives results of tests in which various materials were pyrolyzed in a liter flask containing air or nitrogen, the resultant atmosphere being analyzed for HCN. The results are shown in Table 14. The conclusion drawn was that "....polyurethrane foam does not produce more HCN than do many other natural and synthetic consumer products" and "....it is difficult to understand why cotton and paper produce hydrogen cyanide on pyrolysis unless nitrogen fixation is assumed."

Table 14. Hydrogen cyanide measured in pyrolysis products.

	Hydrogen cyanide (micrograms/gm sample)	
Material	Air	Nitrogen
Paper	1100	182
Cotton	93 130	85
Wool	6500	5900
Nylon	780	880
Polyurethane foam	1200	134

Hydrogen cyanide was determined in the work on burning aircraft interior materials (see page 7). It was generally found in much smaller quantities than CO, or HCL when chlorine-containing materials were burned. Nearly all materials tested yielded HCN in concentrations from a few ppm up to 40 ppm. Wool, urethane, ABS, acrylic, and polyamide materials produced the highest concentrations of HCN. One modified acrylic pile rug sample yielded 90 ppm HCN, the highest concentration observed. The authors state that because the materials studied were from many different manufacturers and contained "plasticizers, fillers, and other additives, it is difficult to relate quantitatively gaseous product concentration with polymer composition." The results given in Table 8 show that in the study on bedding and upholstery fires, (see page 12), HCN was produced in small quantities in each of the five tests. Results presented in Table 6 show that HCN can be evolved at extremely high levels during combustion of wool and woolen materials, while acrylic carpeting and acrilan yield lesser, but still significant amounts of HCN. Hydrogen cyanide is evolved from certain urethane elastomers and urethane foams as is shown in the work of Gaskill (see page 7), and Tables 4 and 5. There were wide variations, depending on ventilation, flaming or non-flaming exposure, and foaming agent, in the amounts of HCN produced.

The studies cited above indicate that woolen materials, urethane, polyamides, and acrylics yield relatively large amounts of HCN on pyrolysis. Flexible urethane foam is now used in large quantities in bedding and furniture. In fact, 316 million pounds out of 653 million pounds consumed in 1970 were used for the above purposes [48]. Only 125 million pounds of flexible foam were used in bedding and furniture in 1965 [56]. Rigid urethane foams are now used in largest quantity in building construction for structural units such as sandwich systems for walls and insulation. The second largest use of rigid foams is in appliance insulation [48]. Rigid foam consumption for these uses increased from 22 million pounds in 1965 to 145 million pounds in 1970 [48,56]. Generally, there would not be as much acrylic material or polyamide (nylon) material present in the ordinary fire as there would be urethanes. Total acrylic consumption in 1970 was 390 million pounds and nylon consumption was 103 million pounds [48]. Acrylics are used primarily in outdoor signs, lighting fixtures, and windows and may be found in the home where they are used for knobs, name plates, and packaging. Acrylic foams are now being used increasingly as drapery backing. Nylon would be found in the home in such articles as bristles, appliances, machinery parts, clothing and carpets.

The above indicates that HCN in the ordinary fire might be found if upholstery, bedding, or wall panelling of newer construction is involved. The quantity of HCN evolved would probably not present a hazard by itself. However, special situations such as fires in clothing stores or rug shops might yield lethal atmospheres due to HCN alone. Relatively low concentrations of HCN in combination with other toxic fire gases may, as will be discussed later, produce toxic synergistic effects.

F. Nitrogen Oxides

Nitrogen dioxide (NO_2) is the most important oxide of nitrogen to be considered as a toxic hazard in a fire situation. Most nitric oxide (NO) formed in a fire would be rapidly converted to NO_2 in the presence of oxygen and moisture. Nitrogen dioxide has a dark brown color. When inhaled NO_2 acts primarily as a pulmonary irritant. A secondary effect, that of production and subsequent absorption of nitrites in the lungs, is usually obscured by the intense irritating action on respiratory tract tissue [32]. The 1970 TLV for NO_2 is 5 ppm [29]. Humans exposed to atmospheres containing higher NO_2 concentrations, up to approximately 100 ppm, develop bronchitis or pneumonia with eventual recovery [57]. One-half to one hour exposures to about 150 ppm NO_2 and higher usually are fatal.

A type of degeneration of lung tissue, bronchiolitis fibrosa obliterans, fatal in 3 to 5 weeks, may ensue after inhalation of NO_2 in the 150-200 ppm range [57]. Inhalation of concentrations of about 500 ppm usually causes death from pulmonary edema within 48 hours. Nitrogen dioxide is insidious in that the irritating effect on nose and throat may be tolerated even though a lethal concentration is being breathed [32,58]. When NO_2 is no longer present in the inspired air the irritation of nose and throat subside, but a few hours later massive pulmonary edema may develop resulting in death by suffocation.

Nitrogen dioxide has been measured in a few studies in which combustion products of various materials were analyzed. In the study on burning aircraft interior materials (see page 7) NO_2 and/or NO was found in the combustion products of seven of the materials. The materials producing nitrogen oxides were polyamides, ABS, cotton, polyether urethane, and a combination material containing wool and polyester. The highest concentration of nitrogen oxides found was 50 ppm produced by a polyamide. Table 8 indicates very small quantities of NO_2 produced in three instances in the bedding and upholstery tests (see page 12). The results in Table 6 show NO_2 produced in rather small amounts from several materials. Materials which evolve copious quantities of nitrogen oxides on combustion, such as nitrocellulose (pyroxyln) which was formerly used extensively for toys, film, *etc.*, are not used in large quantity today.

Judging from the few available laboratory tests in which nitrogen oxides have been measured, they would present, by themselves, no real threat in the ordinary fire. Small amounts of nitrogen oxides may, however, give rise to synergistic effects in combination with other toxic gases.

The danger of a high concentration of NO_2 is well illustrated by a recent non-fire situation in which firemen were involved [59]. Four firemen were exposed to NO_2 from a leak in a chemical plant. The NO_2 concentration of the contaminated atmosphere was not known, but reddish brown fumes were present. The most severly affected fireman initially experienced only a mild headache and dry cough. Twenty hours after exposure he was admitted to a hospital with acute pulmonary edema and in a deteriorating condition. After surviving this phase of the illness a second acute phase, also survived, appeared about 3 weeks later. The fireman was finally discharged seven weeks after admission, but with some pulmonary impairment. It is interesting to note the varying individual responses of the four firemen to NO_2 exposure. The course of the illness of the fireman discussed above is compared to another of the firemen who suffered only sinusitis, transient respiratory symptoms, and no disabling sequelae. The authors state that, "One wonders what role innate resistance plays in these cases".

G. Phosgene

Phosgene ($COCl_2$) is a colorless gas with the odor of musty hay. Its odor is perceptible at 5.6 ppm, though lesser amounts cause coughing and eye irritation [32]. Phosgene is an irritant whose effects closely resemble those of NO_2. The 1970 TLV for phosgene is 0.1 ppm [29], while 50 ppm is fatal in 1/2 to 1 hour [32].

Coleman and Thomas [43] analyzed for $COCl_2$ in their work on chlorinated plastics. The largest concentration of $COCl_2$ found was 1/1700 the amount of HCl produced. The authors state that "Traces of carbonyl chloride [phosgene] were evolved in some instances, but the quantities were of small account compared with those of the other gases."

Underwriters Bulletin No. 53 [44] cites several unpublished reports in which $COCl_2$ has been found in the combustion products of plastics. Kandybowits [60] found 0.1 ppm $COCl_2$ in the gaseous products of a rigid vinyl plastic, compared to 104 ppm HCl. Fulks *et al.* [61] combusted two samples of polystyrene to which a chlorinated paraffin had been added as an extinquishing agent and found 0.014 wt. percent phosgene evolved based on the weight of the original sample. Hobbs and Patten [54] found 0.0001 gm $COCl_2$/gm sample evolved from a polyvinyl chloride plastic but none from samples of such materials as rayon, nylon, wool, silk, wood, and paper.

Tables 6 and 8 show $COCl_2$ is produced in several instances. Though $COCl_2$ is evidently found only in small amounts during combustion of common materials, it is also very toxic compared to CO, HCl, or NO_2 and would contribute to the overall toxicity of a fire atmosphere. Phosgene would probably be most commonly found in fires involving polyvinyl chloride plastics.

There are several documented cases of deaths in fire situations due to $COCl_2$ when carbon tetrachloride, which may yield $COCl_2$ on combustion, was used as an extinguishing agent [62].

H. Sulfur Dioxide

Sulfur dioxide (SO_2) is a colorless, highly irritating gas, detectable by its odor at 3-5 ppm [32]. The 1970 TLV for SO_2 is 5 ppm [29]. 20 ppm SO_2 causes immediate irritation of eyes and coughing [32], 150 ppm is tolerable for only a few minutes [58], and 400-500 ppm is dangerous for exposures of 1/2 to 1 hour [32].

Sulfur dioxide is formed by the incomplete combustion of sulfur containing materials. Olsen *et al.* (see page 6) found 3.4 percent SO_2 by volume of gas produced on pyrolyzing rubber insulation in nitrogen. No SO_2 was found on combustion in excess air, probably due to oxidation to sulfates. As shown in Table 6, which includes results from the burning of materials in the ASTM E84 Tunnel Furnace (see page 7) SO_2 was evolved predominately from the natural products wool, and oak, and Douglas Fir. The work on aircraft interior materials (see page 7) showed that sulfur containing plastics could produce SO_2 when combusted. Polysulfones, used mostly for alkaline battery cases and electronic parts, produced as much as 150 ppm SO_2. A chlorosulfonated polyethylene yielded about 50 ppm SO_2. Table 8, from the study on bedding and upholstery materials (see page 12), shows SO_2 to be produced in each test, in rather high concentrations. The authors state that "The source of the sulfur dioxide and bromine is a matter of speculation. These gases would not be expected to develop with the bedding and upholstery materials involved." At the levels shown in Tables 6 and 8, SO_2 can exert toxic synergistic effects in combination with other toxic gases, as will be discussed in the section on combinations of gases. There is no common material except sulfur which would yield large quantities of SO_2 on combustion and its irritating nature gives adequate warning of its presence. So by itself, SO_2 would not be a serious hazard in the ordinary fire.

I. Ammonia

Gaseous ammonia (NH_3) is colorless and has a characteristic, extremely sharp odor. It is irritating to the eyes, respiratory tract, and in high concentrations, to the skin. The 1970 TLV for ammonia is 20 ppm [29]. Ammonia is perceptible at the 20 ppm level, physically tolerable for an eight-hour day at the 100 ppm level, and may be fatal for half-hour exposures at 1700 ppm [58].

Ammonia is produced on combustion of a variety of nitrogen containing materials. Olsen *et al.* (see page 6) found NH_3 in concentrations from about 1-7 percent in the gaseous combustion products of wool and silk. It has been found in the pyrolysis products of acrylonitrile polymer [63], nylon [64], phenolic and melamine resins combined with fillers [65], and PVC and acrylonitrile foamed with certain agents [65]. Table 8 indicates NH_3 was formed in two tests.

From the data available, it is difficult to postulate how much NH_3 might be found in a fire situation. However, its characteristic odor and unbearable irritating effects at sublethal concentrations would probably give adequate evidence of its presence.

J. Hydrogen Sulfide

Hydrogen sulfide (H_2S) is of concern in fires if sulfur-containing materials are involved. It is colorless, but is easily detectable at low concentrations by its characteristic rotten-egg odor. The odor threshold concentration of H_2S is 0.18 ppm [66] while the 1970 TLV is 10 ppm [29].

Hydrogen sulfide may act both as an irritant and asphyxiant. Exposure to relatively low concentrations (20-150 ppm) causes eye irritation and inhalation of slightly higher concentrations may result in pulmonary edema [67]. A half hour exposure to 800-1000 ppm may be fatal due to paralysis of the respiratory center of the brain. Olsen *et al.* (see page 6) found that rubber insulation and woolen material evolved large amounts of H_2S during thermal decomposition in nitrogen. Combustion of these materials in air (see Table 2) also produced H_2S, though in smaller quantities (0.1 to 0.4 percent), because H_2S itself is combustible. Madorsky [64] found H_2S as a product of the pyrolysis of certain vulcanized natural rubbers. The results in Table 8, from the bedding and upholstery tests, (see page 14), indicate H_2S was produced in each test. The results in Table 6 show small amounts of H_2S were evolved from red oak and wool.

Hydrogen sulfide would generally not be of much concern in the usual fire because only relatively small amounts would be present and because of the warning given by its characteristic odor.

K. Miscellaneous Halides and Halogens

Chlorine (Cl_2), bromine (Br_2), Hydrogen bromide (HBr), hydrogen fluoride (HF), ethyl bromide (CH_3CH_2Br), methyl bromide (CH_3Br) and some other halogenated compounds act as pulmonary irritants and some may produce protoplasmic poisons when inhaled. For example, HF yields sodium fluoride on contact with respiratory tissue and methyl bromide may be absorbed causing injury to kidneys and the central nervous system. Irritation of the skin and eyes may also result from contact with these materials.

These substances would be involved in fire situations primarily through the use of extinguishing agents such as chlorobromomethane (CH_2BrCl) and trifluorobromomethane (CBrF3) or because of the pyrolysis of halogenated plastics.

A study of the pyrolysis products of the extinguishants CH_2BrCl and $CBrF_3$ indicates many different halogen compounds are produced [68]. On pyrolysis in a hydrogen-oxygen flame at 800 °C, $CBrF_3$ yielded primarily HF, HBr, and Br_2, and some other compounds with empirical formulas CH_2Br_2, $CHBr_2Cl$ and CCl_4. It was found that under the pyrolysis conditions used, the products of $CBrF_3$ were less toxic to rats than those of CH_2BrCl. Carbon tetrachloride, which is by itself toxic and which yields the highly toxic $COCl_2$ when pyrolyzed, has largely been replaced by other halogenated methanes for use as extinguishants. A red-yellow highly irritating gas, ClO_2, with a 1970 TLV of 0.1 ppm [29] is formed on combustion of several materials (see Tables 6 and 8).

The major fluoro-plastics in use today are chlorotrifluoroethylene, polyvinylidene fluoride, polytetrafluoroethylene (TFE) and fluorinated ethylene-propylene (FEP). These are used mainly for electrical insulation, metal finishing and in applications where corrosive materials are handled. Study of the toxicity to rats of the pyrolysis products of polychlorotrifluorethylene indicates that particulate matter may cause death rather than other toxic byproducts [69]. Small amounts of carbonyl fluoride (COF_2), COFCl, and species with COCl groups were found on analysis of the break-down products.

Several studies have been made on the pyrolysis products of TFE [70-73]. The major product on pyrolysis in air at 500 ° to 650 ° was COF_2. Pyrolysis above 650 °C yielded mostly CF_4 and CO_2. Experiments on animals indicated COF_2 was the principal toxic agent of pyrolysis of TFE at 500 °C. In the investigation on burning aircraft interior materials (see page 7), HF was found in the products of combustion of nearly every fluorine-containing material. Materials combusted included coatings (both polyvinyl fluoride and polyvinylidene fluoride) and TFE seals and insulation. The TFE seals yielded 90 ppm HF under non-flaming conditions, the highest concentration of HF found. Products of fluorocarbon pyrolysis have been implicated in several cases of human illness in non-fire situations. For example, the pyrolysis products from Teflon impregnated asbestos tape on the exhaust manifold of a power unit in an airplane caused toxic reactions in 39 of 40 personnel on board [74], but there was no sensory indication that a toxic or irritating substance was present. The specific causative agent of the illness was never determined, but symptoms were aggravated by an oil mist present and the high altitude.

In most cases, warning of the presence of a toxic halide or halogen would be given by the sharp odor and noticeable irritating action on the respiratory tract. An obvious hazard from these compounds exists in situations during or soon after a fire where an extinguisher containin a halogenated methane is used. The small amount of fluroplastics found in the ordinary fire situation probably minimizes their contribution to the toxicity of the fire atmosphere.

L. Other Irritants

A number of organic materials classed as irritants are formed in combustion processes. There may be intermediates formed in the early development of a fire which later undergo further oxidation or they may themselves be the end products of certain kinds of combustion processes.

Chemically, these substances fall into the class of oxygenated organic compounds, principally aldehydes, ketones, and acids. Those commonly encountered are formaldehyde, acetic anhydride, acetaldehyde, acetic acid, formic acid, furfural, and acrolein. All these materials are irritants, all are combustible, and most have pungent acrid odors. The 1970 TLV's range from 0.1 ppm for acrolein to 200 ppm for acetaldehyde [29]. Levels at which they are dangerous or fatal are not well established, but like most irritants, tolerable levels are probably well below toxic levels. Among the many products of combustion of cellulosic materials such as wood, cotton, and newspaper, are acetaldehyde, formaldehyde, acetic acid, formic acid, and furfural [44,75]. The pyrolysis products of cotton cellulose, for example, may contain at least 37 compounds [64].

Synthetic organic compounds may produce irritants during combustion. Some irritants of importance are octafluoroisobutylene (from Teflon) and toluene diisocyanate from polyurethanes. The 1970 TLV for toluene diisocyanate is only 0.02 ppm [29].

Madorsky [64] presents a compilation of the many degradation products of organic polymers when pyrolyzed in air, inert atmospheres, or vacuum.

In fire situations, it is likely that these irritants will be adsorbed on or associated with particulate matter (smoke). These irritants, then, should be suspected in the early stages of smokey, poorly ventilated fires. Warning of their presence would ordinarily be given by visual evidence of smoke and by their irritating action on respiratory tract and eyes. More concerning their physiologic effects in conjunction with particulate smoke is discussed on page 67.

M. Miscellaneous Simple Asphyxiants and Gases with Anesthetic Effects

Gases classified by Henderson and Haggard [32] as simple asphyxiants act chiefly by excluding oxygen from the lungs and usually cause no other effects than those of oxygen deficiency. Nitrogen, helium, argon, hydrogen, and methane are examples of gases which may act as simple asphyxiants. Irritant gases, CO_2, and other gases, in addition to their primary physiological effects, may exclude oxygen from the inhaled atmosphere and act as simple asphyxiants. Certain simple asphyxiants may be produced as intermediate products of combustion during the course of a fire, for example, hydrogen (see Figures 1 and 2) and hydrocarbons such as methane and ethane [64]. However, the concentration of these simple asphyxiants would have to be inconceivably high in order to dilute the oxygen below a safe limit. A high concentration of primary asphyxiant existing in a fire situation is not a hazard *per se* because there is no systemic toxic effect exerted and the actual hazard would be due to displacement of oxygen. In special situations where large amounts of simple asphyxiant are released in an enclosed space, for example, a natural gas line break or rupture of a gas cylinder, precautions must be taken because of the probable low oxygen concentration. Mention should be made of a fire situation where a chemical extinguishant such as $CBrF_3$ or CH_2BrCl is being or was used. These compounds may act as simple asphyxiants due to their displacement of oxygen from the immediate area. If high enough concentrations of these chemicals are inhaled, other systemic effects could also result [76].

During the combustion process, gases with drug-like or anesthetic properties may be evolved, usually in relatively small amounts. Examples of those which may be found in pyrolysis products are propane and higher paraffins, olefins, and benzene. The major physiological effects of these compounds are exerted after they are absorbed into the blood stream. In certain situations, firemen are exposed to and inhale gasoline vapor, which has anesthetic properties. The danger of inhaling gasoline vapor, is well illustrated by a recent incident in Australia [77]. Two individuals in an airplace accident were trapped and forced to inhale gasoline fumes of unknown concentration, one for five minutes, the other for 25 minutes. When the individuals were removed to a hospital in satisfactory condition, fractures they received had to be set and they were anesthetized with halothane. The combination of the anesthetic and gasoline absorbed by the body through inhalation caused death to both individuals from fat embolism within about 3 days.

Generally, gases acting as simple asphyxiants or as anesthetics must be present in relatively high concentrations to exert any appreciable immediate physiological effect and would not be of consequence by themselves in the usual fire.

N. Smoke

For the purposes of this discussion, smoke will be defined as the non-gaseous airborne products of combustion. Smoke particles are predominately carbon, on which may be adsorbed irritants such as organic acids, aldehydes, or HCl. In addition to particles, smoke may also contain droplets of condensed combustion products. Smoke particles may be of small enough size to be inhaled deeply into the lungs. According to Thomas [75], "The effect of inhaling such particles on pulmonary function has not been evaluated acutely or clinically. Clinically, the inhalation of smoke particles appears to do little harm other than produce a mild irritation of the tracheobronchial tract with some cough, increased secretions, and complaints of substernal burning." Thomas also states that more damage may be done by smoke particles which become lodged in the nose and pharynx. These particles may be swallowed, causing nausea and vomiting. Eye irritation also results from exposure to smoke. It is pointed out in the paper by Thomas that fire casualties labelled as "overcome by smoke" (denoting asphyxia) may not be suffering from asphyxia, but from toxic gas inhalation, ingestion of smoke, heat, heart attack, or hyperventilation. Careful diagnosis of the problem is essential in properly treating the victim. Autian [78] states that smoke inhaled into the lungs may, depending on particle size, migrate into the blood stream or be entrapped in the lung tissue and over a long period of time lead to malignant tissues.

A major hazard of smoke is its obscuration of vision, which coupled with its irritating effects, causes fear and panic and hinders escape from a smoke filled enclosure.

Smoke is evolved from nearly all materials during the combustion process, production being generally greater in poorly ventilated enclosures. Smoke particles are good adsorbents and may carry other combustion products characteristic of the particular material combusted or adsorbable products from nearby burning materials. For example, HCl might be adsorbed on smoke from chlorine containing materials, SO_2 on smoke from sulfur containing materials, and ammonia from nitrogenous materials. Little information is available on the chemical composition of most smokes. Certain wood smokes have been fairly extensively investigated because of their use in the food processing industry. For example, smoke from hard maple was found to contain C_1 to C_{10} acids, valeraldehyde, crotonaldehyde, ethanal, butanal, and other compounds [79]. Other investigators found 21 carbonyl compounds in wood smoke and identified 16, such as formic acid, acetic acid propionaldehyde, and acrolein [80].

Mention should be made here of the carcinogens in certain smoke, which may have a long term effect on one who has inhaled large quantities of smoke or inhaled smoke intermittenly over a long period of time. It is well known that wood smoke contains polycylic hydrocarbons which may exhibit carcinogenic activity. For example Rhee *et al.* [81] found such compounds as 3,4-benzopyrene, fluorene, phenanthrene, and chrysene, all of which may be carcinogens, in sawdust smoke.

O. Combinations of Toxic Gases

Thus far, we have been concerned with the effect of single gases and at this point the obvious should perhaps be stated. This is, that in no combustion is it likely that a single product is formed except in the case of combustion of hydrogen where water would be the only product. It is evident from the experimental work cited that high concentrations of CO, CO_2, and other toxic gases are associated with low oxygen concentrations. This is well illustrated, for example, by Figures 1, 2, and 3, and Tables 2, 3, and 7. Therefore, what should be considered in judging an atmosphere in regard to the associated toxicity is the effect of combinations of gases, both those which are toxic individually and those which might be innocous by themselves.

The psychological and physiological effects of a combination of two toxic substances may simply represent the sum of the two, in which case the effect would be additive. The effect may be many fold greater than the sum of the effects of each alone, in which case the effect is defined as a synergistic effect. In the event that one substance counteracts the effect of the other, the effect is antagonistic.

Several studies have been made of the physiological effects and toxicity of combinations of gases. The effects of a low oxygen atmosphere, 8.5 percent, were shown to disappear when 3 percent CO_2, which increases the ventilatory rate, was added to the atmosphere [82]. Here, CO_2 exerts an antagonistic effect. Zapp [83] found that the effects on goats of a low oxygen, high CO atmosphere were more lethal than either alone. Five goats were exposed to 2.7 percent CO in air, three were exposed to 3 percent oyxgen in nitrogen, and nine were exposed to a mixture of 2.7 percent carbon monoxide and 3 percent oxygen in nitrogen. The average time of respiratory cessation in the various groups of animals was as follows: 2.7 percent CO in air - 3.03 minutes, 3 percent O_2 in N_2 - 4.56 minutes, 2.7 percent CO and 3 percent O_2 in N_2 - 1.9 minutes.

In work with white rats, it was found that adding 10 - 20 ppm HCN to atmospheres containing CO in sub-lethal amounts, 2000 ppm CO under the experimental conditions, caused fatalities [53]. HCN alone did not cause fatalities below 50 ppm. It was postulated that the HCN increased the respiratory rate of the rats, resulting in an increased CO intake. This higher CO intake would cause carboxyhemoglobin levels equilvalent to much higher atmospheric carbon monoxide levels and caused death in a relatively short time period.

Two fairly extensive studies have been performed on the effect of varying O_2, CO_2, CO, heat and other toxic gases in the atmosphere to which white mice were exposed [17,84]. In the first study in 1968 at Southwest Research Laboratory [84], groups of ten white mice were exposed to atmospheres of varying CO, CO_2, O_2, and temperature for 4 hours in a 1 cu. ft. chamber. One, two, and three variable tests, that is variable from 21 percent O_2, 0.0 percent CO_2, and 85 °F, were conducted. On comparing single-variable to two-variable experiments, it was generally found that levels which were not lethal alone could be lethal when combined. For example, there were no survivors in an atmosphere containing 16 percent oxygen and 0.075 percent CO, yet there were 10 survivors in one case and 7 in another at 0.075 percent CO. There were no deaths at 16 percent oxygen. With three variables, the levels required to produce a given effect were further decreased. For example, 95 °F, 0.05 percent CO, and 5 percent CO_2 killed nine animals, but any one or two of these variables was not lethal. There was some evidence that CO_2, when combined with CO exerted an antagonistic effect. Post mortem examinations of animals killed during the four-hour exposure period showed congestion of the vascular system and lungs, which the authors postulated was produced by a disruption of the thermoregulatory center of the brain.

In 1969, the effects of varying O_2, CO, CO_2, and temperature (primary variables) with the addition of variable amounts of HCl, NO_2, SO_2, HCN, and certain combustion products were studied at Southwest Research Laboratories [17]. Two exposure chambers, a 4 cu. ft. flow chamber and a 10 cu. ft. static chamber, were used for the tests. Adequate provisions were made for mixing, monitoring, and analysis of all gases concerned and for temperature control. The flow-through chamber was used to determine the effect of the primary variables and noxious gases, the static chamber for primary variables and combustion products. Tests in the flow chamber with HCl were abandoned because much of the HCl adsorbed on the chamber walls and furnishings. Usually ten white mice were exposed for periods ranging from 4 to 24 hours, while physiological responses and deaths were recorded during the tests. All animals that died during exposure in the chambers were autopsied. After exposure tests, surviving animals were observed for 10 days then killed and about 50 percent of the total autopsied.

Considering only primary variables, additive toxic effects were noted, except for the effects of CO_2, which could be additive or antagonistic depending upon conditions. Definite synergistic effects were noted when NO_2, HCN, or SO_2 were added to a combination of the primary variables. For example, an atmosphere of 16 percent O_2, 0.075 percent CO, 30 percent CO_2, and 100 °F produced no deaths in 4 or 24 hours. Addition of 10 ppm NO_2 to the above mixture produced two deaths in four hours. With NO_2 in air, 100 ppm was required to produce any deaths. Similar results were obtained with SO_2 and HCN. For example, 25 ppm SO_2 produced 3 deaths and 10 ppm HCN caused 2 deaths. It is stated that if only additive effects had occurred, 75 ppm NO_2, 700 ppm SO_2, and 75 ppm HCN would have been needed to produce 1 - 3 deaths with the above combination of primary variables.

In the static tests, control of gas concentrations was somewhat difficult to maintain. However, addition of combustion products of certain materials such as wool, Douglas fir, and polyvinyl chloride to the primary variables indicated increased toxicity. For example, the combustion products of Douglas fir and 1100 ppm CO produced three deaths, 1100 ppm CO alone produced no deaths. The authors state that "study of additional products indicated that HCl, which was generated in sufficient quantity in combination with other gases and smoke, may be extremely toxic and should be studied in detail". Presumably this statement is made because 1500 ppm CO and the combustion products of polyvinyl chloride which would contain HCl (see Table 6 from this study) resulted in ten deaths, whereas 1500 ppm CO in air resulted in two deaths.

Autopsies on all animals that died during the four hour exposures showed only congestion of the lungs and vascular system. No lesions or irritation of the upper respiratory tract were noted. The authors state that these "are the typical findings when death is due to heat prostration and/or heat and anoxia." Examination of animals that survived the four hours exposure ten days after exposure showed no lesions or congestion.

It may be concluded from the relatively few studies available that the hazards of combinations of toxic gases are greater than might be suspected based upon the toxicity of the individual components of a combination. More work is necessary to better define the problems associated with combinations of toxic gases and to elucidate the mechanisms of this action.

A recent study [85] has produced the interesting conclusion that combinations of CO, CO_2 and NH_3 are less hazardous in terms of ability to function than are the individual gases. The authors have measured a time interval described as "time of useful function" which represents the length of time after the beginning of exposure to toxic gases during which subjects, in this case laboratory mice, are still capable of escape from the toxic environment. It was found that the time of useful function TUF was longer in combination of CO and CO_2 and in combinations of CO and NH_3 than when their substances were present alone but at the same concentration. The TUF was even greater in atmospheres containing similar concentration of CO, NH_3 and CO_2.

It might be concluded from the relatively few available studies that combinations of toxic gases do not simply act additively one on another but rather that the effect is not predictable from the action of the individual substance. More work is obviously needed in order to better define the physiological response to the many combinations which are likely to be encountered in a real fire situation.

5. RECOMMENDATIONS AND CONCLUSION

Toxic gases are a major cause of fire casualties to firemen and civilians, as the available statistics show. The overall toxic gas problem however, needs more accurate and detailed definition from a statistical standpoint. Present statistical surveys are inadequate either because the sample is too small or invalid statistical methods are used in gathering and analyzing data. In describing fire casualties, the term "overcome by smoke" as generally used may cover several different causes of casualty, such as hypoxia due to oxygen deficiency or carbon monoxide, hyperventilation, or even heat exhaustion. "Overcome by smoke" should have an explicit definition, for example, inhalation and ingestion of smoke, causing nausea. Thus defined, and restricted to cases where this was the medical diagnosis of the cause of injury, the above term would yield pertinent information in statistics classifying fire injuries. The United Kingdom Fire Statistics would serve as a good model for an overall U. S. fire casualty survey.

More detailed information of the circumstances surrounding firemen incapacitated or injured by smoke and gases would help define the breathing mask problem. It would be well to know, for example, for each casualty, whether a mask was being worn, and if so what kind of mask, the specific nature of the injury received, the type of fire being fought and an assessment of toxic gases present. Standard forms for collecting this data, which is presently not available on a nationwide basis, could be distributed to fire departments.

This report has shown that in the residential fire, where toxic gases would be most commonly of concern, a lethal combination of oxygen deficiency and toxic gases may easily occur. In the early stages of a typical residential fire, initiated by a small source in a room, smoke and combustible irritants would be the predominant toxic materials in the fire atmosphere. As the fire builds up, combustible irritant gases are burned, oxygen concentration decreases, and CO and CO_2 increase. The ratio of CO to CO_2 produced by the fire is dependent on ventilation. Generally with better ventilation, less CO is formed. At flashover, that is when all combustible materials burst into flame almost simultaneously, the oxygen concentration decreases sharply and CO and CO_2 show marked increases. Simultaneous high concentrations of CO, CO_2 and the presence of certain irritants such as HCl, NO_2 and SO_2 are thus usually associated with low oxygen concentrations. It is probably this combination of factors which is responsible for most fire casualties from toxic gases, rather than CO alone.

A fire atmosphere containing a non-lethal concentration of CO by itself, could easily cause a fatality due to additive or synergistic toxic effects of low oxygen and other toxic gases present. The fatality would probably be attributed to CO, since there would be little evidence of the action of the other gases. Respiratory protection against more than high CO levels is thus necessary for those involved in fire situations.

Since so many variables such as ignition source, materials, ventilation, *etc.* are involved in any real fire, it is difficult to accurately predict the composition of a fire atmosphere at any given time or place. Some reasonable conclusions have been made concerning what materials produce specific toxic gases and the general levels at which these gases might be expected in a fire situation.

As production figures indicate, there is a large and increasing usage of certain plastics, particularly polyvinyl chlorides and urethanes, in both furnishings and construction of buildings. Usage of natural materials also changes with changes in technology. The "average" fire atmosphere of today will thus be different from that of the past or future. Fire atmospheres could be better characterized if analyses for toxic gases were performed at real fires. This could be done by using detector tubes or other simple measuring devices.

The psychological and physiological effects of different levels of toxic gases have no absolute appearance threshold and the effects themselves may vary considerably depending on the exposed individual. Individual characteristics such as age, health, or "innate resistance" are important in determining the response of an individual to a given toxic atmosphere. Several studies show that small amounts of gases wuch as HCl, NO_2, HCN, and SO_2, when combined with toxic atmospheres containing CO, CO_2, and low O_2 concentrations, produce synergistic toxic effects when respired by animals. Many other irritant gases such as HCl, NO_2, HCN, and SO_2 are likely to be present at low concentrations in fire atmospheres. It would be informative to better define the effects of various combinations of toxic gases and the mechanism of their action.

Firemen should be informed as to what toxic gases to expect in a particular fire situation and what physiological and psychological effects these gases might exert. They should further be taught to assess the toxicity of a fire atmosphere from visual observation of the surroundings and from any odors or irritating effects produced by gases present in the atmosphere.

VI. REFERENCES

[1] "IAFF Annual Death and Injury Survey", Pamphlet reprinted from *International Fire Fighter*, November 1969.

[2] "IAFF Annual Death and Injury Survey", Pamphlet reprinted from *International Fire Fighter*, November 1970.

[3] Smoke Inhalation Deaths Up, *Fire Engineering* 121, No. 11, 80 (1968).

[4] "United Kingdom Fire Statistics 1965", Her Majesty's Stationery Office, London (1967).

[5] "United Kingdom Fire Statistics 1966", Her Majesty's Stationery Office, London (1968).

[6] "United Kingdom Fire Statistics 1967", Her Majesty's Stationery Office, London (1969).

[7] "United Kingdom Fire and Loss Statistics 1968", Her Majesty's Stationery Office, London (1970).

[8] Utech, H. P., Injury Statistics and the Design of Fire Fighters' Protective Clothing and Equipment, Office of Fire Research and Safety, NBS, Unpublished report.

[9] Utech, H. P., Statistical Survey of Injuries to D. C. Fire Department Firemen, Office of Fire Research and Safety, NBS, unpublished report.

[10] Injuries to Fire Department Personnel, *Fire J.* 63, No. 2, 23 (1969).

[11] The Single Fatality Fire, *Fire J.* 63, No. 1, 34 (1969).

[12] A Fire Record: Hospitals, *Fire J.* 64, No. 2, 14 (1970).

[13] Gregory, K. L., Malinoski, V. F., and Sharp, C. R., Cleveland Clinic Fire Survivorship Study, *Arch. Environ. Health* 18, 508 (1969).

[14] Olsen, J. C., Ferguson, G. E., and Sheflan, L., "Gases from Thermal Decomposition of Common Combustible Materials, *Ind. & Eng. Chem.* 25, 599 (1933).

[15] Gross, D., Loftus, J. J., Lee, T. G., and Gray, V. E., Smoke and Gases Produced by Burning Aircraft Interior Materials, NBS Building Science Series 18, February 1969.

[16] Gaskill, J. R., Smoke Development in Polymers During Pyrolysis or Combustion, *J. Fire and Flammability* 1, 183 (1970).

[17] Pryor, A. J., Johnson, D. E., and Jackson, N. N., "Hazards of Smoke and Toxic Gases Produced in Urban Fires, Southwest Research Institute, San Antonio, Texas, OCD Work Unit 2537B, September 1969.

[18] Fire Tests in Room of Dwelling Give Data on Gases, Temperature, *Fire Engineering* 107, No. 5, 408 (1954).

[19] Yuill, C. H., The Life Hazard of Bedding and Upholstery Fires, *J. Fire and Flammability* 1, 312 (1970).

[20] Hafer, C. A. and Yuill, C. H., "Characterization of Bedding and Upholstery Fires", NBS Contract No. IST-792-5-69, SWRI Project No. 3-2610, Southwest Research Institute, San Antonio, Texas, March 31, 1970.

[21] British Fire Tests of Fiberboard, *National Fire Protection Association Quarterly* 45, No. 3, 218 (1952).

[22] Shorter, G. W., McGuire, J. H., Hutcheon, N. B., and Legget, R. F., The St. Lawrence Burns, *National Fire Protection Association Quarterly* 53, No. 4, 300 (1960).

[23] Pryor, A. J., Full-Scale Fire Tests of Interior Wall Finish Assemblies, *Fire J.* 63, No. 2, 14 (1969).

[24] Butler, C. P., "Measurements of the Dynamics of Structural Fires", OCD Work Unit 2561A, SRI Project PYU-8150, Stanford Research Institute, Menlo Park, California 94025, August 1970.

[25] Gordon, G. S., and Rogers, R. L., "A Report of the Medical Findings of Project Monoxide", The John P. Redmond Memorial Fund of the IAFF, Merkle Press, Washington, D. C. (1969).

[26] Baumberger, J. P., Leong, H. C., and Neville, J. R., Oxygen Delivery Rate of Human Blood, *J. Appl. Physiol.* 23, No. 1, 40 (1967).

[27] Courville, C. B., Forensic Neuropathology XI. The Asphyxiant Gases, *J. Forensic Science* 9, 19 (1964).

[28] Sakurai, Y., The Study of the Skin Permeability of Carbon Monoxide and Measurement of Carboxyhemoglobin in Blood, *Japan J. Legal Med.* (Tokyo) 17, 314 (1963).

[29] "Threshold Limit Values of Airborne Contaminants Adopted by ACGIH for 1970", American Conference of Governmental Industrial Hygienists, 1014 Broadway, Cincinnati, Ohio (1970).

[30] Schulte, J. H., Effects of Mild Carbon Monoxide Intoxication, *Arch. Environ. Health* 7, 524 (1963).

[31] Forbes, W. H., Sargent, F., and Roughten, F. J. W., The Rate of Carbon Monoxide Uptake by Normal Men, *Amer. J. Physiol.* 143, 594 (1945).

[32] Henderson, Y., and Haggard, H. W., "Noxious Gases and the Principles of Respiration Influencing Their Action", Reinhold Publishing Corporation, New York, New York (1943).

[33] Monaco, B., Intoxication from Carbon Monoxide and Carbon Monoxide Determination and Investigations in a Large Workshop Producing City Gas, *Rass. Med. Indust.* 33, 495 (1964).

[34] McFarland, R. A., Dunlap, J. W., Hall, W. A., and Moseley, A. L., "Human Factors in the Design of Highway Transport Equipment. A Summary Report of Vehicle Evaluation", Harvard School of Public Health, June 1953.

[35] The Effects of Carbon Monoxide, *Fire J.* 61, No. 4, 46 (1967).

[36] Pryor, A. J., and Yuill, C. H., "Mass Fire Life Hazard", OCD Work Unit 2537A, NRDL TRC-63, Southwest Research Institute, San Antonio, Texas, September 1966.

[37] Los Angeles Fire Department Tests - Fire Detection Systems in Dwellings, *National Fire Protection Association Quarterly* 56, No. 3, 201 (1963).

[38] Fires and Fire Losses Classified, 1969, *Fire J.* 64, No. 5, 65 (1970).

[39] Thomas, D. M., What Smoke Can Do to Your Body, *Fire Engineering* 122, No. 8, 46 (1969).

[40] McFarland, R. A., Anoxia: Its Effects on the Physiology and Biochemistry of the Brain and on Behavior in "The Biology of Mental Health and Disease", Hoeber, New York (1952).

[41] Claudy, W. D., "Respiratory Hazards of the Fire Service", National Fire Protection Association, Boston, Mass. (1957).

[42] "Report of Incident Resulting in Two Deaths, 1513 Hampshire West Court, October 30, 1970", Department of General Services, Division of Fire Prevention, Montgomery County, Maryland, unpublished report.

[43] Coleman, E., and Thomas, C., The Products of Combustion of Chlorinated Plastics, *J. Appl. Chem.* 4, 378 (1954).

[44] Underwriters Laboratories Inc., Bulletin of Research No. 53, "Survey of Available Information on the Toxicity of the Combustion and Thermal Decomposition Products of Certain Building Materials under Fire Conditions", July 1963.

[45] Yarborough, V. A., and Haskin, J. F., Spectrometric Study of the Gaseous Products from the Combustion of 'Vinylite' Sheeting, Union Carbide Plastics Co., unpublished report (1950).

[46] Cornish, H. H., and Abar, E. L., Toxicity of Pyrolysis Products of Vinyl Plastics, *Arch. Environ. Health* 19, 15 (1969).

[47] Plastics Hold to Record 6 Billion lb., *Modern Plastics* 38, No. 5, 82 (1961).

[48] Annual Review and Forecast, *Modern Plastics* 48, No. 1, 65 (1971).

[49] Technical News from NBS, STR-4017, November 1969.

[50] How Hazardous is PVC Wire Insulation in a Fire?, *Modern Plastics* 47, No. 4, 97 (1970).

[51] Stark, G. W. V., Toxic Gases from PVC in Household Fires, *Rubber and Plastics Age* 50, No. 4, 283 (1969).

[52] Bimonthly Fire Record, Office Building, Hydrogen Chloride from Wire Insulation, *Fire J.* 64, No. 5, 73 (1970).

[53] Moss, R. H., Jackson, C. F., and Saberlick, J., Toxicity of Carbon Monoxide and Hydrogen Cyanide Gas Mixtures, *Arch. Ind. Hyg. and Occup. Med.* 4, 53 (1951).

[54] Hobbs, A. P., and Patten, G. A., Products of Combustion of Plastics and Other Common Solids, Dow Chemical Co., Midland, Michigan, unpublished report (1962).

[55] McDermott, W. H., and Critchfield, F. E., Thermal Degradation of Polyurethane to Hydrogen Cyanide, Union Carbide Plastics Co., unpublished report, (1961).

[56] Annual Review and Forecast, *Modern Plastics* 42, No. 5, 76 (1965).

[57] "Air Quality Criteria for Nitrogen Oxides", Environmental Protection Agency, Air Pollution Control Office Publication No. AP 84, Washington, D. C., January 1971.

[58] "Matheson Gas Data Book", 4th Edition, Herst Litho Inc. New York (1966).

[59] Tse, R. L., and Bockman, A. A., Nitrogen Dioxide Toxicity--Report of Four Cases in Firemen, *J. Am. Med. Assoc.* 212 No. 8, 1341 (1970).

[60] Kandybowits, A., Toxicity of Rigid Vinyl - VCA-3354 and VCA-3606, Union Carbide Plastics Co., United States Testing Co. Inc., unpublished report (1961).

[61] Fulks, B. D., Morris, R. J., Jr., and Lamdein, W. J., Polystyrene Resins, Identification of Combustion Products from Self Extinguishing Formulations, Union Carbide Plastics Company, unpublished report (1960).

[62] Fawcett, H. H., Carbon Tetrachloride Mixtures in Fire Fighting, *Arch. Ind. Hyg. and Occup. Med.* 6, 435 (1952).

[63] Burlant, W. and Parsons, J., Pyrolysis of Polyacrylonitrile, *J. Polymer Science* 22, 249 (1956).

[64] Madorsky, S. G., "Thermal Degradation of Organic Polymers", Wiley (1964).

[65] Coleman, E. H., Gaseous Combustion Products from Plastics, *Plastics* 23, No. 10, 416 (1959).

[66] Sleik, H., and Turk, A., "Air Conservation Engineering," Connor Engineering Corporation, Danbury, Connecticut (1953).

[67] Sax, N. I., "Dangerous Properties of Industrial Materials", 3rd Edition, Reinhold, New York (1968).

[68] Haun, C. C., Vernot, E. H., Geiger, D. L., and McNerney, J. M., The Inhalation Toxicity of Pyrolysis Products of Bromochloromethane (CH_2BrCl) and Bromotrifluoromethane ($CBrF_3$), *Am. Ind. Hygiene Assoc. J.* 30, No. 6, 551 (1969).

[69] Birnbaum, H. A., Scheel, L. D., and Coleman, W. E., The Toxicology of the Pyrolysis Products of Polychlorotrifluoroethylene, *Am. Ind. Hygiene Assoc. J.* 29, 61 (1968).

[70] Scheel, L. D. Lane, W. C., and Coleman, W. E., The Toxicity of Polytetrafluoroethylene Pyrolysis Products--Including Carbonyl Fluoride and a Reaction Product, Silicon Tetrafluoride, *Am. Ind. Hygiene Assoc. J.* 29, 41 (1968).

[71] Coleman, W. E., Scheel, L. D., and Gorski, C. H., The Particles Resulting from Polytetrafluoroethylene (PTFE) Pyrolysis in Air, *Am. Ind. Hygiene Assoc. J.* 29, 54 (1968).

[72] Coleman, W. E., Scheel, L. D., Kupel, R. E., and Larkin, R. L., The Identification of Toxic Compounds in the Pyrolysis Products of Polytetrafluoroethylene (PTFE), *Am. Ind. Hygiene Assoc. J.* 29, 33 (1968).

[73] Scheel, L. D., McMillan, L., and Phipps, F. C., Biochemical Changes Associated with Toxic Exposures to Polytetrafluoroethylene Pyrolysis Products, *Am. Ind. Hygiene Assoc. J.* 29, 49 (1968).

[74] Nuttal, J. B., Kelly, R. J., Smith, B. S., and Whitside, C. K., Inflight Toxic Reactions Resulting From Fluorocarbon Resin Pyrolysis, *Aerospace Medicine* 35, 676 (1964).

[75] Thomas, D. M., and Connor, E. H., Management of the Patient Overcome by Smoke, *J. of the Kentucky Med. Assoc.* 66, 1051 (1968).

[76] Van Stee, EE. W., and Bock, K. C., Short-Term Inhalation Exposure to Bromotrifluoromethane, *Toxicology and Applied Pharmacology* 15, 164 (1969).

[77] Delayed Petrol Intoxication, *The Medical Journal of Australia* 2, No. 1, 3 (1969).

[78] Autian, J., Toxicologic Aspects of Flammability and Combustion of Polymeric Materials, *J. Fire and Flammability* 1, 239 (1970).

[79] Porter, R. W., Bratzler, L. J., and Pearson, A. M., Fractionation and Study of Compounds in Wood Smoke, *J. Food Sci.* 30, 615 (1965).

[80] Love, S. and Bratzler, L. J., Tentative Identification of Carbonyl Compounds in Wood Smoke by Gas Chromatography, *J. Food Sci.* 31, No. 2, 218 (1966).

[81] Rhee, K. S., and Bratzler, L. J., Polycyclic Hydrocarbon Composition of Wood Smoke, *J. Food Sci.* 33, No. 6, 626 (1968).

[82] Gellhorn, E., Carbon Dioxide and Oxygen Deficiency, *The Am. J. of Psychiatry* 93, No. 4, 1413 (1937).

[83] Zapp, J. A., Jr., "Toxicology of Fire", Army Chemical Center Mediccal Division, Special Report No. 4, April 1951.

[84] Pryor, A. J., Fear, F. A., and Wheeler, R. J., "Mass Fire Life Hazard--Experimental Study of the Life Hazard of Combustion Products in Structural Fires", OCD Work Unit 2537A, AD672 035, Southwest Research Institute, San Antonio, Texas, March 1968.

[85] Gaume, J. G., Burtek, P. and Rostami, H. J., Experimental Results on Time of Useful Function (TUF) After Exposure to Mixtures of Serious Contaminants, *Aerospace Medicine* 42, No. 9, 987 (1971).

ADDITIONAL REFERENCES RELATED TO FIRE GASES

Fire Gases, General

1. "Breathing Apparatus for the Fire Service", National Fire Protection Association, 60 Batterymarch St. Boston, Massachusetts (1966).
2. Easton, W. H., "Irritating Vapors Produced by Burning Cellulose Materials", *Journal of Industrial Hygiene and Toxicology* 27, 211 (1945).
3. Easton, W. H., Smoke and Fire Gases, *Industrial Medicine* 11, 466 (1942).
4. National Fire Protection Association Committee on Fire Gas Research, Fire Gas Research Report, *National Fire Protection Association Quarterly* 45, No. 3, 280 (1952).
5. Robertson, A. F., "Analysis of IMCO Fire Tests of Deck Covering Materials", National Bureau of Standards Report 10 045.
6. Williams, L. L., Toxicity of Fire Gases, *Fire Engineering* 112, No. 5, 372 (1959).

Toxicity of Gases and Pyrolysis Products

7. Aviado, D. and Salem, H., Acute Effects of Air Pollutants on the Lungs, *Arch. Environmental Health* 16, 903 (1968).
8. Conner, E. H., DuBois, A. B., and Comroe, J. H., Jr., Acute Chemical Injury to the Respiratory Tract and Lungs, *Anesthesiology* 23, 538 (1962).
9. Fitzpatrick, W., and Yeager, L. B., Respiratory Complications from Military Screening Smoke Bomb, *Quart. Bull. of Northwestern Univ. Medical School* 26, 313 (1952).

10. Greendyke, R. M., Accidental Death Due to Hydrofluoric Acid, *Journal of Forensic Science* 9, 383 (1964).

11. Leong, K. J., and MacFarland, H. N., Hazards from Thermal Decomposition of Epoxy Resins, *Arch. Environmental Health* 7, 675 (1963).

12. Lewis, C. E., and Kerby, G. R., An Epidemic of Polymer-Fume Fever, *JAMA* 191, No. 5, 375 (1965)).

13. MacFarland, H. N., and Leong, K. J., Hazards from the Thermodecomposition of Plastics - Polyurethane and Polyurethane Coated Nylon, *Arch. Environmental Health* 4, 591 (1962).

14. MacFarland, H. N., The Pyrolysis Products of Plastics-Problems in Defining Their Toxicity, *American Industrial Hygiene Association Journal* 29, 7 (1968).

15. Marks, J., Regiseal, an Industrial Hazard, *Proceedings of the Mine Medical Officers' Association* 47, 18 (1967).

16. Milliken, J. A., Waugh, D., and Kadish, M. E., Acute Interstial Pulmonary Fibrosis Caused by a Smoke Bomb, *Canadian Medical Association Journal* 88, 36 (1963).

17. Oettel, H., "Health Dangers During the Manufacture, Processing, and Decomposition of Synthetic Products", National Bureau of Standards Report 9833 (1968).

18. Paisley, D. P. G., Isocyanate Hazard from Wire Insulation: An Old Hazard in a New Guise, *British Journal of Industrial Medicine* 26, No. 1, 79 (1969).

19. Peters, J. M., Studies of Isocyanate Toxicity, *Proceedings Royal Society of Medicine* 63, 372 (1970).

20. Robbins, J. and Ware, R., Pulmonary Edema from Teflon Fumes, *New England Journal of Medicine* 271, 360 (1964).

21. Salem, H., and Cullumbine, H., Inhalation Toxicities of Some Aldehydes, *Toxicology and Applied Pharmacology* 2, 183 (1960).

22. Stone, H. H., Respiratory Burns: A Correlation of Clinical and Laboratory Results, *Annals of Surgery* 165, No. 2, 157 (1967).

23. Tepper, L. B., Hazards to Health; Teflon, *New Enngland Journal of Medicine* 267, No. 7, 349 (1962).

24. Tschumy, W., Pulmonary Infiltration with Eosinophilia due to Smoke Inhalation: Report of a Case and Comment on Pathogenesis, *Ann. Internal Med.* 49, 665 (1958).

25. Use of Pills for Smoke Poisoning Rapped, *International Rescuer*, 10, May-June 1963.

26. Walworth, H., and Virchow, W., Industrial Hygiene Experiences with Toluene Diisocyanate, *American Industrial Hygiene Association Journal* 20, 205 (1959).

27. Wilson, R. and McCormick, W., Acrylonitrile--Its Physiology and Toxicology, *Industrial Medicine* 18, 243 (1949).

28. Wilson, R. and Wilson, G., Toxicology of Diisocyanates, *ournal of Occupational Medicine* 1, 488 (1959).

9. Zapp, J. A., Jr., Hazards of Isocyanates in Polyurethane Foam Plastic Production, *Arch. Industrial Health* 15, 324 (1957).

30. Zapp, J. A., Jr., Toxic and Health Effects of Plastics and Resins, *Arch. Environmental Health* 4, 125 (1962).

Gases from the Thermal Decomposition of Plastics

31. Effect of Burning PVC, *Fire Engineering* 24, No. 2, 58 (1971).

32. Grimaldi, J. V., The Hazards of Synthetic Plastics, *Mechanical Engineering* 72, No. 12, 987 (1950).

33. Hilado, C. J., "Flammability Handbook for Plastics", Technomic Publishing Co., Stamford, Connecticut (1969).

34. Sinclair, J. E., A Simple Method of Identifying Common Burning Plastics, *Fire Engineering* 121, 10, 58 (1968).

35. Thrune, R. I., Gases Released When Fire Resistant Epoxy Resins Are Burned, *American Industrial Hygiene Association Journal* 24, 475 (1963).

Gases Produced by Burning Structures

36. Labes, W. G., The Ellis Parkway and Gary Dwelling Burns, *Fire Technology* 2, 287 (1967).
37. Shaffer, E. L., and Eickner, H. W., Corridor Wall Linings-Effect on Fire Performance, *Fire Technology* 5, No. 1, 243 (1969).

Analysis of Fire Gases

38. Boettner, E. A., and Weiss, G., An Analytical System for Identifying the Volatile Pyrolysis Products of Plastics, *American Industrial Hygiene Association Journal* 28, 535 (1967).
39. Crump, N., and Bartels, T., Toxic Gas Contaminants in Enclosed Environments, *Contamination Control* 9, No. 1, 20 (1970).
40. Fish, A., Franklin, H. H., and Pollard, R. T., Analysis of Toxic Gaseous Combustion Products, *J. Appl. Chem.* 13, 506 (1963).
41. Lee, T. G., "Analytical Methods for Measurement of Toxic Components of Gaseous Products in Fires - A Survey", National Bureau of Standards Report 9612 (1967).

Carbon Monoxide

42. "Air Quality Criteria for Carbon Monoxide", U. S. Department of Health, Education, and Welfare, National Air Pollution Control Administration Publication No. AP-62, Washington, D. C., March 1970.
43. Breysse, P., Chronic Carbon Monoxide Poisoning, *Industrial Medicine and Surgery* 30, 20 (1961).

44. "Carbon Monoxide, a Bibliography with Abstracts", U. S. Department of Health, Education, and Welfare, Public Health Service Publication No. 1503, Washington, D. C. (1966).

45. Chronic Carbon Monoxide Poisoning, *New England Journal of Medicine* 261, 1248 (1959).

46. Roughton, F. J. W., The Average Time Spent by the Blood in the Human Lung Capillary and Its Relation to the Rates of CO Uptake and Elimination in Man, *Amer. J. Physiol.* 145, 239 (1945).

GLOSSARY

ABS - Acrylonitrile-Butadiene-Styrene, polymers (plastics) consisting of the three aforementioned types of polymer molecules.

Adsorption - adhesion of a gas on a surface.

Asphyxia - symptoms produced when insufficient oxygen interferes with normal respiratory processes.

Blowing agent - foaming agent, a chemical additive which causes a plastic material to expand when heated.

Br_2 - bromine, a dark brown, irritating gas.

Carboxyhemoglobin (COHb) - a union of carbon monoxide with hemoglobin which prevents normal uptake of oxygen.

$CBrF_3$ - bromotrifluoromethane, a relatively non-toxic liquid or vapor used as a fire extinguishant.

CCl_4 - carbon tetrachloride, a toxic liquid or vapor formerly used as a fire extinguishant.

CH_2BrCl - bromochloromethane, a relatively non-toxic liquid or vapor used as a fire extinguishant.

Cl_2 - chlorine, a highly irritating, toxic gas.

ClO_2 - chlorine dioxide, a red-yellow irritating gas formed during combustion of certain materials.

CO - carbon monoxide, a colorless, odorless toxic gas formed during combustion of carbon-containing materials.

CO_2 - carbon dioxide, a colorless, odorless gas, toxic at high concentrations, formed during combustion of carbon-containing materials.

$COCl_2$ - phosgene or carbonyl chloride, a highly toxic, irritant gas.

COF_2 - carbonyl fluoride, a highly toxic, irritant gas.

Combustion - burning, the rapid combination of oxygen and a fuel.

Co-polymer - a polymer (plastic) containing two or more different kinds of molecules.

Edema - swelling due to the accumulation of excess fluid in any body tissue.

Foaming Agent - see blowing agent.

H_2 - hydrogen, an odorless, colorless, combustible gas sometimes formed in fires.

Halide - chemical compounds containing a halogen and other non-carbon elements.

Halogen - group of elements which includes fluorine, chlorine, bromine and iodine.

HCl - hydrogen chloride, an acrid, colorless gas.

HCN - hydrogen cyanide, a highly toxic, colorless gas.

Hemoglobin - coloring matter of red blood cells which combines with oxygen and liberates it as required for metabolic processes in the body.

HF - hydrogen fluoride, an irritating, colorless gas.

H_2S - hydrogen sulfide, an irritating colorless gas with the odor of rotten eggs.

Hyperventilation - increased pulmonary ventilation causing decrease in normal carbon dioxide concentration in the body, manifested by faintness, dizziness, or even unconsciousness.

NH_3 - ammonia, an irritating gas with a characteristic pungent odor.

NO - nitric oxide, an irritating gas.

NO_2 - nitrogen dioxide, an irritating red-brown gas, highly toxic.

O_2 - oxygen, a colorless, odorless gas making up 21 percent of the normal atmosphere.

Organic - any material containing carbon.

Physiological - characteristics of the processes and functions occuring in living organisms.

ppm - parts-per-million, as used here a measure, by volume, of gas concentrations.

PVC - polyvinylchloride, a chlorine containing plastic.

Pyrolysis - thermal decomposition.
SO_2 - sulfur dioxide, a colorless, irritating gas.
TLV - threshold limit value, the time weighted concentration of a particular substance which may be tolerated by most humans for an 8 hour day and 40 hour week with no adverse effects.
Toxicology - the study of poisons.