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INHALATION TOXICITY OF PYROLYSIS PRODUCTS OF MONOBROMOMONOCHLOROMETHANE (CB) AND MONOBROMOTRIFLUOROMETHANE ($CBrF_3$)

C. C. HAUN, E. H. VERNOT, J. D. MacEWEN
D. L. GEIGER, J. M. McNERNEY, and R. P. GECKLER

AEROJET-GENERAL CORPORATION

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AEROSPACE MEDICAL RESEARCH LABORATORIES
AEROSPACE MEDICAL DIVISION
AIR FORCE SYSTEMS COMMAND
WRIGHT-PATTERSON AIR FORCE BASE, OHIO

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FOREWORD

This is one of a series of reports describing toxicological research performed in the Toxic Hazards Research Unit. This report is concerned with the inhalation toxicology of the pyrolysis products of monobromomonochloromethane (CB) and monobromotrifluoromethane ($CBrF_3$), materials of interest to the Air Force as fire extinguishers. The experiments reported are a part of a continuing program of research conducted by Aerojet-General Corporation under Contract No. AF 33(657)-11305 for the Toxic Hazards Division, Biomedical Laboratory, Aerospace Medical Research Laboratories, Wright-Patterson Air Force Base, Ohio. The contract was initiated in support of Project No. 6302, "Toxic Hazards of Propellants and Materials," and Task No. 630201, "Toxicology." A. A. Thomas, M. D., and K. C. Back, Ph. D., were contract monitors for the Aerospace Medical Research Laboratories.

J. D. MacEwen, Ph. D., is the principal investigator for the research program. This report is identified as Aerojet-General Corporation Report No. 3320. This research was conducted over a 9 month period beginning September 1965 and completed in June 1966.

This technical report has been reviewed and is approved.

WAYNE H. McCANDLESS
Technical Director
Biomedical Laboratory
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ABSTRACT

The toxicities of the pyrolysis products of two fire extinguishant compounds, CH_2ClBr and $CBrF_3$, were investigated using albino rats and 14 day LC_{50} values were determined for single 15-minute exposures. Both fire extinguisher compounds, currently used by the USAF for aircraft fires, were pyrolyzed at 800 C in a hydrogen-oxygen flame. The pyrolysis products of each compound were examined and the principal constituents were identified and quantitated. The determined LC_{50} value of 2300 ppm for pyrolyzed $CBrF_3$ produced a hydrogen fluoride concentration of 2480 ppm consistent with the reported LC_{50} value for a single 15-minute exposure to this gas. Monobromomonochloromethane pyrolysis products were found to have a LC_{50} of 465 ppm (as CH_2ClBr) under the experimental parameters tested. The toxic response producing this LC_{50} value appeared to result from a mixture of hydrogen chloride, hydrogen bromide, and bromine gases.

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SECTION I

INTRODUCTION

Monobromotrifluoromethane ($CBrF_3$) has been suggested as a replacement for monobromomonochloromethane (CB) as a fire extinguishing compound, because it is essentially nontoxic in its natural form and exhibits greater thermal stability than most other halogenated fire extinguishing materials. The inhalation toxicity of both of these compounds had been studied in some detail but little was known of the nature and toxicity of their pyrolysis products formed when used as fire extinguishants.

Chambers and Krachow (ref. 1) reported that albino rats were able to tolerate concentrations of $CBrF_3$ as high as 834,000 ppm for periods up to 15 minutes without adverse effects. Higher concentration of this gas produced anoxia in the laboratory animals. Chambers and Krachow also reported an approximate lethal concentration (ALC) resulted from the pyrolysis of 14,000 ppm $CBrF_3$. Comstock et al (ref. 2) reported that delayed deaths in rats occurred after 15-minute exposures to 20,000 ppm CB while deaths during exposure occurred only in exposures above 27,000 ppm. Svirbely et al (ref. 3) found the $LC_{50/7\ hr}$ value for mice to be 2273 ppm. A 15-minute ALC_{50} of 65,000 ppm unpyrolyzed CB for rats has also been reported as compared to 834,000 ppm for $CBrF_3$ reported by Engibus and Torkelson (ref. 4).

As the result of the study of vaporizable fire extinguishants by Engibus and Torkelson, more comprehensive investigations were recommended of the toxicity of pyrolyzed fire extinguisher agents to be undertaken to establish the applicability of these materials to U S Air Force fire protection problems.

The experiments described were conducted to define the toxicity of $CBrF_3$ pyrolysis products and to attempt to identify the pyrolysis products responsible for the observed toxicity. Samples of CB were also pyrolyzed and investigated for comparative purposes.

SECTION II

MATERIALS AND METHODS

ANIMAL EXPOSURE FACILITIES

Animal exposure facilities of the Air Force Aerospace Medical Research Laboratories as described elsewhere (ref. 5) were used for the experiments being reported. In particular, the Longley inhalation exposure

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chambers were used. These chambers (shown in figure 1) are maintained at 72 + 5 F and 50% + 10% RH. Air flow is variable up to 50 cfm and the flow maintained for a particular experiment was used in part to effect the desired contaminant concentration. The Longley chambers have a 4-foot cubical center section made of 3/8-inch thick, transparent plastic with a stainless steel frame. The chamber has a truncated cone-shaped lower section similar to Rochester chamber design. The upper section of the chamber is composed of four individual truncated cones which permit the chamber to be subdivided into units of 2 or 4 sections using either an independent air supply for each or a common supply for all. In the current experiments, the chamber was subdivided into the four compartments. Each subchamber has a volume of 0.6 M^3 in the subdivided condition. When fully opened, the chamber is approximately 2.5 M^3 in volume. The individual compartments are divided into a lower and upper level by means of a stainless steel, expanded metal grating.

Individual air-sampling ports are located in each of the four chamber compartments so that samples for chemical analysis of the chamber air may be obtained.

Special baffle plates are located in the upper portions of the chambers to assure a uniform concentration and also a frontal movement of the contaminant when exposures are begun. As a result of this feature, almost square wave exposures can be accomplished; in short acute exposures, such as the ones being reported, this is most important.

PYROLYSIS METHOD AND INTRODUCTION INTO CHAMBER AIR

Contaminant Generation and Administration

A special apparatus for pyrolyzing materials was constructed, using commercially available components. The pyrolyzer was placed just upstream from the chamber within the air supply duct. Desired concentrations were achieved by a combination of controlling chamber air flow and test material flow. A schematic of the system as used with $CBrF_3$ is shown in figure 2.

The pyrolysis unit consisted of an atomizer-burner assembly (Beckman Model 4060) mounted in a 4-inch stainless steel spool piece. A small quartz window was installed in the spool piece to permit continuous observation of the combustion process and to permit placement of an adjustable chromel-alumel thermocouple in the oxygen-hydrogen flame. The pyrolysis of the test materials in all experiments reported herein was conducted at 800 C which produced a 32 mv signal from the thermocouple. The

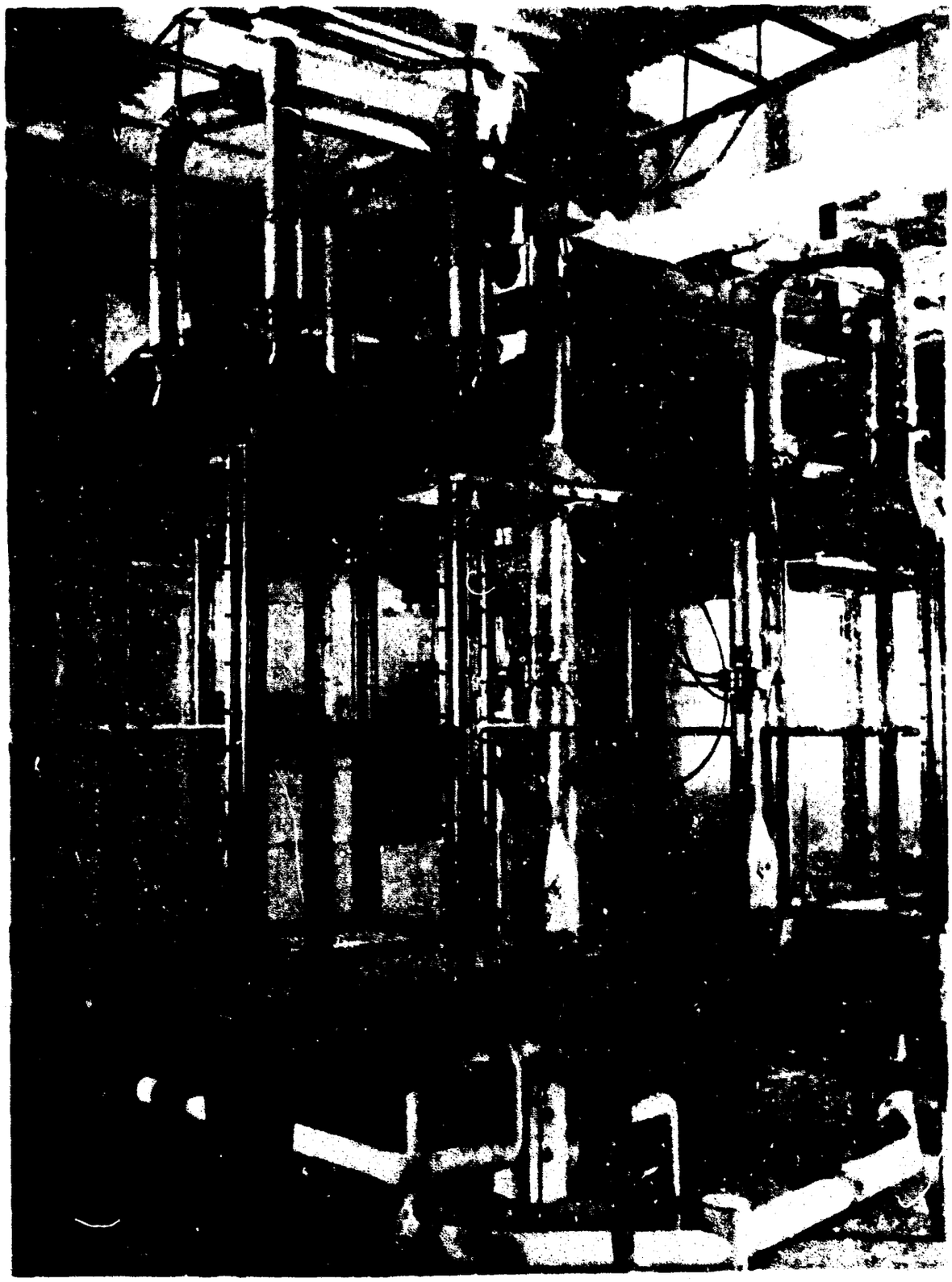


Figure 1
Longley Exposure Chambers

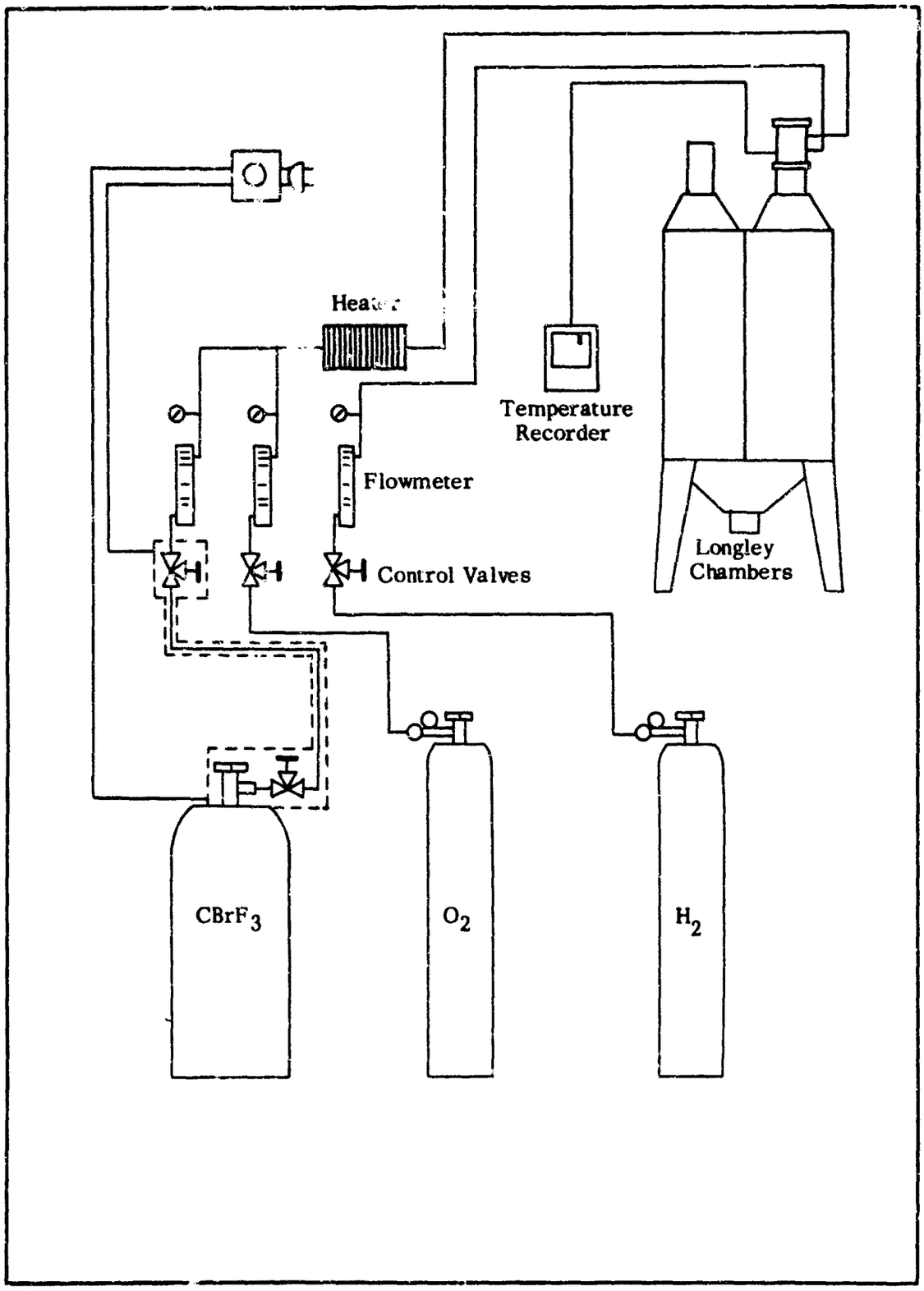


FIGURE 2
Schematic of $CBrF_3$ Pyrolysis System

thermocouple signal was transmitted to a millivolt recorder which was used to monitor the flame temperature.

The pyrolyzer burner assembly had three input lines; two for the combustion materials oxygen and hydrogen, which were mixed at the burner tip. The third line led to a capillary aspirator tube which was used for introduction of CB into the flame but not for $CBrF_3$. The metered flow of $CBrF_3$ was premixed with a known amount of oxygen and the capillary aspirator was not used.

Desired chamber concentrations of CB were established by metering the CB through a dual syringe feeder into the capillary aspirator and then into the oxygen-hydrogen flame. The experimental apparatus is shown in schematic form in figure 3.

Since $CBrF_3$ is a gas obtained in pressurized cylinders, the desired chamber concentrations were obtained by passing the gas through a flow meter and the feed rate was controlled by a micrometer metering valve. The sample was then blended with a controlled flow of the oxygen gas prior to introduction into the flame. It was necessary to wrap the gas supply tubing with heating tape since the $CBrF_3$ underwent adiabatic expansion at the metering valve and would become liquified if not rewarmed. A modest amount of heat revaporized the $CBrF_3$ before blending with hydrogen.

Chlorobromomethane for the experiments described herein was obtained from Air Force supplies of fire extinguisher fluid and manufactured under military specification MIL-B-4394-B. Two supply sources were used for $CBrF_3$. Most of the $CBrF_3$ experiments were conducted with material obtained from Dow Chemical Company meeting military specification MIL-B-12218-A. However, one series of exposures was carried out using more highly purified material obtained from DuPont Chemical Corporation meeting the newest military specification, MIL-M-12218-B.

Chamber air samples were collected in a tonometer for analysis of test materials. The unpyrolyzed test material concentrations were established with preset gas flow rates and chamber air flow rates before ignition of the pyrolysis unit. A second air sample was collected for analysis of CB or $CBrF_3$ after ignition of the pyrolysis unit and the net difference in concentration was assumed to represent the concentration of pyrolyzed test agent. The concentrations of test agents fed into the chamber were also evaluated by flow measurements of the air supply and contaminant feed supply.

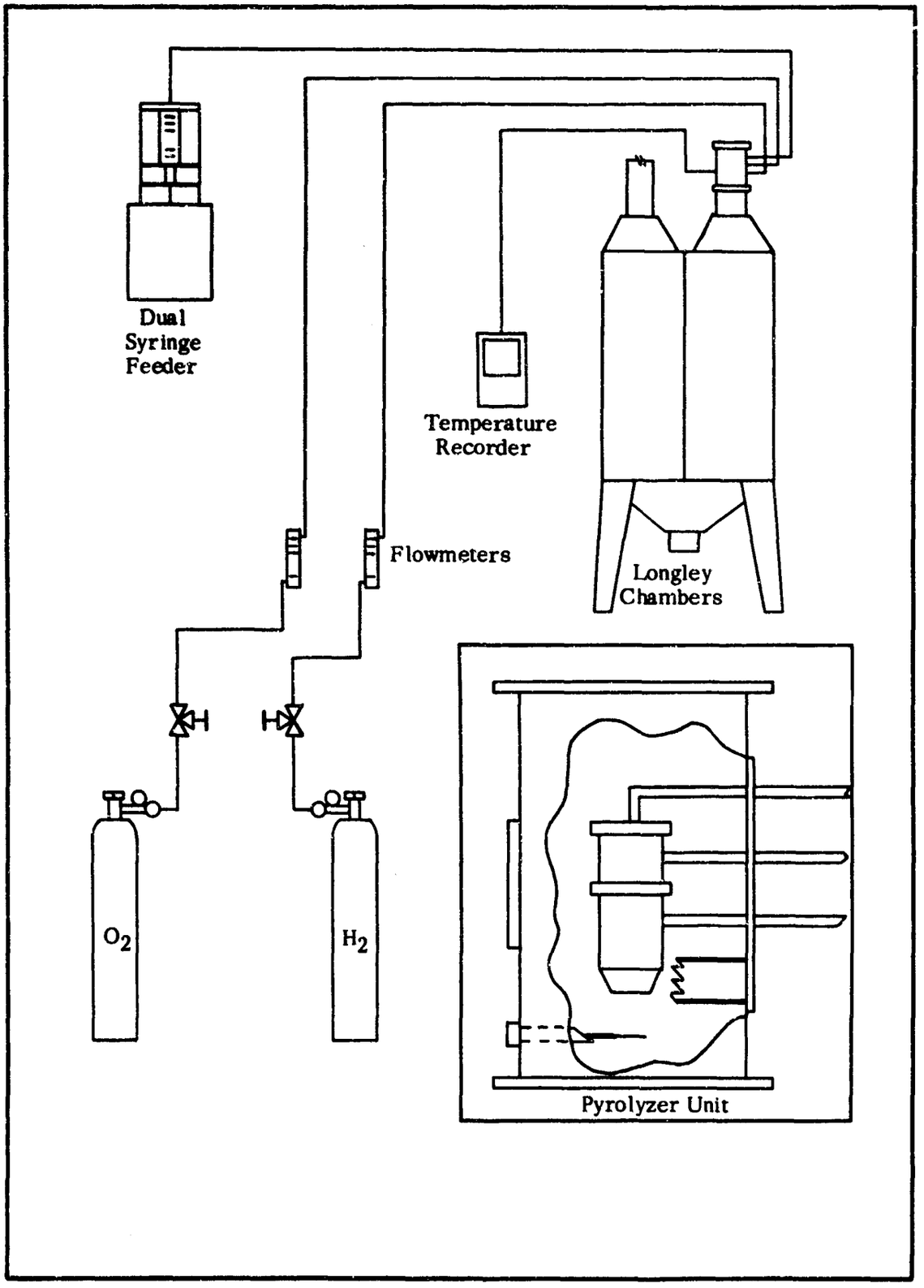


FIGURE 3
Schematic of CB Pyrolysis System

ANALYTICAL CHEMISTRY METHODS

Monobromomonochloromethane and Its Pyrolysis Products

Monobromomonochloromethane is capable of being transformed into many products in a hydrogen-oxygen flame. These include HCl, HBr, phosgene ($COCl_2$), $COBr_2$, and a variety of halogenated hydrocarbons. Since all of these may contribute to the toxicity of the pyrolysate, a scheme of analysis was devised which would yield quantitative data on these pyrolysis products.

The method used for total strong acid (HCl + HBr) analysis was the back titration with HCl after absorption in NaOH, using bromphenol blue as indicator (Kolthoff and Sandell (ref. 6)). Theoretically, bromphenol blue indicator with a pH range of 3.0-4.6 titrates Na_2CO_3 as if it were NaOH, and therefore CO_2 should not be determined in an acid mixture. For the determination of HBr and HCl, potentiometric titrations of Cl^- and Br^- with $AgNO_3$ solution were used (Bowers et al (ref. 7)).

Analysis for elemental bromine was conducted by sample collection in chloroform using a glass fritted midget impinger and measuring absorbance of the solution at a wavelength of 412 mμ (Snell and Snell (ref. 8)). The bromine analyses were verified by sample collection in KI solution, followed by the back titration of liberated iodine with sodium thiosulfate (Kolthoff and Sandell (ref. 6)). Chlorine and phosgene were determined by a gas chromatographic technique described by Priestly (ref. 9). Individual halogenated hydrocarbons were identified and their concentrations determined using a combination of gas chromatography and mass spectrometry described by Bieman (ref. 10)).

$CBrF_3$ and Its Pyrolysis Products

Analysis was performed to determine the chamber air concentration of unpyrolyzed $CBrF_3$, HF, HBr, BR_2 and halogenated hydrocarbons. HBr and Br_2 were also determined by the methods previously described for CB and its pyrolysis products.

Hydrogen fluoride concentrations were determined by the method of Rodgers and Yasuda (ref. 11) which involved sample absorption in NaOH, followed by neutralization and decolorization of ferric salicylate.

Unpyrolyzed $CBrF_3$ was determined by a gas chromatographic method using a molecular sieve column. Under the conditions used, air is

held back but $CBrF_3$ is not, and therefore $CBrF_3$ can be detected and measured separate from air. The gas chromatographic conditions are as follows:

Column - 8' x 1/4" SS Molecular Sieve 5A, 60-80 mesh.
Temperature - column 120 C, injector - 100 C, detector - 150 C.
Thermal conductivity detector, 250-ma current.
Carrier gas - helium, pressure - 50-psi., flow rate - 80-ml/min.

Five ml samples of chamber atmosphere are injected into the gas chromatograph, and the concentration of unpyrolyzed $CBrF_3$ determined from the $CBrF_3$ peak height. The peak height is measured from the forward base line to the vertex.

Standards are prepared by mixing appropriate volumes of $CBrF_3$ and air (1 ml $CBrF_3$ in 1000 ml air = 1000 ppm).

The state of hydration of the Molecular Sieve column is important in the retention of air and not $CBrF_3$. Therefore, a small amount of water (0.25 ml) is injected into the molecular sieve gas chromatographic column at weekly intervals and a new calibration curve must be prepared daily.

To determine individual halogenated hydrocarbons, a sample of the organic pyrolysis products from the exposure chamber atmosphere was introduced into a mass spectrometer and the resulting mass spectrum analyzed for the presence of carbon-halogen compounds.

EXPERIMENTAL ANIMALS

Male albino rats, 6-8 weeks of age, were obtained for the experiments from Greenacres Laboratory. These animals originated from germ-free Wistar rats obtained from the Lobund Institute and were disease-free with respect to common respiratory and intestinal forms of rodent disease. Before and after exposures, the animals received Rockland mouse diet ad libitum. Rat weights were recorded on the day of exposure and, for survivors, 3-, 7-, and 14-days postexposure, at which time the animals were killed. Tissue samples were taken from lung, kidney, liver, spleen, and heart and submitted for histopathologic examination.

Exposures were carried out in the following fashion. Animals were placed in cages within the exposure chamber; the pyrolysis unit was ignited and timing of the 15-minute exposure begun. During animal exposures, combustion temperatures were continuously monitored and air samples were collected for chemical analysis of unpyrolyzed test agent and its thermal degradation products. The animals were continuously observed for

signs of toxic response both during exposure and for approximately 4-hours postexposure. The animals were then held 14 days for postexposure observation.

SECTION III

EXPERIMENTAL RESULTS

ANALYTICAL CHEMISTRY

Varying concentrations of CB and $CBrF_3$ in air were subjected to pyrolysis and the resulting mixtures analyzed for the appropriate decomposition products. The unpyrolyzed original material was also examined for minor contaminating constituents. The quantities of inorganic acids, halogens and phosgene formed by the pyrolysis of CB are presented in table I for various concentrations of CB. The same data are presented as mole percentages in table II. Complete pyrolysis of CB to HCl and HBr would have yielded 100-mole percent of HBr and 200 mole percent of strong acid. Complete conversion of the bromine portion of the molecule to Br_2 would also have led to 100 mole percent of pyrolyzed CB. Theoretically, the sum of HCl and HBr concentrations should equal that of strong acid. In actuality, the mole percent yield of acid measured (69 ± 8) was higher than the sum of the two strong acids which may indicate a possible error in the strong acid titration procedure due to the presence of CO_2 or a contribution to the strong acid value by trapped bromine.

The analyses indicate that approximately 50% of the pyrolyzed CB chlorine is converted to HCl and only insignificant amounts to chlorine and phosgene. In contrast to this finding, only 4% of the pyrolyzed bromine is found as HBr, while over 10% is oxidized to free Br_2.

The carbon-halogen compounds and their relative concentrations in unpyrolyzed CB are compared in table III with the organic compounds found after pyrolysis. The individual compounds were separated and identified using a gas chromatograph in combination with a mass spectrometer. The concentrations listed are percentages of the total amount of carbon-halogen compounds as measured using the gas chromatographic peak height.

A number of new organic compounds not contained in the original CB have been produced during pyrolysis, and in these new compounds the relative concentration of bromine has been increased. The formation of bromine containing organic compounds offers a partial explanation of the fate of bromine on pyrolysis.

Table I

Pyrolysis Products Formed During Combustion of CH_2BrCl at 800 C (ppm)

Measured Pre-Ignition Conc.	Unpyrolyzed CH_2BrCl Conc.	Pyrolyzed CH_2BrCl Conc.	Strong Acid	HCl	HBr	Cl_2	Br_2	$COCl_2$
550	360	190					11	
750	490	260					18	
1000	650	350	270			<1		<0.2
1000	650	350	230					
1575	900	675		350	36			
2000	1275	725	470	380	23			
3000	1975	1025					45	

Table II

Average Mole Percent of Compounds Formed During Pyrolysis of CH_2BrCl at 800 C

Strong Acid	HCl	HBr	Cl_2	Br_2	Phosgene
69 ± 8	52 ± 4	4.3 ± 1.0	<0.35	11.2 ± 2.5	<0.07

Table III

Carbon-Halogen Compounds in Untreated Monobromomonochloromethane and in Pyrolysate

Parent Material		Chamber Air Samples of Pyrolysate	
Compound	% Total Organics	Compound	% Total Organics
CH_2Cl_2	1.00	CH_3Cl	0.015
CH_3NO_2	0.21	CH_2Cl_2	0.74
CB	98.60	CH_3NO_2	0.15
CH_2Br_2	0.19	CB	96.20
	100.00	CH_2Br_2	1.44
		CCl_4	0.005
		$CHBr_2Cl$	1.27
		CCl_3Br	0.18
			100.00

Table IV

Concentration of Pyrolysis Products Produced by Ignition of Monobromotrifluoromethane at 800 C (ppm)

Unpyrol. $CBrF_3$	Pyrol. $CBrF_3$	HF	HBr	Br_2
3920	2340	2280		283[1] 227[2]
3800	2070	2370	160	236[2]

Notes: 1. Spectrophotometric method
2. Volumetric method

The pyrolysis of $CBrF_3$ produced only 3 major inorganic constituents; namely HF, HBr and Br_2 as shown in table IV.

One-third of the available fluorine from the pyrolyzed $CBrF_3$ was apparently converted into HF and one-third of the available bromine into HBr and Br_2 with much more bromine going to Br_2 than the HBr.

A clue to the fate of the remaining pyrolyzed fluorine was obtained from the mass spectrum of the pyrolysis products of $CBrF_3$. In addition to the expected mass spectrum of $CBrF_3$, a very high peak at mass number 85 was obtained. This is equivalent to the fragment - OCF_3. The highest mass number measurable was approximately 282 which would correspond to the molecule:

$$CF_3O\text{-}CH_2CH\ (OCF_3)_2.$$

The mass number 85 is much the highest in the pyrolysis product mass spectrum indicating that a significant amount of -OCF_3 containing product is formed.

Not all of the pyrolyzed bromine and chlorine in the case of CB or the pyrolyzed bromine and fluorine in the $CBrF_3$ could be accounted for by analysis. The material balance did not yield 100% of the material introduced into the chambers for pyrolysis and the loss of these materials may be explained by their reaction with the chamber itself. The exposure chamber and the air diffuser system are constructed of type-304 stainless steel which is readily attacked by halogen acids (HCl, HBr, and HF) and by bromine according to Monypenny (ref. 12) and to the Stainless Steel Handbook (ref. 13). Observation of the exposure chamber after each pyrolysis experiment revealed that the metal had been attacked by these acid gases and indeed small amounts of green chromium salts were leached out of the metal and deposited on its surface.

ANIMAL EXPOSURE

Using the exposure methods described in an earlier section, a series of inhalation exposures were conducted on rats with the results presented in table 5 for CB and in tables VI and VII for $CBrF_3$. These tables present the concentration of unpyrolyzed and pyrolyzed material with the resulting mortality in groups of exposed rats. The results of animal exposures to $CBrF_3$ meeting military specification MIL-M-12218-A are presented in table VI and exposure data from $CBrF_3$ meeting MIL-M-12218-B specifications are shown in table VII. A statistical comparison of the data in these 2 tables did not demonstrate significant differences. The response of rats exposed to pyrolysis products of both CB and $CBrF_3$ was fairly uniform

Table V

Results of Exposure to the Pyrolysis Products of CH_2BrCl

Nominal Metered Conc. ppm	Actual Meas. Conc.	Pyrol. CB Conc.	% Pyrol. CB of Actual Meas.	Mort. Ratio	% Mort.	Day of Death Post Exposure 0	1	2
500	550	190	34.5	0/20	0			
1000	1075	355	33.0	4/20	20	3	1	
1000	1050	360	34.3	10/20	50	10		
1000	1050	450	42.9	9/20	45		9	
1000	1050	460	43.8	15/20	75	13		2
1000	1000	500	50.0	7/20	85	6	1	
1500	1575	675	42.8	17/20	85	17		
1500	1650	800	48.5	16/20	80	16		
2000	2100	900	43.0	19/20	95	19		
3000	3050	1025	33.5	19/20	95	18		1
3000	3213	1413	44.0	20/20	100	20		

Table VI

Results of Exposure to the Pyrolysis Products of $CBrF_3$
Military Specification MIL-B-4394-B

Nominal Metered Conc.	Actual Meas. Conc.	Pyrolysis $CBrF_3$ Conc.	% Pyrolysis $CBrF_3$ of Actual Meas.	Mortality Ratio	% Mortality	Day of Death-Post Exposure 1	2	3	4	5	6	7	8	9	10	11	12	13	14
3500	3400	1700	50.0	0/10	0														
4000	4000	1950	48.7	5/10	50				3	2									
4000	4000	2100	52.5	5/10	50				4	1									
4000	4000	2300	57.5	5/10	50	1		1	3										
5000	5300	2750	52.0	6/10	60	1			2	3									
6000	5950	3075	51.8	6/10	60	1	1		1	1		1				1			
6000	6050	3250	53.8	8/10	80	2		1	2	1									2
7000	7150	3780	52.9	9/10	90	5	3		1										
8000	7900	4475	56.5	9/10	90	1	1	5	2										

All concentrations in ppm.

Table VII

Results of Exposure to the Pyrolysis Products of $CBrF_3$
Military Specification MIL-B-12218-A

Nominal Metered Conc.	Actual Meas. Conc.	Pyrolyzed $CBrF_3$ Conc.	% Pyrolysis of Actual	Mortality Ratio	Days After Exposure 1	2	3	4	5	6	7
4000	4000	2270	56.8	4/10	1	1			1		1
6000	6090	3840	57.5	10/10	10						
6000	6090	3250	53.4	10/10	10						
4000	4300	1850	43.0	5/10	1		2	2			

although dose dependent. Typical reactions included lacrimation, excessive salivation, hyperactivity (although no convulsions occurred), labored breathing or gasping and, finally, prostration and unconsciousness. Time to death differed in the two series. As may be seen from the tables, there was a large number of delayed deaths in the groups exposed to $CBrF_3$ pyrolysis products. With CB products, on the other hand, no deaths occurred after the third day subsequent to exposure. Fourteen days after exposure, survivors were killed, gross pathology observed and tissue samples taken for histopathology evaluation.

The mortality data were used to calculate LC_{50} values by the modified Litchfield-Wilcoxon technique (ref. 14). The data and best fit lines for CB and $CBrF_3$ pyrolysis products are plotted in figure 4. The 15-minute LC_{50} value for CB pyrolysis products is 465 ppm; analysis of the data yielded a range of 424-511 at the 95% confidence level. $CBrF_3$ pyrolysis products produced a 15-minute LC_{50} value of 2300 ppm with a range of 1890-2799 at the 95% level of confidence.

During the postexposure period, weights of the surviving animals were taken. Following every exposure, weight loss was demonstrated after 3 days followed by resumption of growth. Data are presented in table VIII for CB pyrolysis products and table IX for $CBrF_3$ pyrolysis products. A small but significant dose response of approximately 1% weight loss per 100 ppm pyrolysis products is also shown in table IX. The variability of the data in table IX does not permit a dose response to be shown. In addition, the weight loss caused by $CBrF_3$ pyrolysis products is greater than for CB pyrolysis products by about 7% at the end of three days in those rats that survive 14-days postexposure.

SECTION IV

PATHOLOGY

MONOBROMOMONOCHLOROMETHANE

The inhalation of the pyrolysis products of monobromomonochloromethane by albino rats produced rapid deaths in affected animals, usually occurring within the first 8 hours postexposure. An occasional rat, however, died on the second or third postexposure day with all other animals showing rapid recovery from the initial shock of their exposure. The survivors appeared healthy by the fourteenth day of postexposure and were rapidly reestablishing their normal growth pattern.

A uniform pathologic response was observed in all rats that died regardless of the actual exposure concentration of inhaled monobromomono-

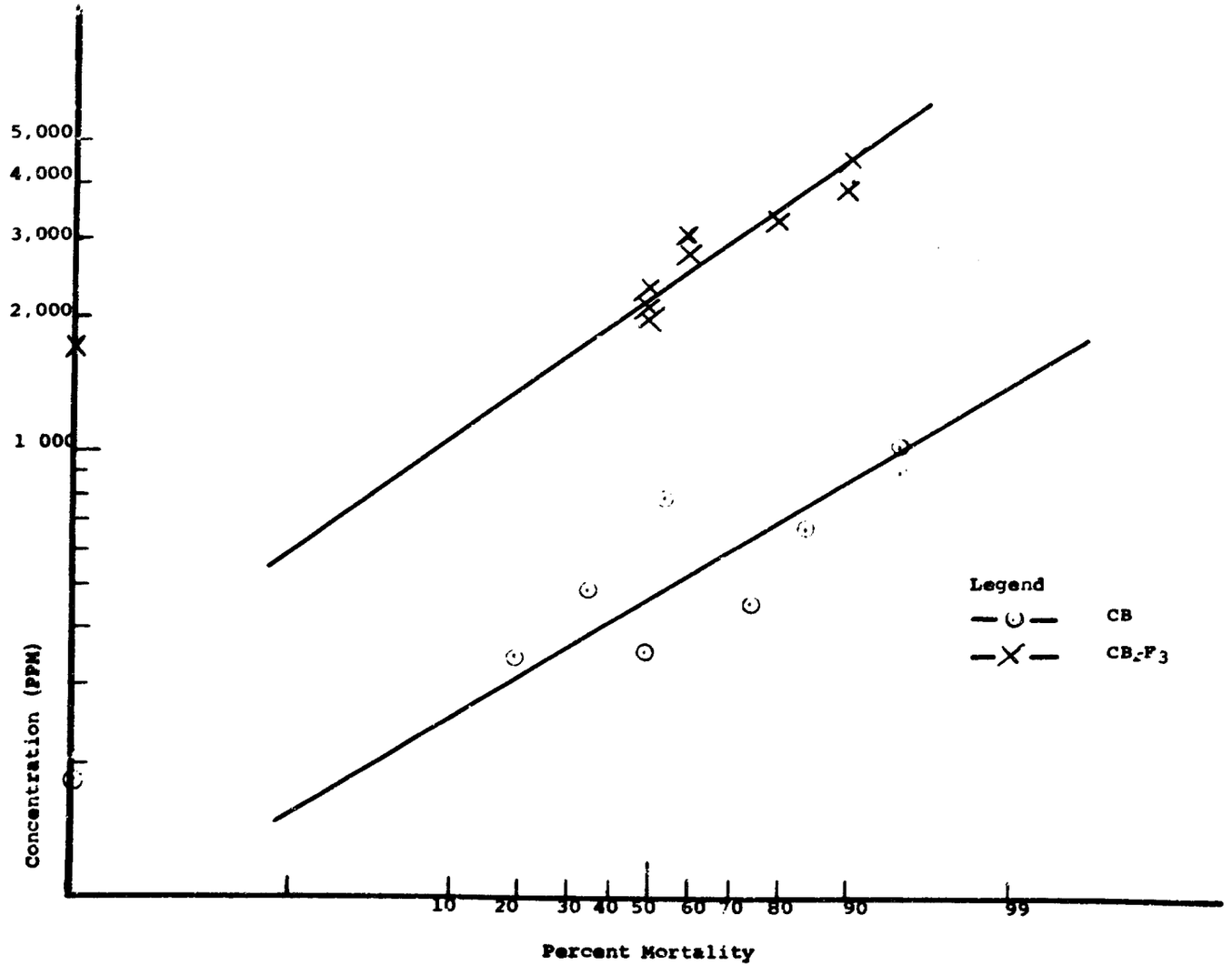


FIGURE 4
Mortality Versus Concentration of Pyrolysis Products of (CB) Monobromomonochloromethane and (CBrF3) Monobromotrifluoromethane Probability Plot

Table VIII

Mean Weights of Rats Surviving Exposure to the Pyrolysis Products of CH_2BrCl

(Grams Body Weight)

Exposure ppm as CH_2BrCl	Day Post Exposure				Number of Rats
	0	3	7	14	
190	202	193	212	215	20
355	204	188	204	208	16
360	211	197	210	238	10
450	250	231	246	267	11
460	203	176	192	224	5
500	256	232	244	269	12
675	278	242	242	266	3
800	228	194	210	258	4
900	223	199	171	213	1
1025	200	175	195	218	1
1413	100% Mortality				

Table IX

Mean Weights of Rats Surviving Exposure to the Pyrolysis Products of $CBrF_3$

Exposure ppm as $CBrF_3$	Day Post Exposure				Number of Rats
	0	3	7	14	
1700	235	208	220	230	10
1850*	196	144	h. d.	201	5
1950	224	185	197	211	5
2100	182	151	150	178	5
2270*	193	179	191	217	6
2300	205	n. d.	184	207	5
2750	189	172	178	207	4
3075	201	160	164	164	4
3250	208	156	163	216	4
3780	220	198	183	216	1
4475	201	158	164	203	1

*Material meeting military specification MIL-B-4394-B. Other data are from material meeting MIL-B-12218-A.

chloromethane pyrolysis products. The response was generally limited to pulmonary tissue due to the rapid onset of effects and resultant deaths. Widespread pulmonary edema and congestion with patchy areas of hemorrhage were seen in all lobes of the lung. No significant pulmonary changes were observed in surviving rats killed on the fourteenth postexposure day.

MONOBROMOTRIFLUOROMETHANE

The mortality pattern observed in albino rats exposed to the pyrolysis products of $CBrF_3$ by the inhalation route was one of delayed response. The majority of animals that died as a result of their exposure succumbed between the third and fifth postexposure day although occasional deaths were observed up to the fourteenth day. In the highest concentration tested, near or at the LC_{100} level, animal deaths were more rapid and occurred during exposure or within the next few hours. The immediate deaths resulting from exposure to the pyrolysis products of $CBrF_3$ were characterized by severe pulmonary changes of diffuse congestion, edema, and hemorrhage, with some emphysematous reaction in a portion of the animals.

In those animals displaying the more typical mortality pattern of delayed death, pulmonary changes were also significant but not as acute in nature. The lungs were congested with focal hemorrhage and mild interstitial edema. A frequent finding was cellular infiltration of the alveolar spaces with interstitial pneumonitis and proliferative and fibrotic peribronchitis. The incidence of renal tubular necrosis, pericarditis and occasional myocardial necrosis was also noted. Animals receiving inhalation exposures higher than the LC_{50} level consistently exhibited signs of mucous membrane and corneal irritation. The noses of these animals were crusted with flakes of blood and scab formation occurred shortly after exposure. Most rats had a brown granular exudate surrounding swollen eyelids and many exhibited a dense white corneal opacity. In animals surviving $CBrF_3$ pyrolysate, exposure at our near the LC_{50} level, slight chronic changes such as mild pulmonary congestion and emphysema were observed although these animals appeared to be healthy and were returning to a normal growth pattern.

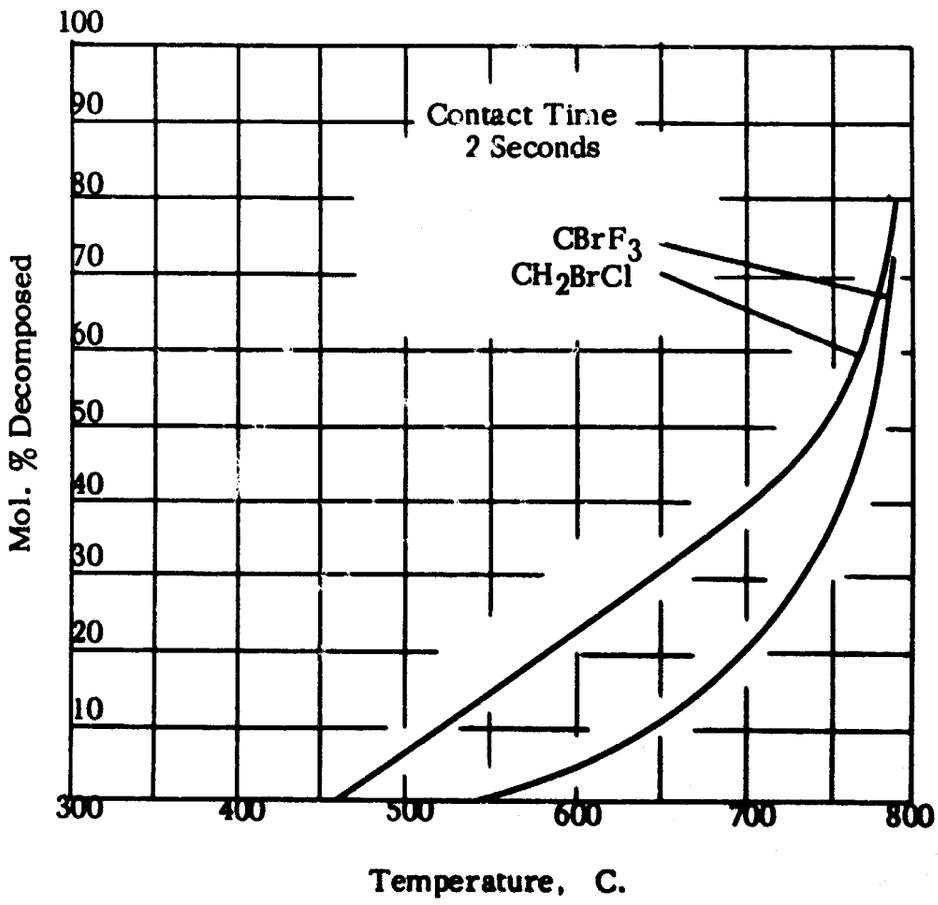
SECTION V

DISCUSSION AND CONCLUSIONS

The data reported in the preceding sections support the contention, certainly, that $CBrF_3$ and its pyrolysis products are less toxic than CB and its pyrolysis products. In comparing these new data with those in the literature, it is most important to know the temperature and other conditions of pyrolysis accurately. A plot of thermal decomposition versus temperature of CB and $CBrF_3$ is shown in figure 5 (data from reference 4). The

FIGURE 5

Thermal Decomposition of Two Fire Extinguishant Compounds



flame temperature used in the present work was maintained at 800 C which would be expected to yield essentially complete pyrolysis; however, the analytical data revealed that pyrolysis of CB ranged from 33% to 50%. The amount of $CBrF_3$ pyrolyzed was generally higher, ranging from 50% to 57%. The test material introduced into the flame apparently failed to remain long enough for complete pyrolysis. Treon et al (ref. 15) performed experiments in which $CBrF_3$ was pyrolyzed in an Inconel tube heated at various temperatures up to 1090 C. At 1090 C, 61% was pyrolyzed; again, a short contact time is the most logical reason for incomplete pyrolysis. The studies on the toxicity of $CBrF_3$ pyrolyzed at 1090 C reported by Treon et al are the only data in their experiments comparable to those being reported here. Exposure to 16,944 ppm $CBrF_3$ (57% pyrolyzed) produced 100% mortality after 15 minutes. Eight of ten rats exposed to 6,972 ppm $CBrF_3$ (which was 61% pyrolyzed) died. The latter figure is to be compared with 9/10 rats dying in THRU experiment 143-22 (table 6). In this experiment, 7900 ppm $CBrF_3$ was 56.5% pyrolyzed. Treon et al also reported weight losses and recoveries similar to those found in the experiments described in this report. Hydrogen fluoride comprised approximately 35% of the pyrolysis products produced from $CBrF_3$. An HF concentration of 2480 ppm was formed at the $CBrF_3$ LC_{50} value of 2300 ppm. A 15-minute LC_{50} value for hydrogen fluoride was reported by Carson et al (ref. 16) for several animal species. For albino rats, the LC_{50} value was 2689 ppm with 95% confidence limits of 2397-3016 ppm. Therefore the mortality observed in our experiments undoubtedly resulted from the hydrogen fluoride in the mixture. The weight losses observed are also consistent with HF exposures.

The approximate lethal dose (ALD) of 14,000 ppm reported by Engibus and Torkelson (ref. 4) for $CBrF_3$ pyrolyzed at 800 C is considerably higher than the LC_{50} value observed in the current experiments. The two methods of pyrolysis were different. In the earlier experiments, the material was pyrolyzed in a monel metal tube filled with iron filings maintained at 800 C. Acid gases formed during pyrolysis could react with the iron filings and might not be present in the animal exposure chamber or be present at lower concentrations, resulting in a higher apparent ALD Value.

As mentioned earlier, the degree of pyrolysis is critically dependent on the temperature at which pyrolysis occurs. Referring again to figure 5, at 700 C, less than 20% pyrolysis occurs. Thus, a difference of a few degrees will result in a wide variation in the concentration of products to which the animals are exposed and in the mortality observed. Differences found between data in the literature and the experiments reported here may be attributed to differences in the actual temperature of pyrolysis.

Animals exposed to the pyrolysis products of CB did not exhibit delayed deaths to the degree shown by animals exposed to products of

$CBrF_3$. In the case of CB pyrolysis products, all deaths occurred within the first 3 days whereas with pyrolyzed $CBrF_3$ the majority of deaths occurred during the fourth and fifth days with scattered deaths continuing throughout the 14 day observation period. The 15-minute LC_{50} value of 465 ppm for pyrolysis products of CB is significantly lower than the value for pyrolyzed $CBrF_3$ (2300 ppm) and in both cases the pyrolysis products are also more toxic than unpyrolyzed material. Analytical chemistry data from the pyrolysis products showed that, among the inorganic constituents, HCl was the major component. Elemental halogens were in the minority as was phosgene. The observed mortality cannot be attributed to these materials alone, however, and must be due to the mixture of both inorganic and organic compounds arising during pyrolysis.

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13. ABSTRACT

The toxicities of the pyrolysis products of two fire extinguishant compounds, CH_2ClBr and $CBrF_3$, were investigated using albino rats and 14 day LC_{50} values were determined for single 15-minute exposures. Both fire extinguisher compounds, currently used by the USAF for aircraft fires, were pyrolyzed at 800 C in a hydrogen-oxygen flame. The pyrolysis products of each compound were examined and the principle constituents were identified and quantitated. The determined LC_{50} value of 2300 ppm for pyrolyzed $CBrF_3$ produced a hydrogen fluoride concentration of 2480 ppm consistent with the reported LC_{50} value for a single 15-minute exposure to this gas. Monobromomonochloromethane pyrolysis products were found to have a LC_{50} of 465 ppm (as CH_2ClBr) under the experimental parameters tested. The toxic response producing this LC_{50} value appeared to result from a mixture of hydrogen chloride, hydrogen bromide, and bromine gases.

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Monobromotrifluoromethane ($CBrF_3$)						
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