PB86-203874

Industrial Hygiene Study: Extent of Exposure to Hydrazines

Clayton Environmental Consultants, Inc.
25711 Southfield Road
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Contract No. 200-82-2521

Date of Report:
February, 1986

Report Number:
136.5

U.S. Department of Health and Human Services
Public Health Service
Centers for Disease Control
National Institute for Occupational Safety and Health
Division of Surveillance, Hazard Evaluations and Field Studies
Cincinnati, Ohio 45226

50272-101

REPORT DOCUMENTATION PAGE	1. REPORT NO.	2.	3. Recipient's Accession No.

4. Title and Subtitle

Industrial Hygiene Study Extent Of Exposure To Hydrazines, Clayton Environmental Consultants, Inc., Southfield, Michigan

5. Report Date 86/02/00

6.

7. Author(s) Anonymous

8. Performing Organization Rept. No. IWS-136-5

9. Performing Organization Name and Address

Division of Surveillance, Hazard Evaluations and Field Studies, NIOSH, U.S. Department of Health and Human Services, Cincinnati, Ohio

10. Project/Task/Work Unit No.

11. Contract(C) or Grant(G) No.

(C)

(G)

12. Sponsoring Organization Name and Address

13. Type of Report & Period Covered

14.

15. Supplementary Notes

16. Abstract (Limit: 200 words)

Walk through surveys of facilities handling hydrazine (302012) were conducted. Eight facilities were surveyed. These included installations where hydrazines were used as propellants, hydrazine production sites, sites where hydrazine was used as an aircraft emergency power unit fuel, and sites where hydrazine was used in boiler water treatment. At all facilities, employers and employees were aware of the need to avoid exposure and had developed hydrazine handling systems, work practices, and personal protective equipment programs to minimize the risk of exposure. Hydrazine production activities generated time weighted average (TWA) exposures that were generally well below 0.1 part per million, primarily because the production processes involved closed systems. Using hydrazines as propellants involved potential exposures while loading or unloading spacecraft and in related propellant transfer operations and while testing spacecraft components that utilized hydrazines. The authors conclude that TWA exposures to hydrazine compounds are relatively low. The number of exposed workers is also small. Current manufacturing methods are relatively new as is large scale propellant and emergency power unit usage. The accumulated person/years are relatively low, and it is unlikely that suitable cohorts exist for retrospective exposure studies.

17. Document Analysis a. Descriptors

b. Identifiers/Open-Ended Terms

NIOSH-Publication, NIOSH-Author, NIOSH-Survey, Field-study, Chemical-industry-workers, Chemical-properties, Environmental-hazards, Time-weighted-average-exposure, Hazardous-materials, Biological-monitoring, Exposure-levels, IWS-136-5

c. COSATI Field/Group

18. Availability Statement	19. Security Class (This Report)	21. No. of Pages 58
	20. Security Class (This Page)	22. Price

CONTENTS

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Acknowledgements

This project could not have been accomplished without the assistance of the NIOSH Project Officers, Charles S. McCammon Jr. and John M. Fajen.

This study was supported by the National Cancer Institute, Division for Cancer Cause and Prevention, through the Interagency Agreement on Research on Occupational Carcinogens (Y-01-CP-60605).

The cooperation of the companies and agencies which participated in the study is greatly appreciated. The review and comments by the members of these organizations were very helpful. Any errors or omissions remain those of the author.

Preface

NIOSH has been granted the authority and responsibility under the Occupational Safety and Health Act of 1970 to conduct field research studies in industry, evaluate findings, and report on these findings. Section 20(a)7 of this Act states that NIOSH shall conduct and publish industrywide studies of the effects of chronic or low-level exposure to industrial materials, processes, and stresses on the potential for illness, disease, or loss of functional capacity in aging adults. Section 22(e) provides the authority to enter into contracts, agreements, or other arrangements with appropriate public agencies or private organizations for the purpose of conducting studies relating to responsibilities under the Act. For this purpose NIOSH established a contractual agreement with Clayton Environmental Consultants, Inc. to perform an extent of exposure study of hydrazines and its compounds (Contract No. 200-82-2521). The funding for this work was provided by the Division for Cancer Cause and Prevention, National Cancer Institute, through the Interagency Agreement on Research on Occupational Carcinogens (Y-01-CP-60605).

Hydrazines are a class of compounds with over 300 derivatives. Animal studies have suggested that long-term exposure to hydrazine and several hydrazine compounds may increase the risk of cancer. Data on the extent of worker exposure to hydrazine and its more common derivatives are very limited and in most cases do not exist.

To assess whether or not the consequences of exposure to hydrazine should be further evaluated, it is necessary to determine who is exposed to hydrazine, how significant is the extent of exposure, and how reliable are the sampling and analytical methods used. This extent of exposure study was undertaken to address these questions. This report contains a discussion of sampling and analytical methods, brief descriptions of the facilities surveyed, discussion of results, and recommendations based on the results.

The study was designed to be done under three tasks: (1) a literature evaluation, (2) walkthrough industrial hygiene surveys at selected facilities, and (3) comprehensive industrial hygiene surveys where warranted. After each task, the information and data were reviewed and evaluated prior to progressing to the next task which was modified accordingly. Because of the information obtained during the walkthrough surveys, only limited onsite evaluation under Task 3 was considered necessary.

Abstract

The National Institute for Occupational Safety and Health (NIOSH) contracted with Clayton Environmental Consultants, Inc. (CEC) to conduct an industrial hygiene assessment of the extent of exposure to hydrazine compounds. The study was initiated because a growing number of these compounds have been shown in laboratory research to be known animal carcinogens, and because there is a lack of workplace exposure data.

This report discusses production and uses of hydrazine compounds, reviews and summarizes toxic effects of these compounds, summarizes relevant exposure standards, describes sampling and analytical methods relevant to exposure assessment, and summarizes observations made during surveys conducted at eight U.S. facilities where selected hydrazines were produced and/or used.

Observations reported include descriptions of operations and job titles of potentially exposed personnel, exposure control techniques in use, health and safety programs, and discussions of air sampling data reviewed or collected. In summary, the air sampling data showed that, with one exception, 8-hour, time-weighted average (TWA) personal exposures to the hydrazine compound(s) in use during normal operations ranged from below the limit of detection to 0.1 ppm--exposures that were below current OSHA permissible exposure limits of 0.5 to 5 parts per million (depending upon the specific compound) and near the current NIOSH-recommended exposure limits of 0.03 to 0.14 ppm (depending upon the specific compound).

Discussions and recommendations relevant to the study as a whole are also reported. In brief, the study suggests that growth in usage is anticipated, and exposure appears most likely, where hydrazines are used as fuels or propellants, such as in the space shuttle program, or as an emergency power unit fuel in jet aircraft used by the Air Force. In these applications, it is exposures from spills or unanticipated releases that are of major concern. Consequently, work practices and personal protective equipment which minimize exposure in such situations are necessary. The normal TWA personal exposures were low or nondetectable except in accident situations (spills). Nevertheless, personnel were all well protected with respiratory and skin protection at the sites visited in connection with this study. In addition, emergency procedures for spills and unanticipated releases were developed at most sites visited.

This report was submitted in partial fulfillment of Contract No. 200-82-2521 by CEC under the sponsorship of NIOSH.

List of Tables

List of Figures

INTRODUCTION

Under the terms of the authority and responsibility given to the National Institute for Occupational Safety and Health (NIOSH) to develop needed information regarding potentially toxic substances in industry, NIOSH contracted with Clayton Environmental Consultants, Inc. to conduct an industrial hygiene study of the extent of exposure to hydrazine compounds. Hydrazines were selected by NIOSH for study because a growing number of the compounds have been shown in laboratory research to be known animal carcinogens (see Toxicity section of this report) and therefore suspected human carcinogens[1] and because there is, at the time of this study, a lack of workplace exposure data.

STUDY GOALS

The following goals were established for this study:

- Describe job titles of exposed workers and exposure levels.
- Determine significance of recurring and non-routine exposures.
- Determine reliability of exposure data (gleaned from exposure records provided by the facilities visited, or collected as part of an industrial hygiene evaluation at the facility visited).

STUDY OBJECTIVES AND SCOPE

To meet the study goals, the following objectives for this study were established:

(1) Document production and use of hydrazine compounds.

(2) Briefly review and summarize the toxic effects of hydrazines.

(3) Summarize relevant exposure standards.

(4) Describe sampling and analytical methods relevant to exposure assessment of hydrazines.

(5) Conduct industrial hygiene surveys at selected workplaces where hydrazines are produced or used.

(6) Identify job types and describe specific jobs where hydrazine exposures may occur at the selected facilities.

(7) Describe current industrial hygiene and safety practices including engineering controls, work practices, administrative controls, and biological and environmental sampling and control procedures utilized by the selected hydrazine handling companies and organizations.

(8) Document exposures to hydrazines and relevant process or production changes occurring during the site surveys that could affect the interpretation of hydrazines exposure data.

Walkthrough and indepth industrial hygiene surveys to accomplish these objectives were made at eight U.S. facilities where selected hydrazines were produced and/or used. The surveys were conducted during the period of February 1983 through February 1984 by the contractor and NIOSH personnel.

LIMITATIONS OF STUDY

The industrial hygiene data measured or gathered during the study represent evaluations of worker exposures to the hydrazines and related workplaces selected for the study. Accordingly, workplace exposures and exposure scenarios may not be necessarily reflective of exposures associated with manufacture or use of hydrazines in workplaces that were not evaluated. Exposures evaluated in this study may not necessarily reflect possible variations in exposure due to seasonal or operational changes. An attempt was made to evaluate exposures to the selected hydrazines for each situation as encountered. No abnormal exposure situations were encountered; therefore, the reported exposure measurements are considered to represent only those exposures associated with normal operating conditions. This study was also highly dependent on data available from the facilities and organizations which participated in the study.

BACKGROUND

Hydrazine and common hydrazine derivatives were discovered between 1887 and 1893 and first synthesized in 1906 by Raschig.[2] The first major use of hydrazine was as a fuel during World War II for rocket-powered German fighter planes. Commercial production in the United States started in 1953.

NIOSH lists more than 300 hydrazine derivatives in the "Registry of Toxic Effects of Chemical Substances."[1] Physical and chemical properties of hydrazine and some of the major hydrazine derivatives are presented in Table I.[3,4,5]

MANUFACTURING METHODS OF HYDRAZINE

Many methods for the preparation of hydrazine have been used. In the United States, hydrazine has been produced primarily by two methods, the Raschig process and the Ketazine process.[2] Current production is primarily by the Ketazine process.

The Raschig process is based on the oxidation of ammonia with hypochlorite according to the following overall reaction:

$$2NH_3 + NaOCl \longrightarrow N_2H_4 + NaCl + H_2O$$

TABLE I

Physical and Chemical Properties of Hydrazine and Some Hydrazine Derivatives

	Hydrazine	Methylhydrazine	1,1-Dimethylhydrazine	1,2-Dimethylhydrazine	Phenylhydrazine
Chemical Abstracts name	Hydrazine	Hydrazine, methyl-	Hydrazine, 1,1-dimethyl-	Hydrazine, 1,2-dimethyl-	Hydrazine, phenyl-
CAS Registry no.	302-01-2	60-34-4	57-14-7	540-73-8	100-63-0
Formula	H_2NNH_2	CH_3NHNH_2	$(H_3C)_2NNH_2$	$CH_3NHNHCH_3$	$C_6H_5NHNH_2$
Physical and chemical properties					
Molecular weight	32.0	46.1	60.1	60.1	108.14
Physical form	Clear colorless liquid	Clear liquid	Clear colorless liquid	Clear colorless liquid	Colorless oily liquid
Odor	Fishy	Ammonia-like	Fishy	Fishy	Faint, aromatic
Boiling point	113.5 °C	87 °C	63 °C	80-81 °C	243.5 °C (dec.)
Melting point	2 °C	-20.9 °C	-57 °C	-9 °C	19.5 °C
Density	1.0083^{20}_{4}	0.874^{20}_{4}	0.791^{20}_{4}	0.8274^{20}_{4}	1.0978^{20}_{4}
Vapor pressure	14.4 mm Hg at 25 °C	49.6 mm Hg at 25 °C	156.8 mm Hg at 25 °C	69.9 mm Hg at 25 °C	1 mm Hg at 71.8 °C
Flammability					
Flash point	52 °C	21 °C	1 °C	Flammable	88 °C
Explosive limits	47-100%	2.5-97 ±2%	2.5-95%		
Ignition temperature	518 °F	(auto) 196 °F	480 °F		
Vapor density	1.1 (air = 1)	1.6 (air = 1)	1.94 (air = 1)		3.7 (air = 1)
Solubility					
Water	Miscible	Miscible	Miscible	Miscible	Sl. soluble
Alcohol	Miscible	Miscible	Miscible	Miscible	Miscible
Ether	Miscible	Miscible	Miscible	Miscible	Miscible

(Reference 3,4,5)

Olin Corporation has in the past used an adaption of the Raschig process; liquid chlorine is absorbed in dilute sodium hydroxide to form sodium hypochlorite. The sodium hypochlorite is mixed with aqueous ammonia; chloramine is then formed and then reacted with excess ammonia to form hydrazine. The Olin Raschig process flow sheet is shown as Figure 1.

In the ketazine process, ammonia is oxidized by chlorine or chloramine in the presence of aliphatic ketones. Intermediates, such as hydrazones, ketazines, or diaziridines, are formed and converted to ketazines with excess ketone. After complete consumption of oxidizing agents (Cl_2, NaOCl, NH_2Cl), the intermediates can be hydrolyzed to hydrazine or its salts. The ketazine process as adapted by Bayer Chemicals is shown as Figure 2.[2]

PRODUCTION OF HYDRAZINES

Hydrazine and its Salts

Currently, three major producers in the United States have hydrazine production capacities of approximately 16,500 metric tons per year.[2,6,7,8] Small amounts may be manufactured by other producers as well.

One of the major producers reportedly has about 9,500 metric tons of capacity per year, and about 3,000 metric tons of this is dedicated to the U.S. government, mainly for fuels for aerospace applications. Hydrazine producers estimated the total demand in 1982 at about 9,000 metric tons. Industry sources estimate that annual growth in the next five years will average about 8 to 10%. One of the predicted major areas of growth is in the use of hydrazines as chemical blowing agents. The blowing agents are used in the manufacture of some types of vinyl flooring and in automotive foam cushioning.

Hydrazine Derivatives

The major hydrazine derivatives produced in the United States are 1,1-dimethylhydrazine, methylhydrazine, and phenylhydrazine.[9] In 1978, NIOSH estimated the production of certain hydrazine derivatives as shown in Table II.[10]

USES OF HYDRAZINES

Hydrazines are used as rocket fuels, and in water treatment as an oxygen scavenger to control corrosion. Hydrazines are also used in the production of a number of other materials including agricultural chemicals, chemical blowing agents, pharmaceutical drugs, photographic developing compounds, dyestuffs, explosives, stabilizers and antioxidants, and as a fuel in fuel cells. Percent consumption on a world-wide basis for applications of hydrazines is listed in Table III.[7,11]

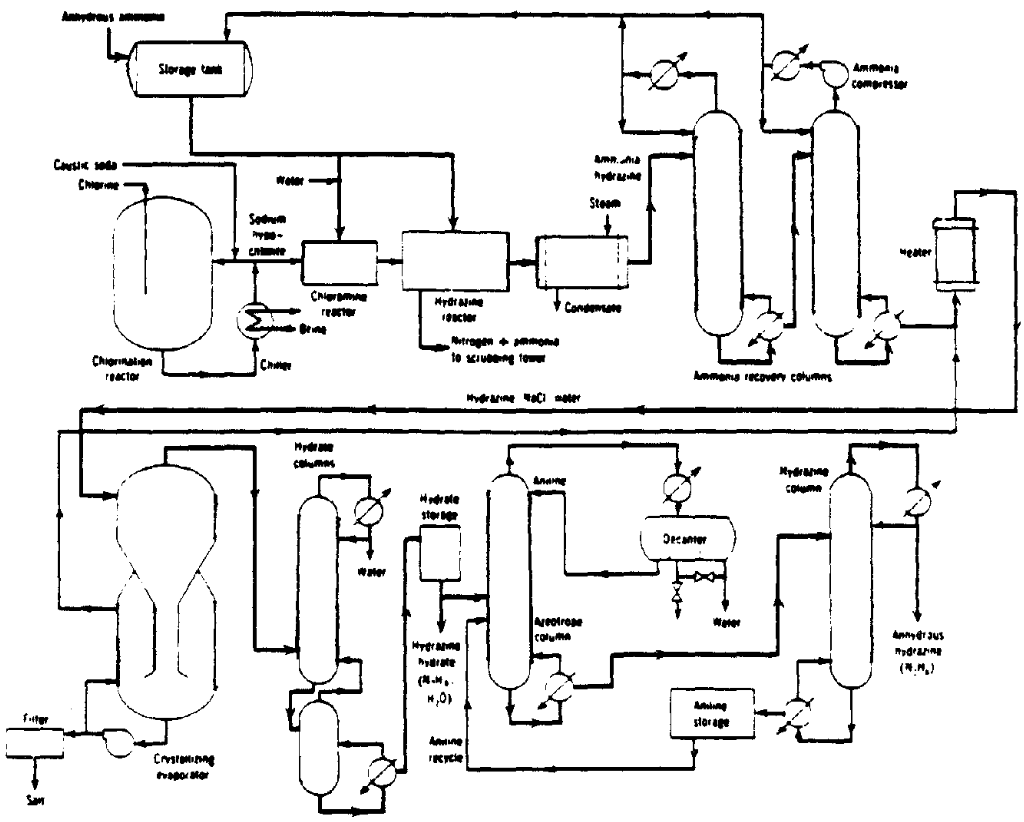

Figure 1. Olin Raschig process flow sheet [2].

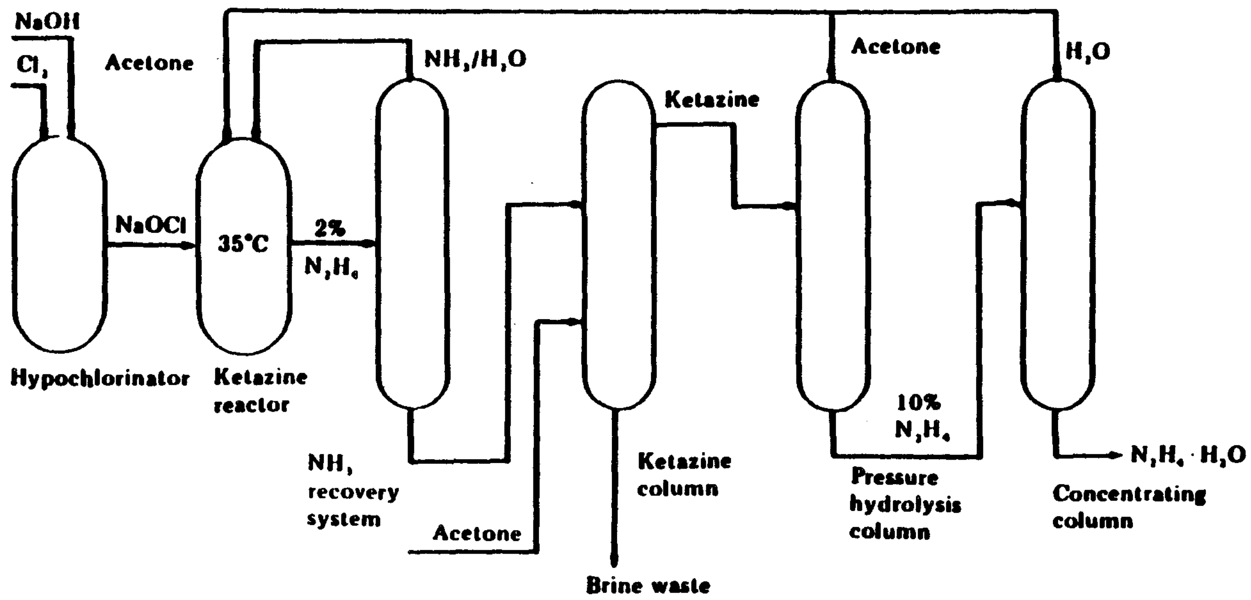

Figure 2. Bayer-Ketazine process flow sheet [2].

TABLE II
Production Amounts of Hydrazine Derivatives

Compound	Production, (Metric tons/year)
1,1-Dimethylhydrazine	450-900
1,2-Dimethylhydrazine	Small quantities
Methylhydrazine	90
Phenylhydrazine	Unknown

Source: NIOSH estimate (1978)[10].

TABLE III
Worldwide Application of Hydrazine and Its Derivatives

Application	Consumption, %
Synthesis of agricultural chemicals (herbicides and pesticides)	40
Blowing agents for foamed plastics	33
Water treatment	15
Rocket fuels, synthesis of pharmaceutical drugs, and fire chemicals	12

Reference 7, 11.

Propellants

Hydrazine rocket fuels include hydrazine, 1,1-dimethylhydrazine, and methylhydrazine. Aerozine-50, which was used to power the Titan II launch vehicle for the Gemini spacecraft as well as other Titan missiles, contains an equal mixture of hydrazine and 1,1-dimethylhydrazine and an oxidizer, nitrogen tetroxide. Since 1981, large amounts of hydrazine and methylhydrazine have been used for the voyages of the space shuttle.(12)

Estimates made in the early 1960s indicated that rocket fuel consumed 80% of the hydrazines produced in the U.S. However, while the fuel use is still significant in various space and military programs, more recent figures indicate that it may represent only about 20% of U.S. consumption.(13)

Water Treatment

In boiler water treatment, hydrazine acts as an oxygen scavenger to control corrosion. For water treatment applications, hydrazine is usually purchased as a 35% solution in water and further diluted to the required concentration. Some water treatment supply and service companies sell special formulations of hydrazine with other necessary boiler water treatment chemicals. Hydrazine is reportedly one of the best scavengers used in high temperature, high pressure systems such as utility boilers where no dissolved solids can be tolerated. Approximately 4,000 tons of hydrazines per year are used in boiler systems.

While public utilities are generally the major customers of hydrazine for boiler treatment, pulp and paper mills, textile mills, and chemical processing plants are also large users. Hydrazine can also be used as a corrosion inhibitor in closed system cooling water and in the petroleum industry, and for chromium reduction in process wastewater treatment.

Synthesis of Agricultural Chemicals

Many hydrazine derivatives are used as pesticides and herbicides in agriculture. The earliest hydrazine derivative with extensive agricultural application was maleic hydrazide, a plant growth regulator. Hydrazine production is often captively used for the synthesis of agricultural chemicals.

Blowing Agents

Blowing agents are used to produce foaming actions in polymers to form pores or cells. The most important are hydrazine derivatives; they release nitrogen as a major gaseous decomposition product. Some of the most common hydrazine-based blowing agents used in the U.S. are listed in Table IV.(2,14)

TABLE IV
Common Blowing Agents

Compound	Trade Name
Azodicarbonamide	Celogen AZ
Kempore	
Azocel	
4-Methylbenzene sulfonylhydrazide	Celogen TSH
4,4'-Oxybis(benzene-sulfonylhydrazide)	Celogen OT
4-Methylbenzene sulfonyl-2-(aminocarbonyl)-hydrazide	Celogen RA

Reference 2,14

Other Uses

Hydrazine derivatives are also used in areas listed below:

- pharmaceutical drugs, such as isonicotinic acid hydrazide [CAS No. 54-85-3]
- photographic developing compounds, such as stabilizers, fog-inhibitors, and spectral sensitizers (hydrazine derivatives such as triazoles, tetrazole, and tetrazonium salts).
- dyestuffs - metal complexes based on formazans
  - 2-hydroxynaphthazine, a yellow dye
- explosives - nitrate, perchlorate, and azide salts
- stabilizers for fuel additives and antioxidants (as a result of the chelating and reducing power of hydrazine derivatives)
- fuel cells - using hydrazine and oxygen as a fuel

SUMMARY OF TOXICOLOGY

Since little information is available from the study of human populations, animal studies provide the primary source of data on the toxicity associated with the production and application of hydrazines.[10,15] Major target organs and systems include the skin and eyes, central nervous system, the liver, the blood, and the kidneys.

Hydrazine compounds have caused dermatitis and have potential for skin absorption. The central nervous system is also affected by a number of compounds, resulting in effects such as restlessness, breathing difficulties, convulsions, vomiting, and lethargy.[16] The inhalation of hydrazine by mice at levels of 30 ppm - hours/week cumulative exposure resulted in severe fatty degeneration in the liver.[17]

Oral administration or injection of hydrazine sulfate has produced multiple pulmonary tumors in CBA mice and liver, lung, and breast tumor in Cb rats.[10] In 1981, MacEwen et al released the results of a four-species inhalation study, in which multiple concentrations of hydrazine were administered to rats, mice, hamsters, and dogs.[18] The exposures were for 6 hours/day, 5 days/week for one year; rodents were observed 12 to 18 months following termination of exposure and the dogs were observed for 38 months. Tested concentrations included 0.05, 0.25, 1.0, and 5.0 ppm. At 5 ppm and 1 ppm, respectively, microscopic nasal carcinomas in rats, and benign tumors of the nasal epithelium were observed. Benign respiratory tumors were also observed in mice and hamsters. When the 21 dogs were sacrificed after 38 months of observation, two tumors were found in one animal exposed at 0.25 ppm; however, the authors interpreted these findings as incidental.

Animal testing has also shown teratogenic and other reproductive effects. Studies by subcutaneous injection of hydrazine in rats resulted in death or stillbirth of all off-spring.[19] Hydrazine demonstrated mutagenic activity in the mouse host-mediated assay, Ames test, *Drosophila melanogaster*, and Chinese hamster cells. Mutagenicity was not demonstrated in the dominant lethal assay.[15]

Table V briefly summarizes the acute and chronic toxicity data of hydrazine and its derivatives and their salts.

OCCUPATIONAL HEALTH STANDARDS FOR HYDRAZINE COMPOUNDS

Standards for occupational exposures have been developed for hydrazine and three of its derivatives (1,1-dimethylhydrazine, methylhydrazine, and phenylhydrazine). The exposure limits established, adopted, and recommended by the Occupational Safety and Health Administration (OSHA), the American Conference of Governmental Industrial Hygienists (ACGIH), and NIOSH, respectively, are indicated in Table VI.[10,21,22]

The Committee on Toxicology of the National Academy of Sciences has recently (November 1983) evaluated short-term exposures to hydrazine and has prepared exposure guidelines.[15] A concentration-time multiplier concept with a safety factor of 10 was used. Guidelines were issued for emergency exposure limits (EEL), short-term public limits (STPL), and short-term public emergency limits (SPEL) as follows:

Exposure Time	TWA Limits for Indicated Exposure Time		
	EEL (ppm)	STPL(ppm)	SPEL (ppm)
10 min.	3.6	1.8	3.6
30 min.	1.2	0.6	1.2
60 min.	0.6	0.3	0.6
2 hours	0.3	0.15	0.3
4 hours	0.15	0.075	0.15
8 hours	0.075	0.0375	0.075
12 hours	0.05	0.025	0.05
16 hours	0.0375	0.018	0.0375
24 hours	0.025	0.012	0.025

SAMPLING AND ANALYTICAL METHODS

A summary of integrated sampling and analytical methods for hydrazines is presented in Table VII. Most of these methods as well as certain direct-reading methods were reported to have been used at or in the sites visited during the course of this study. The specific methods used by the contractor or safety and health personnel at each company or agency are described in detail in later sections of this report.

Table V

Toxicity Data of Hydrazine and its Derivatives

Substance	LD_{50}, mg/kg							Additional Information
	Rat			Mouse				
	Oral	Intravenous	Intraperitoneal	Oral	Intravenous	Intraperitoneal	Subcutaneous	
Hydrazine			76			163		Animal carcinogen LC_{50}: 570 ppm/4 hour (rat) 252 ppm/4 hour (mouse)
Hydrazine, 2HF					56			
Hydrazine, HCl	128	118	126	126	122	133		
Hydrazine, H_2O	129			83				Experimental carcinogen; research chemical
Hydrazine, H_2SO_4 (1:1)	601		230	704		152		Animal carcinogen
Acetyl hydrazine						153		
Benzyl hydrazine						100	68	
Benzyl hydrazine, 2HCl								Positive carcinogen in animal
Benzyl hydrazine, HCl				90		50		
Butyl hydrazine, H_2SO_4						120		
1,2-Diethyl hydrazine								Positive carcinogen in animal

Table V (cont.)

Toxicity Data of Hydrazine and its Derivatives

Substance	LD_{50}, mg/kg							Additional Information
	Rat			Mouse				
	Oral	Intra-venous	Intraper-itoneal	Oral	Intra-venous	Intraper-itoneal	Subcu-taneous	
1,2-Diethyl hydrazine, 2HCl								Animal teratogen
1,1-Dimethyl hydrazine			102			125	12	Positive carcinogen in animal LC_{50}: 252 ppm/4 hour (rat) 172 ppm/4 hour (mouse 392 ppm/4 hour (hamst
1,1-Dimethyl hydrazine, HCl	196	191	210	426	402	466		
1,2-Dimethyl hydrazine	100							Positive carcinogen in animal
1,2-Dimethyl hydrazine, HCl	257	281	262	58	47	56		
1,2-Dimethyl hydrazine, 2HCl	100							Animal carcinogen; research chemical; no evidence of U.S. production/importation
1,1-Diphenyl hydrazine, 2HCl								Research chemical; no evidence of U.S. production/importation
Ethyl hydrazine, HCl								Positive carcinogen in animal
Ethyl hydrazine, H_2SO_4						140		

Table V (cont.)

Toxicity Data of Hydrazine and its Derivatives

Substance	LD_{50}, mg/kg							Additional Information
	Rat			Mouse				
	Oral	Intra-venous	Intraper-itoneal	Oral	Intra-venous	Intraper-itoneal	Subcu-taneous	
Heptyl hydrazine, H_2SO_4						150		
Hexyl hydrazine, H_2SO_4						90		
Methyl hydrazine	33		21	57				Positive carcinogen in animal LC_{50}: 74 ppm/4 hour (rat) 143 ppm/4 hour (hamst
Methyl hydrazine, HCl	58		58	59				
Methyl hydrazine, HNO_3	133	38	43					
Methyl hydrazine, H_2SO_4						160		Positive carcinogen in animal; research chemical; no evidence of U.S. production/importation
Pentyl hydrazine, HCl								Positive carcinogen in animal
Pentyl hydrazine, H_2SO_4						250		
Phenethyl hydrazine				130		135	150	Positive carcinogen in animal
Phenethyl hydrazine, 2HCl						100		
Phenethyl hydrazine, HCl				125				

Table V (cont.)

Toxicity Data of Hydrazine and its Derivatives

Substance	LD_{50}, mg/kg							Additional Information
	Rat			Mouse				
	Oral	Intra-venous	Intraper-itoneal	Oral	Intra-venous	Intraper-itoneal	Subcu-taneous	
Phenethyl hydrazine, H_2SO_4	210			156	157	166	125	
Phenyl hydrazine	188							
Phenyl hydrazine, HCl								Positive carcinogen; researc chemical; no evidence of U.S production/importation

References (1, 10, 15, 20)

15

TABLE VI
Exposure Limits for Hydrazine and its Derivatives

Chemical	Exposure Limits (ppm)				
	OSHA PEL[1]	ACGIH TLV[2]			NIOSH-Recommended Standard
		TWA*	STEL**	CEILING***	
Hydrazine	1	0.1	—	—	C 0.03
1,1-Dimethylhydrazine	0.5	0.5	1	—	C 0.06
Methylhydrazine	—	—	—	0.2	C 0.04
Phenylhydrazine	5	5	10	—	C 0.14

[1]PEL - Permissible Exposure Limit: An employee's exposure in any 8-hour workshift of a 40 hour work week shall not exceed this level measured as an 8-hour TWA.

[2]TLV - Threshold Limit Value: Refers to airborne concentrations of substances and represents a condition under which it is believed that nearly all workers may be repeatedly exposed day-after-day without adverse effects.

* TWA - Time-weighted average for an 8-hour workshift of a 40-hour workweek

** STEL (short-term exposure limit): A 15-minute TWA exposure which should not be exceeded at any time during a work day even if the 8-hour TWA is within the TLV. Exposures at the STEL should be no longer than 15 minutes and should not be repeated more than four times per day. There should be at least 60 minutes between successive exposures at the STEL.

*** Ceiling - concentration not to be exceeded at any time

C Denotes ceiling concentration - the maximal concentration which cannot be exceeded in any 2-hour period

Note: All the exposure limits carry the "skin" notation, warning of the potential for percutaneous absorption; these specific concentration limits are based on the presumption that there is no concurrent exposure via the skin and oral ingestion routes.

ACGIH lists hydrazine, methylhydrazine, and 1,1-dimethyl hydrazine in its A2 category, i.e., industrial substances suspect of carcinogenic potential in humans.

Hydrazine air sampling techniques include adsorption of hydrazines on a solid sorbent or absorption in a liquid medium. Generally, a solid sorbent is favored because it is easier to handle for personal sampling than a liquid. Other factors, such as collection efficiency, stability, and the nature of the subsequent analytical methods also need to be considered in the selection of a sampling method.

Many analytical methods, such as titration, colorimetric, manometric, and gas chromatographic methods, have been used to quantify hydrazines, and are reported in the literature. Among them, NIOSH has published both gas chromatographic and colorimetric methods.[10,23]

In considering analytical methods, sensitivity and specificity are important factors. In instances when more than one hydrazine may be present simultaneously, the analytical method(s) selected should be specific for individual hydrazines. For separation of specific hydrazines in a mixture, gas chromatography is recognized as the best method.

Hydrazines have been collected on a sulfuric acid-coated silica gel sorbent for subsequent derivatization and gas chromatographic analysis. This method (NIOSH Method P&CAM 248) offers the advantage of allowing determination of more than one hydrazine in a single sample. Tests have shown adsorption efficiency was independent of vapor concentration and humidity. At a flowrate of 0.2 liter/minute, sampling can be continued for a full workshift with virtually 100% collection efficiency. Desorption efficiency reportedly may decrease, especially for methylhydrazine, as the detection limit is approached; however, the reduction in desorption efficiency is compensated for by preparing and desorbing standards using the collecting medium. Based on a 96-liter air sample, the detection limits are 0.02 ppm for hydrazine, 0.05 ppm for methylhydrazine, 0.02 ppm for 1,1-dimethylhydrazine, and 0.001 ppm for phenylhydrazine.

Hydrazines can also be collected in midget bubblers containing an acid medium, such as dilute hydrochloric acid, with analysis by colorimetric techniques using phosphomolydic acid or p-dimethylaminobenzaldehyde. At a flowrate of 1 liter/minute, the collection efficiency was nearly 100% in NIOSH validation tests for such methods. However, the NIOSH methods based on these techniques recommend sampling times of 2 hours or less, requiring collection of sequential samples to determine 8-hour, TWA concentrations. The detection limits and validation ranges for these techniques are indicated in Table VII.

A sampling and analytical method for hydrazine, developed by the U.S. Air Force, employs sulfuric acid-coated firebrick as the collecting medium, with analysis by a p-dimethylaminobenzaldehyde technique.[24]

The method was tested at sampling rates ranging from 0.2 to 1.0 liters per minute for sampling periods from 4 minutes to 8 hours, with better

TABLE VII

Summary of Integrated Sampling and Analytical Methods and Their Detection Limits

Method	Sampling Media	Analytical Method	Flowrate L/min.	Lower Limit of Detection (ppm)	Validation Range (ppm)
NIOSH (P&CAM 248)	Tube containing sulfuric acid-coated silica gel	2-Furaldehyde derivatization, gas chromatography	0.2 (8 hours)	Hydrazine: 0.002 Methylhydrazine: 0.05 1,1-Dimethylhydrazine: 0.02 Phenylhydrazine: 0.001	— — — —
NIOSH S-237 NIOSH S-143 NIOSH S-160	Bubbler containing 10-15 mL 0.1 M - HCl	Colorimetry* Colorimetry** Colorimetry**	1 (2 hours)	Hydrazine: 0.02 1,1-Dimethylhydrazine: 0.01 Phenylhydrazine: 1	0.45-2.6 0.25-1.1 2.3-10.
NIOSH S-149	Bubbler containing 15 mL 0.1 M - HCl	Colorimetry**	1.5 (15 min.)	Methylhydrazine : 0.02	0.090-0.41
USAF***	Tube containing sulfuric acid-coated fire brick (Gaschrome-R)	Colorimetry*	0.05 (3 hours)	Hydrazine: 0.05	—
MDA****	Direct reading	—	—	Hydrazine: 0.05	—

* Color reagent: p-dimethylaminobenzaldehyde.

** Color reagent: phosphomolybdic acid.

*** Reference 24

**** Source: Catalogue for Model 3060 Autospot, MDA Scientific, Inc., Park Ridge, Illinois.

than 90% overall recovery for concentrations ranging from 0.036 to 20.6 ppm. The authors indicated that a concentration of 0.05 ppm could be measured over sampling times as short as slightly over two minutes or as long as 3 hours using flowrates of 4.0 to 0.05 liters per minute, respectively.

The widely used colorimetric analytical techniques using phosphomolybdic acid or p-dimethylaminobenzaldehyde for color development are prone to interference by hydrazines other than the specific compound for which they were validated, but provide satisfactory detection limits and specificity when only one hydrazine is present.

Direct-reading methods using detector tubes, paper tapes, and electronic instruments have been developed for hydrazines. Since most uses of hydrazine entail not only an integrated exposure but also sudden, accidental exposure, it is highly desirable to obtain direct-reading results. Although these methods can be used for qualitative tests, they often lack specificity and sensitivity.

Detector tube product literature indicates detection limits ranging from 0.05 to 0.5 ppm, depending on the manufacturer, and reports interferences by other hydrazines, imines, amines, and acid gases.

Currently, MDA Scientific, Inc. produces the Autospot Toxic Gas Detector, Model 3060, which can be used to measure airborne hydrazine. The detection limit, according to product literature, is 0.05 ppm. The detection principle is based on the color change produced on chemically impregnated paper tape due to the presence of airborne hydrazine.[25] The MDA Monospot sensor reportedly is also capable of measuring hydrazine.

Direct-reading equipment based on electrochemical principles has been produced by Interscan and Energetic Sciences. These instruments have often been developed for government agencies and are currently undergoing testing for use as indicators of hydrazine exposure.

SITE SURVEY DESIGN AND PROCEDURES

After reviewing literature pertaining to the toxic effects of hydrazines, and documenting of production and uses of hydrazines, it was decided to focus the site survey objective on those facilities that produce or use hydrazine compounds with known toxicity (primarily suspected carcinogenicity) or produce or use significant quantities of hydrazines. Effectively, this limited the prospective survey population to producers and users of hydrazine, 1,1,-dimethylhydrazine (DMH), and methyl-hydrazine (monomethylhydrazine).

Companies and agencies using these compounds were contacted and walkthrough surveys were solicited. Contacted companies included all known hydrazine producers, major producers of the hydrazine derivatives of interest, hydrazine propellant users, and boiler system operators.

Surveys and conferences were scheduled with, and completed at, three hydrazine and hydrazine-derivative manufacturers, one Air Force base, an aircraft manufacturer, and three sites where hydrazines-fueled space vehicle propulsion systems and power units were used or tested. Many boiler system operators were also contacted. Permission was not obtained to evaluate this use of hydrazines with a site visit. However, monitoring data were received from a major utility which described the extent of exposures measured during the addition of hydrazine to the boiler water system.

Information obtained during the visits is discussed in the chapter on Facilities Surveyed. That information included:

- Physical description of site and identification of hydrazine(s) used.
- Description of operations involved in hydrazine(s) usage.
- Description of workforce and recordkeeping system.
- Description of medical and industrial hygiene program.
- Description of exposure data when obtained.

With respect to the last item, samples for measurement of hydrazine exposure concentrations were collected (as part of an in-depth industrial hygiene survey) at only one of the eight facilities visited. This was due to the infrequency of activities associated with potential exposures. Most of the hydrazine concentration data presented in this report was obtained from documents provided by the facilities visited.

During the walkthrough surveys, it was observed that employees who were engaged in exposure-generating activities were wearing respiratory protection and protective clothing. Therefore, monitoring data reported may not necessarily represent actual worker exposure.

FACILITIES SURVEYED

Walkthrough surveys were conducted at seven facilities where hydrazines are used, handled, or tested. In addition, an eighth facility was visited and hydrazine exposure monitoring was conducted to determine exposures occurring in that manufacturing facility.

The facilities, designated as Sites A through H, are briefly described in this chapter. The chapter includes review of the activities or processes with potential exposure to hydrazines, descriptions of health and safety programs that have been established at these sites, details of measurement methods when reportable, and exposures which occur as a result of the activities or processes carried out at the facilities.

Site	Use of Hydrazines
A	Hydrazines-fueled propulsion system and power unit testing
B	Hydrazine production
C	Air Force fighter base
D	Hydrazines-fueled propulsion system testing
E	Fighter assembly plant
F	Space craft launching
G	Formerly hydrazine producer, currently derivative supplier
H	Hydrazine production facility

SITE A

Description of the Site

This site, a major government installation, provides facilities for a variety of operational, administrative, and testing activities related to the space program. The site, built in the early 1960s, is located in the south central U.S. on several hundred acres. Over 3,000 government employees and approximately 9,000 contractor personnel work here.

Use of hydrazines (hydrazine, monomethylhydrazine, and to some extent, 1,1-dimethylhydrazine) at the site is limited to the thermo-chemical test area (TTA). In this area, engines, power units, and components of engines which utilize hydrazines as propellants are tested. The TTA is separated from the normal traffic areas, and is isolated in the northwest area of the complex. Access is strictly controlled. Such testing has been done periodically for about 20 years at the site.

The TTA consists of an administration/laboratory building and four test areas, each separated by up to several hundred yards. Hydrazines were used in two test buildings.

Description of Operations

Space-craft components (currently, primarily shuttle components) are performance-tested in the TTA. This requires the operation of the propulsion and fuel systems. The fuel for the auxiliary power unit (APU) on the shuttle is monopropellent grade (99.5% pure) anhydrous hydrazine.

Hydrazines are received in 55-gallon drums and stored in a designated and posted area. The fuel is moved around the facility in small portable tanks; the loading and offloading of hydrazines is accomplished with nitrogen pressure. At each test cell, the hydrazine fuel to be used is loaded into test fuel cells (both underground tank and run tank, as necessary) and into the space vehicle component fuel cells.

The exhaust from testing using hydrazines fuels, as well as line-purge gases, are vented to a wet (water) scrubbing system located at each building. The scrubber water (as well as any water used to wash down hydrazine in the event of a spill or leak) is directed to a nearby holding pond. The pond water is periodically batch-treated with chlorine (with and without aeration) and discharged offsite.

It was estimated that, at most, 50 gallons of hydrazines are used each month.

Description of Work Force and Recordkeeping System

Although a large number of people (over 12,000) are employed at the site, only a small number (about 100) work in the TTA. Of these, approximately five to 10 employees, primarily test engineers, deal directly with the hydrazine propellants at each of the two test areas currently using hydrazines. Current research involves the testing of engine and component performance.

As employees using hydrazines are primarily contractor personnel, the number of employees has tended to vary, depending on the level of effort in the research program.

The records for each employee (civil service or contractor) are complete and have been retained to this date. Civil service and contractor personnel have examinations at a common clinic so their records are similar. Employment records are kept by the contractor and would vary with each contractor. The contractor operating the TTA has performed limited environmental testing. Results of the testing are maintained by the contractor.

Description of Medical and Industrial Hygiene Program

The medical monitoring program at Site A is run by an independent contractor. A clinic, located onsite, is fully staffed and provides medical examinations. Civil service and contractor personnel receive annual medical examinations; contractor personnel throughout the site receive medical examinations designed for their specific jobs. TTA workers receive a pulmonary function test, an initial chest x-ray, blood evaluation (blood count and liver enzymes), and urinalysis. TTA personnel also are potentially exposed to a variety of other chemicals, e.g., other fuels and oxidizers, as well as hydrazines, so the medical examination is not limited to evaluation relevant to only hydrazines exposure.

Site industrial hygiene support is provided by three industrial hygienists on the medical program contractor's staff. The hygiene support is site wide and not directed specifically to hydrazine areas. The site also maintains an environmental laboratory where industrial hygiene and environmental samples of a wide variety can be analyzed. The laboratory appears to be well staffed and equipped.

The contractor handling hydrazine provides industrial hygiene support through its safety program in the TTA area, and is directly responsible for hydrazine monitoring and other industrial hygiene program elements directed toward hydrazine exposure.

During each procedure which may cause hydrazine release, test personnel wear full-body protective clothing with air-supplied respirators. Air sampling is done following each test, before respiratory protection is discontinued, to document hydrazine levels.

The only engineering control in use in the test cells is the provision of exhaust gas scrubbers and independent air supply to the test control rooms.

Exposure Data

Results of hydrazine sampling at Site A were made available by the facility. Samples were collected using impingers and analyzed by colorimetry (a modified version of NIOSH Method P&CAM 237). The method does not distinguish between hydrazine and methylhydrazine. Tests conducted 30 to 40 days after tests in which hydrazine propellants were used showed trace (0.01 to 0.02 mg/m^3) background hydrazines levels.

Area air samples in the vicinity of the wastewater holding pond showed concentrations up to 0.11 ppm when aeration was occurring. Hydrazine concentrations in the holding pond water were 240 ppm as monomethyl hydrazine or 48 ppm as hydrazine.

Personal sampling has not been done at Site A. During each activity that entails potential hydrazine or methylhydrazine exposure, full body air-supplied suits are worn. The suits are PVC based and equipped with special gloves.

SITE B

Description of the Facility

Site B is a large chemical plant in the south central United States with diverse production and manufacturing units including production of hydrazine hydrate.

The plant was constructed beginning in 1971. The hydrazine unit was built in 1975. Currently, approximately 800 persons are employed at the plant. Operators are site employees; maintenance is by an outside contractor.

Description of Operations

Hydrazine hydrate is produced by the Bayer-Ketazine process, shown previously in Figure 2. Chlorine is reacted with sodium hydroxide to form sodium hypochlorite and sodium chloride. The hypochlorite is reacted with ammonia and acetone forming a dilute hydrazine stream through hydrazine and ketazine intermediates. The hydrazine hydrate is either shipped in bulk or in 30- or 55-gallon drums.

The hydrazine production unit is not enclosed and is not mechanically ventilated. The drumming operation is semi-enclosed and provided with ventilation using a large excess of exhaust air to keep all air movement well away from the operator. The drumming operation is very intermittent and was not observed during the site visits.

Description of Work Force and Recordkeeping System

The hydrazine hydrate unit is operated by about a dozen employees on a three shift/day basis (some employees work in conjunction with an adjacent unit). The employees are involved in monitoring, maintaining, and testing the hydrazine production unit. Few employees have accumulated significant seniority at the unit due to its relatively short existence.

Extensive employment, medical, and exposure records are kept at the site. The employee's personnel file follows that employee as she/he transfers around the company. The personnel record is retained at the site after the employee retires. Therefore, it is possible that detailed records for all past hydrazine hydrate employees will be at various locations. Duplicate records, such as all industrial hygiene sampling results, are maintained at the site.

Description of Medical and Industrial Hygiene Programs

A well-equipped clinic is maintained at the site. Emergency care as well as routine medical examination facilities are provided. Pre-employment and periodic (annual) examinations are given to all employees. No unique tests are provided to hydrazine unit employees.

The site also has a well-staffed health and safety group. Comprehensive safety and health programs are in place, including those for respiratory protection, operating and emergency procedures, and on-going air monitoring. Examples of program elements are detailed procedures for confined space entry (manway watch, supplied-air respirator, fully equipped secondary staff) and procedures for line opening.

Hydrazine hydrate production is highly automated. When a potential does exist for possible skin contact with hydrazine, protective gloves are worn. Gloves are worn, for example, during quality control sample collection and other line-opening procedures.

The plant offers a voluntary work clothing uniform program (for hydrazine and other areas of the plant). "Dirty" and "clean" sides of a shower area are maintained. Workers enter the facility at the end of the workshift, remove all clothing, and shower. Street clothes are put on in a separate area. The company launders all the work clothing.

Exposure Data

Frequent monitoring has been done to determine TWA exposures to hydrazine and short-term exposures in operations which entail the greatest potential for release of hydrazine. The sample collection medium currently in use is acid-coated firebrick absorbent; analysis is by desorption with dilute sulfuric acid, reaction of p-dimethyl-amino- benzaldehyde to form a yellow complex, and measurement of color intensity at 455 nm. In the past, samples have been collected in midget impingers with an 8% sulfuric acid absorbing solution, with analysis by the same colorimetric technique.

Exposure was assessed by reviewing the company's air sampling records. Typical TWA results showed levels less than 0.01 ppm. Short-term (5 to 10 minutes) samples during specific operations showed levels up to 0.1 ppm. Area samples showed levels up to 0.1 to 0.2 ppm. While the review of exposure data was not exhaustive, the general assessment is that personal exposures are well below the current OSHA limits as well as NIOSH recommendations.

SITE C

Description of Facilities

Site C is located in the southeastern United States. The facility is an integrated Air Force base, housing, in addition to other military units, a squadron of approximately 70 F-16 fighter planes. The presence of the F-16s requires maintenance and support capabilities unique to this aircraft since it is a "fly-by-wire" designed aircraft (that is, all control systems are based on electrical and/or hydraulic systems). It is imperative that emergency power be provided in the event of engine failure. Among these support operations are those for the handling and refilling of the Emergency Power Unit (EPU) fuel cells (bottles) containing 6.8 gallons of H-70 (a 70% hydrazine, 30% water mixture which provides fuel for the EPU upon engine failure). The maintenance squadron oversees these activities, which are carried out in an engine maintenance building and an adjacent service building. The service building houses hydrazine fuel cell refill operations and hydrazine drums. An emergency response trailer houses response equipment such as respirators, protective clothing, oxidizing bleach, and test materials.

The fuel cell refilling service facility was constructed in 1981, replacing a temporary facility which had been used since the F-16s were first assigned to the bases in the late 1970s.

Description of Operations

The operations involving hydrazine at the site include the removal of the hydrazine bottle from the aircraft, refilling the bottle as necessary, and tending aircraft (cleaning potentially contaminated areas on the aircraft and flight line) which have fired the EPU. These activities occur at two locations: on the flight line--just before or after landing--or in the service building.

Activities on the flight line involve stabilizing the EPU system, removal of the fuel bottle, and control and cleanup of any spills. Employees wear gloves, aprons, boots, and face masks during routine bottle handling on the flight line. Spills containment and cleanup is done by employees fully protected with air-supplied respirators, suits, gloves, and boots. This equipment is contained in an emergency response trailer.

Bottle refilling occurs in the service building. Refilling procedures are detailed in written instructions. The refilling stand is similar to that seen at the F-16 production facility (Site E), and is apparently being standardized for F-16 operations. The only ventilation is an overhead fan which is only operational when the heating system is in use. No ventilation was provided in the summer and the building was closed, apparently to protect nearby aircraft in the event of a hydrazine leak.

Description of Work Force and Recordkeeping System

Personnel from the maintenance squadron are the personnel potentially exposed to hydrazine. In addition, some emergency personnel (fire fighters, bio-environmental engineers) may be potentially exposed. All staff who could be exposed receive annual qualification training for handling F-16 hydrazine fuel. Currently, there are 32 trained hydrazine fuel handlers at the site. They perform all flight line and bottle refilling activities.

Detailed records are kept of assignments, medical examinations, and environmental exposures. These records are apparently kept in a central, easily accessible location; they were not available for review.

Description of Medical and Industrial Hygiene Program

The industrial hygiene and safety program at the base, as it impacts the hydrazine-related activities, has three major components--exposure monitoring, personnel protection requirements, and work practice procedures.

Monitoring is performed using detector tubes and the acidified-fire brick/colorimetric procedure. Engineers and fuel handlers perform testing with ortho-tolidine as required to determine the degree of surface contamination, if any, following EPU firing.

During hydrazine bottle refilling, fuel handlers wear boots, gloves, aprons, coveralls, and face shields. Air-supplied respirators are kept nearby for use if a leak develops.

Work practices and procedures have been specified to prevent or limit exposures. The bottle refilling procedures are detailed in step-by-step procedures. Fired EPUs require "safeing" the aircraft, which involves nitrogen lock-out and depressurization, exhaust port check (with detector tubes), and sealing of the EPU cylinder. Currently, about two bottles per week are processed.

A spill requires the following reaction by fuel handlers:

(1) marking and clearing of area with fire department on standby

(2) water wash (with 10% bleach)

(3) clean and test for free hydrazine with ortho-tolidine solution

(4) repeat, as necessary, usually three times

Annual physical examinations are given at the base hospital as part of the fuel handlers' recertification procedure. Standard pre-military physicals are also required. Examination is directed to the following systems or conditions:

- central nervous system
- eyes
- lungs
- liver
- kidneys
- hematopoietic system
- skin
- hypersensitivity to isoniazid or hydrazine

The medical examination also includes: hemocrit, urinalysis, gamma-GT, SGOT, BUN, blood sugar, and chest X-ray.

Exposure Data

Monitoring is performed using firebrick sorbent collection and colorimetric analysis.

Routine, predictable exposures do not occur, so environmental data are limited. Sampling during a spill showed hydrazine levels of 0.04 mg/m^3 for a 38-minute sample and 0.05 mg/m^3 for a 43-minute sample. Monitoring at a temporary fuel tank test stand, in use before the present permanent facility was ready, indicated concentrations of 0.01 and 0.13 mg/m^3 (30-minute samples) and 0.03 and 0.02 mg/m^3 (15-minute samples). The detection limit was 0.013 mg/m^3. The Air Force hydrazine standard (AFOSH Standard 161-13) is 0.13 mg/m^3 (0.1 ppm).

SITE D

Description of Facility

Site D, which began operations in 1963, is located in the southwestern United States and is a major government test facility. Approximately 300 persons perform a large number and range of tests primarily related to the nation's space program. Tests involving the use of hydrazines conducted at the site include testing of propulsion systems, personal protective equipment, materials corrosion, and chemical analytical procedures and instrumentation. The tests are conducted in facilities fairly remote from each other, apparently to limit the risk of physical damage and to minimize the number of employees potentially exposed to a given type of material.

Hydrazines are used in a number of areas at Site D. These include the engine and propulsion system test stands, and the materials testing area. Support areas include the chemistry lab, safety office, and medical clinic (contractor operated).

Description of Operations

Hydrazine fuels (hydrazine and monomethylhydrazine) are used during propulsion systems testing. A variety of engines are or have been tested. Currently, the majority of the tests involving hydrazines are connected with the space shuttle program.

The engine test stand area is the site of the largest use of hydrazines. A fuel storage area is maintained adjacent this site. Hydrazine is received via common carrier (tank truck) or in 55-gallon drums. Each test stand also contains a smaller fuels storage area; fuel is also stored on the test stand vehicle as needed.

Propulsion tests occur as required and not as part of a "routine" schedule. Actual test runs may last only 1 to 2 days. Test set-up and follow-up analysis may take several weeks for each test.

Materials testing is also done. Test materials are exposed in test cells to the compound of interest to determine corrosion and compatibility. Hydrazine currently is and has been used in such testing.

In support of the testing operations described above, as well as being part of other agency-wide studies, hydrazine sampling and analytical methods and personal protective equipment have also been tested at this site.

A potential exists for release of hydrazine during space shuttle landings. Hydrazine is a fuel aboard the orbiter and the orbiter must be checked for leaks. Since this site is an auxiliary site for shuttle landings, the site staff is on alert.

Hydrazine waste streams are vented through scrubbers and the scrubber water directed to a holding pond. The water is treated by chlorination prior to discharge offsite.

Description of Work Force and Recordkeeping System

The workforce at Site D is similar to that of other government operations in the study in that most personnel are contractor staff. Government staff includes facility and area managers.

Hydrazine-using activities occur primarily on the first shift, although some second-shift procedures may be performed when needed. Typically, tests involving use of hydrazine are conducted by 5 to 10 employees. Personnel from two test units are primarily involved. Employees potentially exposed to hydrazine are test engineers and chemists.

The recordkeeping system is quite extensive. Work assignments of personnel are recorded as well as those of contractors and contractor personnel. Detailed medical records are also kept. Records at the site go back to its beginning in 1963. Exposure records, when related to a specific activity, are also maintained.

Description of Industrial Hygiene and Medical Programs

The industrial hygiene program involves the control and monitoring of hydrazine during and after each test. Currently, the internal standards for exposure are 0.1 ppm for hydrazine and 0.2 ppm for monomethyl hydrazine. The chemistry department has been involved with the safety and health group in the monitoring of hydrazines and the testing of various instruments to be used in monitoring. Currently, Ecolyzer and Interscan units are being tested at the site. Results of some testing have been reported in internal reports.

All operations which entail the potential for exposure to hydrazine are performed while the operator is protected with air-supplied protective suits. ILC suits (ILC - Dover Company; Dover, Delaware) (chlorinated polyethylene with supplied air; modified for cooling with vortex tube) or SCAPE suits (self-contained atmospheric protective ensemble) are used. ILC suits are favored due to ease of operation; test stands are equipped with supplied air.

The medical program is run by a contractor. All employees who are required to wear protective equipment or who are exposed to toxic substances receive pre-employment and yearly physical examinations at the medical clinic. One full-time RN, one full-time LPN, and one part-time physician staff the clinic. Exposures to hydrazines requiring treatment have been limited. Only two skin contacts with hydrazine were reported in the past year. These resulted in transient surface burns with skin irritation.

Exposure Data

Monitoring is regularly performed before and after each test at Site D. Testing is done using integrated, colorimetric procedures and direct-reading instruments. Integrated samples are collected with acidified firebrick solid sorbent tubes or in fritted gas bubblers with 0.3 N sulfuric acid. Color is developed by the addition of p-dimethylaminobenzaldehyde and is read at 458 nm. This method reportedly provides a lower limit of detection of 0.02 ppm of monomethylhydrazine in a 25-liter air sample. The results of the monitoring have indicated concentrations primarily below the limit of detection. However, the data do not represent employee exposure since employees are protected with ILC or SCAPE suits.

Because of the nature of the hydrazine-using operations at Site D, there is greater concern regarding short-term, accidental exposures than longer-term, TWA exposure. The site has undertaken an active program of testing direct-reading instruments. Two reports were made available. Test report TR-262-001, Evaluation of MDA Scientific Model 7080 Hydrazine Sensor for the Detection of Monomethylhydrazine and Hydrazine, indicated that the MDA unit was suitable for monitoring sub-ppm levels of hydrazine, but provided erroneous monomethyl- hydrazine indications under field use conditions. A draft report (Interscan Hydrazine Analyzer) indicated that the Interscan unit exhibited similar responses for both hydrazine and monomethylhydrazine, and, while not intended for constant monitoring, was a reliable device for periodic monitoring.

SITE E

Description of the Facility

Site E is a large aircraft manufacturing complex. The current aircraft under production is the F-16, a combat fighter. Since the F-16 is a "fly-by-wire"- designed aircraft (that is, all control systems are based on electrical and/or hydraulic systems), it is imperative that emergency power be provided in the event of engine or generator failure. Accordingly, the F-16 is equipped with an emergency power unit (EPU) which is fueled by hydrazine (H-70: 70% hydrazine, 30% water).

F-16 manufacturing is housed primarily in a large main assembly building with over 16,500 employees. The main building was constructed in the 1940s, during World War II.

Steam for the facility is provided in a boiler plant incorporated into the main assembly building. Four industrial boilers are used for process steam and to develop steam to power the large compressors. Hydrazine is used in treatment of water for the boiler plant.

Description of Operations

The EPU must be installed and tested during assembly of the F-16 aircraft. Accordingly, the EPUs are fired ("green run"), and the hydrazine fuel cells (bottles) refueled and reinstalled. Hydrazine bottles are also refilled as necessary for transient aircraft.

The EPU fuel bottle contains approximately 6.8 gallons or 56 pounds of hydrazine. Bottle refueling and servicing involves three primary functions:

(a) Removal and installation of bottles from the aircraft

Flight line mechanics are responsible for removing and installing hydrazine tanks from the aircraft. A precise sequence of valve opening, line purging, and line disconnections is followed.

(b) Refueling and servicing the bottles

Flight line mechanics are also responsible for refueling the hydrazine tank. Approximately 4 or 5 refill operations per week are conducted. A "Fuel Tank Servicing Stand" is used to fuel the cell (see Figure 3). Hydrazine is removed and loaded by nitrogen pressure. All lines which require venting are vented through water or into the hydrazine reclaim drum. As in tank removal from the aircraft, refueling is controlled by precise step-by-step instructions.

(c) Spill cleanup and response

Flight line mechanics would also respond to any spills of hydrazine which might occur. The cleanup procedure involves the following:

- o Dilution of hydrazine with water to a concentration below the flammable limit (concentrations less than 30%)
- o Containment of the spill
- o Mopping hydrazine/water solution into waste bucket contained in "Hydrazine Cart" (see later discussion)
- o Neutralization with HTH (primarily calcium hypochlorite)
- o Testing with ortho-tolidine solution to verify absence of hydrazine
- o Reneutralization and retesting as necessary

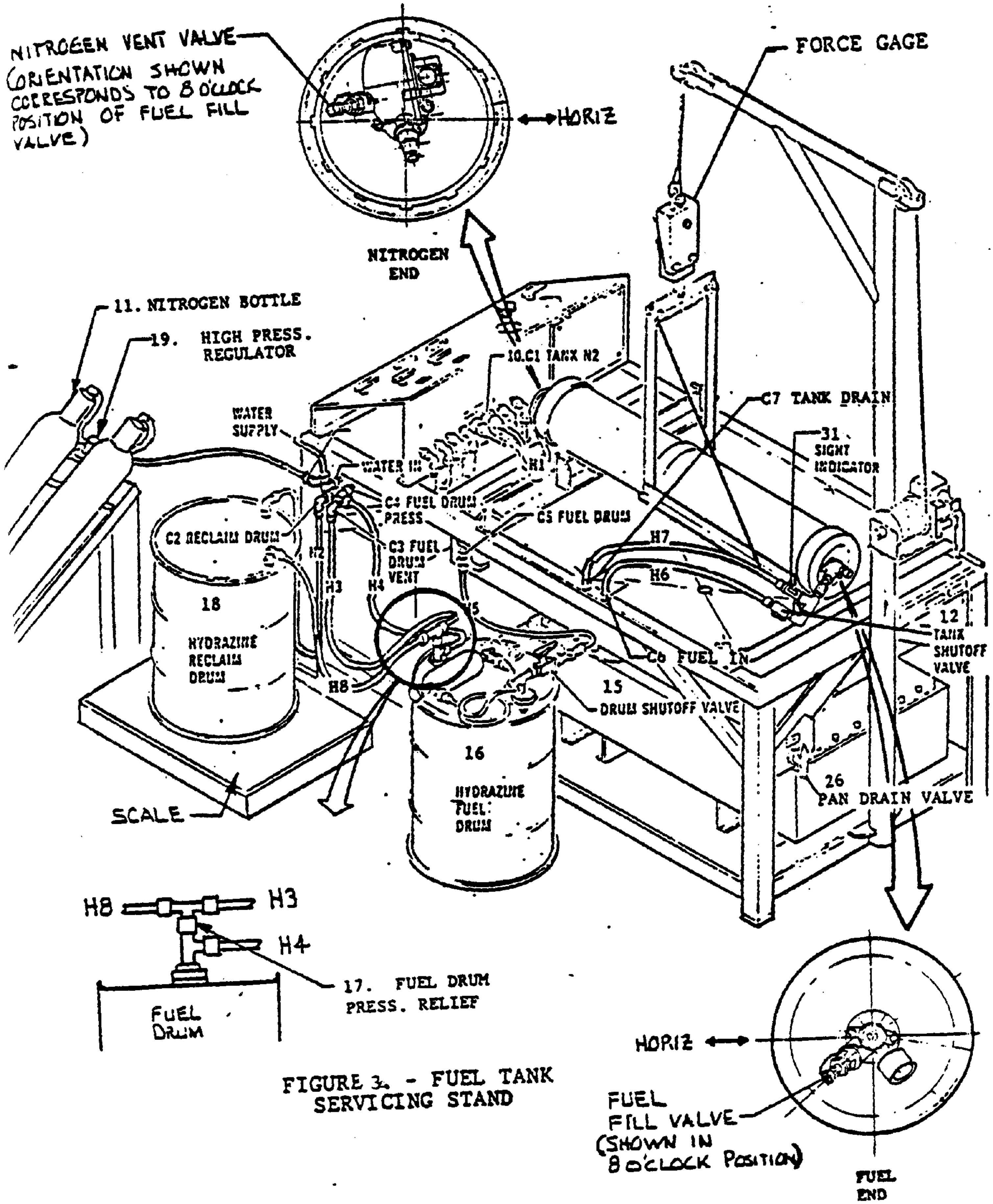

FIGURE 3. - FUEL TANK SERVICING STAND

Also observed was the operation of the power plant, specifically hydrazine addition as an oxygen scavenger. The hydrazine solution (two gallons/boiler every 7 to 10 days) is drawn from 55-gallon stock drums into an open stainless steel bucket for transfer to the day tank from which it is fed into the boiler water as needed.

Description of Work Force and Recordkeeping System

Site E employs approximately 16,500 persons in the F-16 assembly process. Of these, 51 are "certified for hydrazine handling." They handle hydrazine in EPU bottle loading and refilling, EPU test runs, and any spill cleanup. As detailed later, each flight line mechanic who may handle hydrazine is trained in proper precautions and procedures for handling. Accordingly, detailed records on the "certified" employees are kept.

Since each employee who handles hydrazine must be certified, detailed records of work area assignments, training, and physical examinations are kept and maintained at the facility.

Description of Industrial Hygiene and Medical Program

A large industrial hygiene group supported by an AIHA-accredited laboratory is present at the facility. The facility is divided into areas of responsibility; all hydrazine handling areas are in a single hygienist's area of responsibility. Currently, the OSHA standard (1 ppm) is used as the criterion for evaluating hydrazine exposures.

Integrated monitoring for hydrazine has been by adsorption on acid-coated firebrick, elution by water, and colorimetric analysis. Exposures have been monitored by site staff as well as by Air Force personnel. Direct-reading instrumentation has also been used in the past (MDA monitor and Interscan units). Monitoring is done only infrequently.

Detailed instructions have been prepared for each task--including those involving hydrazine. These detail the safety and health precautions incumbent on each step of EPU fuel cell handling.

Protective equipment during bottle refilling includes cotton coveralls, safety shields, a splash apron, and fuel handlers' gloves. Acrylonitrile or butyl rubber gloves are recommended for use. Gloves which are used in spill cleanup are decontaminated and washed. "Hydrazine Carts" are maintained on the flight line. These carts are equipped to provide spill response and contain personal protective equipment, water, chlorination media, and other spill control equipment. Supplied-air respirators are also provided for use during spill cleanup. MSA back packs and air-line units are used. Power room operators are provided face shields, boots, aprons, and gloves for use when handling hydrazine. Gloves are routinely used.

The industrial hygiene program is supported by a comprehensive training staff. Videotapes showing proper hydrazine work procedures and safety precautions are available. Each flight mechanic who handles hydrazine is given annual training, which includes viewing the videotapes. Respiratory protection training is also given in the training segments. Initial training involves a 2-day session; annual recertification is a 1-day course.

Medical examinations are provided to all workers who handle hydrazine fuel. The examination given to hydrazine workers is unique only in that a specific blood test (SMA 24) is included. The plant has an onsite medical staff of two physician's assistants, one medical technician, and a part-time physician (10 hours/week).

Exposure Data

Site E routine testing of hydrazine exposure is through the sulfuric-acid/firebrick collection technique, elution by water, and colorimetric analysis.

Results of area sampling during "green" runs (EPU test runs) indicated concentrations ranging from below the detection limit on the "upwind" side of the aircraft to 0.53 ppm at a point about 5 feet below the EPU exhaust port, based on sampling periods normalized to 15 minutes. (Actual sampling periods on the four dates ranged from 2.5 to 37 minutes because of changes and/or delays in the test sequences, in which the EPU was operated for only a few seconds at a time in each test mode).

The detection limit was not reported; however, hydrazine concentrations (normalized to 15 minutes) as low as 0.01 ppm were reported (0.19 micrograms of hydrazine found in a 7.4 minute sample). The report concluded that, because of the brevity of potential exposures, in which the EPU is fired for only a few seconds at a time and the exhaust cloud dissipates quickly (in 2 minutes or less), there is little risk of TWA exposures above the OSHA standard (1 ppm) or Air Force standard (0.1 ppm).

In a 1978 Air Force study of exposure to hydrazine in the maintenance and refueling of EPU's that have been operated, personal sampling indicated mean full-period, TWA concentrations of 0.03 and 0.19 ppm (standard deviations of 0.02 and 0.15 ppm, respectively) for two technicians (both wearing air line respirators) working at the refill stand. "Excursion" personal samples, of shorter duration (sampling periods are not given in the report) indicated mean peak concentrations of 0.04 and 0.14 ppm (standard deviations of 0.03 and 0.15, respectively), for the same two technicians during periods when peak exposures were anticipated. Modifications have been made in the refill stand since the Air Force study; the present system incorporates the engineering modifications recommended in the 1978 report to reduce exposure from sources identified in the study. The results of personal sampling, including sampling to assess exposures in activities associated with servicing fired EPU's in place on the aircraft (nitrogen depressurization, catalyst purging, and poppet valve replacement) are summarized in Table VIII.

TABLE VIII
Exposures to Hydrazine at Site E*

Task	Number of Samples	Mean Concentration (ppm)	Standard Deviation
Nitrogen depressurization and catalyst purge			
AC-1	6	0.03	0.02
AC-2	6	0.02	0.02
Poppet Valve Replacement			
AC-1	6	0.03	0.04
AC-2	6	0.03	0.02
Refill Stand (full period samples)			
RF-1	11	0.19**	0.15
RF-2	10	0.03**	0.02
Refill Stand (excursion sample)			
RF-1	3	0.14**	0.15
RF-2	4	0.04**	0.03

* Study conducted by the Air Force in 1978.
** Measured concentration; respiratory protection worn during testing.

SITE F

Description of Facility

Site F is located in the southeastern U.S. The primary mission at the site is the launching of space vehicles into Earth orbit using chemically fueled rockets. Currently, a major program at the site is the Space Transportation System (STS), popularly called the "Shuttle Program."

The site controls approximately 150,000 acres. Hydrazine usage is centered in several facilities including:

(a) Fuel Farm and Incinerator

(b) Spacecraft Operations/Industrial Area

(c) Vehicle Assembly Area

Support operations necessary for hydrazine use include administration, medical, and SCAPE suit (self-contained atmospheric protective ensemble) maintenance.

Description of Operations

Hydrazines are used at the site as hypergolic propellants, primarily for the space shuttle and space shuttle payloads. Both monomethyl- hydrazine and hydrazine are used as follows:

(a) Space Shuttle Orbiter

- o Orbital Maneuvering Subsystem (OMS) - monomethylhydrazine
- o Reaction Control Subsystem (RCS) - monomethylhydrazine
- o Hydraulic Power Unit - hydrazine

(b) Space Vehicles (payload operations) - hydrazine, 1,1-dimethyl-hydrazine

Hydrazines are received at a fuel farm, which has three 22,000-gallon tanks and the capability to store 100 55-gallon drums. Fuel is also maintained at the launch pad fuel farm. Detailed operating instructions for the fuel farm are developed.

Potential hydrazine exposure occurs through the loading, testing, and off-loading of fuel on the various vehicles. Currently, most larger hydrazine handling activities in the shuttle program are centered on the launch pad in order to consolidate potential exposures. Smaller amounts of hydrazine are processed onto spacecraft in the cargo operations areas of the site.

Whether hydrazine transfers occur at the fuel farm, operational payload facilities, during cargo operations, or at the pad, they appear to be handled similarly:

(a) An exclusion area is established and secured, whether with or without definition of the exclusion area by computer dispersion modeling. Typically, secured areas range from 200 to 1,500 feet, depending on the wind conditions and the amount of fuel being transferred.

(b) All potentially exposed personnel are protected by self-contained atmospheric protective ensemble (SCAPE) (if the use of SCAPE entails a safety risk, alternative protection may be worn--such as a splash suit).

(c) Air quality is extensively tested and the area cleared through Draeger tube sampling, both before and after each hydrazine transfer.

(d) The details of the transfer or handling operation are written and reviewed by the safety officer with certain minimum requirements.

(e) At a minimum, a buddy system is used with at least one "rescue" employee standing at ready.

Detailed operating instructions are provided for all tasks with potential hydrazine exposures.

Description of Work Force and Recordkeeping System

This facility is similar to others visited during this study in that a large proportion of the workforce is provided through contractors. Approximately 14,000 persons are currently employed onsite; of these, 2,000 are government employees and 12,000 are contractor staff. During launch operations, the number of workers at the facility will often greatly increase.

Recordkeeping appears to have been very thorough and details of work assignments, medical examinations, and exposures are thoroughly documented. The records are currently being computerized. Older records are stored in hard copy fashion and are also dispersed among a variety of contractors.

Description of Industrial Hygiene and Medical Program

Industrial hygiene and safety programs are provided at various levels. The government has a safety and health program onsite, the major base support contractor has industrial hygiene responsibility, and each major contractor provides safety support. A medical program, including an onsite dispensary for emergency treatment, is operated by a contractor.

SCAPE or ILC-Dover suits (totally enclosed, supplied-air) are worn during all hydrazine transfers. A maintenance facility is located adjacent the site. Suits are leak-tested, repaired, and maintained after each use.

Currently, hydrazine exposures are primarily evaluated through the use of Draeger colorimetric tubes, although use of various instruments is under evaluation. A good deal of effort has been expended in evaluating instantaneous and integrated monitoring systems. Most hydrazine transfers are short-term and lend themselves more to direct-reading rather than integrated monitoring. Since hydrazines are handled in pressurized systems, a leak detection and alarm system for monitoring at fixed points is used at the launch pad fuel farm during transfers.

Industrial hygiene and safety programs are supported by an extensive training and system safety program. All staff who handle or are potentially exposed to hydrazines receive toxic propellant training and protective equipment certification every 3 years. Training is supplemented by area walkdowns prior to assignment to the area.

All staff who are required to wear SCAPE suits or other respiratory protection receive a comprehensive physical examination every 3 years, along with SCAPE re-certification. Routine physical examinations (at 3-year intervals) are not directed specifically to hydrazine. However, in the event of a hydrazine exposure, the employee is given an examination consisting of vital signs, history, and physical examination, diagnostic studies, blood evaluation (glucose, calcium, carbon dioxide, and blood count), chest x-ray, and pulmonary function tests. In the case of 1,1,-dimethylhydrazine exposure, 24-hour urine samples are collected for hydroxylysine analysis.

Concentrated (greater than 1%) waste hydrazines-contaminated liquids are currently incinerated at an incinerator located in the fuel farm. Liquids, including wash water, contaminated at levels below 1% hydrazine are sewered and treated. Hydrazine vapors are vented through water/citric acid scrubbers.

Exposure Data

Since personnel are usually protected by SCAPE suits during activities that might release hydrazines into the air, little integrated sampling has been done to characterize TWA or full-shift potential exposures. Extensive leak detection, clearance, and re-entry sampling has been done with Draeger detector tubes; however, results of these tests do not represent exposure. The site is supporting research into a direct-reading instrument which will allow the more rapid "clearance" of areas where hydrazine propellants have been used. Impediments are the presence of ammonia as a potential interference and the frequent need to test in the presence of high humidity. Testing to date has not provided an instrument that is free of ammonia and humidity interference problems.

SITE G

Description of Facility

A visit was made to the corporate headquarters of a former hydrazine producer and current hydrazine derivative producer. The actual sites where hydrazine was formerly produced or used in the production of blowing agents or agricultural chemicals were not available for a walkthrough survey. Access was limited to the corporate headquarters where industrial health and safety programs are managed.

Description of Operations

The manufacturer does not currently produce hydrazine at any of its locations. Production was discontinued approximately 2 years ago. Hydrazine (30% hydrate form) was produced from 1964 to 1981 in one of its southern chemical plants. Approximately 3 to 4 million pounds per year of hydrazine hydrate were produced.

Hydrazine hydrate (roughly 6 to 8 million pounds per year, although exact figures were not available) is still used in the production of certain derivatives at other locations of this company (blowing agents, agricultural chemicals). These derivatives are produced primarily in the South with occasional use in the East. Hydrazine for these processes is received in the 54 or 85% hydrate form, primarily via tank truck.

Any waste hydrazine is treated with hypochlorite (chlorine), held in a holding tank, and disposed of by deep-well injection.

Description of Work Force and Recordkeeping System

Approximately 25 persons were involved in the production of hydrazine hydrate. Employees were involved in the operation, maintenance, and quality control testing at the production site. Less than 25 are now involved in its use in the manufacture of blowing agents and agricultural chemicals.

Medical and employment records are kept at the plant. The company is also currently computerizing exposure records. The current sampling data sheet is detailed, and includes the employee's name, social security number, activity, and necessary sampling and analytical data.

Description of Industrial Hygiene and Medical Programs

A corporate safety and health staff is maintained. Corporate industrial hygiene capabilities are supported at the plant level by technical staff who actually do the required monitoring. The monitoring plan is developed by the corporate industrial hygienist responsible for the particular location.

The industrial hygiene program has been expanded in the last 5 years and most monitoring data start from the late 1970s.

The site also maintains a corporate medical department. Each chemical worker receives an annual medical examination, although it is not specifically addressed to hydrazine exposure.

Employees receive training in the handling and use of hydrazines.

A limited number of employees at the derivatives plant are required to use full protection when handling hydrazines. Full protection includes rubberized suits, gloves, and SCBAs (self-contained breathing apparatus). This level of protection is used during the delivery of hydrazines, a process which entails the greatest exposure risk.

Exposure Data

Monitoring at Site G for hydrazine exposure has increased in the last 5 years. The current ACGIH and NIOSH-recommended standards (0.1 ppm) require the ability to reliably detect low concentrations. The current method is collection on sulfuric acid-coated glass beads. The hydrazine sulfate thus formed is desorbed with water and reacted with p-dimethyl- aminobenzaldehyde to form a yellow-orange-colored complex, and the absorbance is measured spectrophotometrically at 455 nm. The limit of detection is 0.010 ppm in a 40-liter air sample. Impingers were used for sample collection before glass beads were used.

Historical exposure data were provided as shown in Table IX. Most 8-hour, TWA exposures are well below 0.1 ppm. Occasional exposures above 0.1 ppm may occur for limited time periods or in limited areas. Employees in these areas are often protected by use of respiratory protective equipment.

At one time, a concern was expressed about residual hydrazine in derivatives produced at Site G. Testing indicated residual levels in agricultural chemicals ranging from none detected (the detection limit was not specified) to 20 ppm (by weight), levels which have not presented an exposure problem to downstream users.

SITE H

Description of Facility

The Site H facility produces a variety of industrial chemicals, including sodium nitrate, urea, ammonia, nitric acid, toluene diisocyanate, a flame retardant additive, and hydrazine. There are two hydrazine production units, only one of which (the ketazine process plant) was operating during the survey.

The ketazine process plant, in operation since 1979, produces aqueous hydrazine hydrate at a concentration of 65 to 66% by weight (as hydrazine). The stored product is diluted with demineralized water to specified concentrations before shipment in 55-gallon drums or tank trucks.

The ketazine process unit proper is located on a concrete pad (about 250 feet by 75 feet); the unsheltered unit is completely diked, and all sewers discharge to a wastewater treatment plant. The control room is in a building adjacent the unit; the same building houses supervisors' offices and a small process laboratory. The railcar and tank truck receiving and loading racks and the pack-out (drumming) building are remote from the production unit.

TABLE IX

Summary of Hydrazine Monitoring* Data - 1978 through 1981

Site G

Job Category	No. of Samples	% of Samples ppm <0.01	ppm <0.1	ppm <1.0	ppm <2.0**	ppm <12.0**
Boardman	68	80	100			
Outside Tech.	71	70	90	99	100	
Tank Farm Tech.	13	15	85	100		
Day Centrifuge Tech.	8			100		
Total Personal Samples	160	67	89	99	100	
Fixed Point (Area) Samples	89	--	33	91	99	100

*Sorbent collection; colorimetric analysis.

**Values between 2.0 and 12.0 ppm are for area samples. They do not represent worker exposure levels and were non-recurring incidents.

Description of Operations

In the ketazine process at Site H, chlorine piped from tank cars is reacted with a sodium hydroxide solution to form sodium hypochlorite, which is reacted with excess aqua ammonia and acetone from nearby storage tanks to form ketazine and hydrazone. Excess ammonia is recovered and returned to the reactor; the ketazine-rich stream is treated with additional acetone in the ketazine column to ensure that all hydrazine is present as ketazine. The ketazine stream from the ketazine column is hydrolyzed under pressure to form acetone, which is recycled to the ketazine reactor, and aqueous hydrazine, which is concentrated in another column before temporary storage in the day tanks from which the 65 to 66% product is pumped to product storage.

Description of Work Force and Recordkeeping System

The plant operates continuously over 3 shifts. Approximately 1,100 persons work at the entire facility. All employees in the ketazine plant are males.

Jobs with potential hydrazine exposure include those of maintenance (pipefitter, millwright), operation (control board, outside operator), and testing (quality control testing).

The plant maintains current and terminated personnel records. Records contain each employee's work history and exposure profile on a standardized form.

Description of Industrial Hygiene and Medical Program

Two full-time industrial hygienists work at the facility. The industrial hygiene program for the ketazine process area involves routine monitoring for noise, hydrazine, ammonia, ketazine, and radiation (from level indicators).

Personal protective equipment is used in the hydrazine area, primarily during quality control sampling. Protective equipment used includes coveralls, goggles, gloves, hard hats, and if necessary, respirators (Survivair 30-minute self-contained breathing apparatus and Robertshaw 5-minute air-supplied escape units).

The medical program involves a part-time physician and three registered nurses--one certified in occupational health. All employees receive a pre-employment physical. Physical examinations are performed every 5 years for employees under 40 years of age and every 2 years for employees 40 years of age and above. Hydrazine workers also receive a liver function blood test every six months. Physical examinations include chest x-rays, hearing and visual tests, lung function tests, and blood and urine tests.

Exposure Data

Monitoring over two consecutive day shifts was conducted at Site H. Sulfuric acid-coated firebrick was used to collect the samples. Analysis was by the p-dimethylaminobenzaldehyde colorimetric technique. Ammonia concentrations were also monitored (sample collection with sulfuric acid-coated silica gel tubes; analysis by ammonia-specified electrode).

Results are presented in Tables X and XI for hydrazine and ammonia, respectively. Time-weighted average hydrazine exposures ranged from below the limit of detection to 0.27 ppm. Short-term hydrazine exposures (during process stream sampling) of up to 0.91 ppm were also measured.

Ammonia concentrations measured ranged from none detected to 2.9 ppm.

BOILER WATER TREATMENT

A site visit was not made to a large boiler operation (electric power utility), but information on hydrazine exposures was submitted by a southern utility. The information contained the results of air sampling at nine power stations during the addition of hydrazine to the boiler water system. Exposure data are summarized in Table XII. Personal sampling indicated short-term exposures during specific activities (level checking, drum changing, pouring from drums, and level adjustment) ranging from 0.002 to 0.23 ppm (mean value 0.087 for samples indicating detectable levels) during sampling periods ranging from 5 minutes to 50 minutes. Eight-hour, TWA exposures (based on assumed "zero" exposures for the unsampled periods) ranged from less than 0.0002 to 0.005 ppm (mean value 0.002).

Area samples taken in drum storage and hydrazine dispensing areas indicated concentrations ranging from less than 0.002 ppm to 0.09 ppm.

DISCUSSION

Four types of hydrazines workplaces were reviewed during the course of this study: sites where hydrazines are used as propellants, hydrazine production sites, sites where hydrazine is used as an aircraft emergency power unit fuel, and sites where hydrazine is used in boiler water treatment. Several observations regarding hydrazines can be made on the basis of information obtained during this study:

1. Awareness of the acute toxicity of hydrazine and the concern raised by the results of chronic exposure testing in animals have generated a respect for the importance of avoiding exposure in handling hydrazine compounds. At the facilities visited during this study, employers and employees where aware of the need to avoid exposure, and had developed hydrazines handling systems, work practices, and personal protective equipment programs to minimize the risk of exposure.

TABLE X
Results of Hydrazine Sampling - Site H
February 8 and 9, 1984

Sample Number	Sample Date	Description	Sampling Period Start	Sampling Period Stop	Sample Volume (Liters)	Hydrazine Concentration (ppm)
HYD-4	2/8	Board operator	0842	1523	25	<0.003
HYD-22	2/9	Board operator	0738	1454	28	<0.003
HYD-3	2/8	Outside operator	0817	1459	74	0.041
HYD-23	2/9	Outside operator	0743	1454	81	0.008
HYD-1	2/8	Sample operator	0742	1512	57	0.27
HYD-6	2/8	Sample operator, collecting and analyzing samples[a]	0857	0903	5.6	0.68
HYD-11	2/8	Sample operator, sampling and dumping old samples[b]	0933	0943	9.4	0.02
HYD-12	2/8	Sample operator, sampling and analyzing samples[c]	1121	1148	25	0.91
HYD-24	2/9	Sample operator	0800	1510	56	0.041
HYD-28	2/9	Sample operator, sampling hydrolysis overheads and hydrolysis bottoms	1330	1337	6.5	0.06

(a) Sampling concentrator bottoms, dilute caustic, and hypochlorite; analyzing concentrator bottoms sample.

(b) Sampling ketazine overheads, ketazine bottoms, ketazine tray 58, ketazine feed, hydrolysis feed, and hydrolysis bottoms; dumping old samples into pot to recycle waste line.

(c) Sampling ketazine bottoms, ketazine tray 69, hydrolysis trays 72, 68, 62, and 58; analyzing those samples for percent organics; sampling ammonia stripper bottoms, north and south ketazine reactors, ketazine tray 58, hydrolysis overheads, hydrolysis feed, and concentrator bottoms; weighing those samples.

Analytical limit of detection: 0.1 microgram per sample.

TABLE X (continued)
Results of Hydrazine Sampling - Site H
February 8 and 9, 1984

Sample Number	Sample Date	Description	Sampling Period Start	Sampling Period Stop	Sample Volume (Liters)	Hydrazine Concentration (ppm)
HYD-7	2/8	Drumming 54% N_2H_4	0946	1518	17	0.01
HYD-29	2/9	Drumming 35% N_2H_4	1337	1456	7.0	<0.01
HYD-2	2/8	Pipefitter	0752	1513	30	0.025
HYD-21	2/9	Pipefitter	0724	1445	30	0.02
HYD-5	2/8	Instrument man	0847	1521	67	0.002
HYD-25	2/9	Instrument man	0808	1519	77	<0.001
HYD-26	2/9	Millwright	0812	1507	38	<0.002

TABLE XI
Results of Ammonia Sampling - Site H
February 8 and 9, 1984

Sample Number	Sample Date	Description	Sampling Period Start	Sampling Period Stop	Sample Volume (Liters)	Ammonia Concentration (ppm)
NH3-1	2/8	Sample operator	0746	1512	41	0.64
NH3-5	2/8	Sample operator, collecting and analyzing samples[(a)]	1044	1053	8.4	2.9
NH3-22	2/9	Sample operator	0800	1510	35	0.55
NH3-23	2/9	Sample operator, collecting and analyzing samples[(b)]	0925 1054	0953 1100	32	0.82
NH3-3	2/8	Outside operator	0817	1459	34	<0.08
NH3-21	2/9	Outside operator	0745	1454	53	<0.05
NH3-2	2/8	Welder	0756	1512	41	<0.07
American Conference of Governmental Industrial Hygienists TLV (8-hour, time-weighted average)						25

(a) Sampling aqua ammonia and hypochlorite; analyzing aqua ammonia sample.
(b) Sampling aqua ammonia, acetone, ketazine bottoms (brine), ketazine tray 58, ketazine feed, hydrolysis feed, hydrolysis bottoms, and vaporizer; titrating aqua ammonia.

Analytical limit of detection: 2 micrograms per sample.

TABLE XII

Hydrazine Exposures in Boiler Water Treatment
at Nine Electric Power Plants*

Location	Sample Type (Number)	Hydrazine Concentration (ppm)
I	Area (2)	0.006-0.013
II	Area (2)	0.007-0.011
III	Area (4) Personal (1)	0.0031-0.0065 0.071 (14 minutes)
IV	Area (2) Personal (1)	0.002-0.006 0.23 (7 minutes)
V	Area (6) Personal (1)	< 0.0002-0.077 < 0.002 (36 minutes)
VI	Area (4) Personal (2)	0.0032-0.024 0.024 (28 minutes) 0.099 (5 minutes)
VII	Area (4) Personal (1)	0.016-0.033 0.162 (9 minutes)
VIII	Area (5) Personal (2)	0.0017-0.024 0.065 (37 minutes) 0.023 (10 minutes)
IX	Area (4) Personal (1)	0.002-0.09 0.02 (50 minutes)

*Data submitted by a southern utility in a written communication.

2. Use of hydrazines as propellants involves potential exposures during: (1) loading/unloading of the spacecraft and related propellant transfer operations, and (2) testing of spacecraft components which utilize hydrazines. During hydrazine propellant handling at the sites visited, the worst-case exposure potential is assumed; accordingly, full-body supplied-air suits are worn whenever hydrazine is loaded, unloaded, or moved in vessels or pipes. Areas are "cleared" prior to resumption of activities without this protection. Airborne hydrazine concentration measurements made in propellant transfer operations are essentially instantaneous and are not intended to reflect personal exposures.

3. Hydrazines production activities generate TWA exposures generally well below 0.1 ppm, primarily because the production processes involve closed systems. However, certain operations (centrifuging, outdoor activities, routine process stream sampling, and maintenance work) appear to entail a somewhat greater risk of exposure. The use of personal protective equipment was noted during such activities at the producers visited. Process stream sampling appears to present the greatest recurring risk of exposure; TWA exposures were generally within established limits (0.04 to 0.27 ppm), but excursions up to 0.91 ppm were noted.

4. In recent years, the use of hydrazine as a fuel in military aircraft emergency power units (EPUs) has resulted in an increase in the handling of small amounts of hydrazine. Routinely, this handling should not result in TWA exposures approaching current limits and exposure recommendations. The use of proper safeguards during EPU fuel cell handling and refilling (a widely used fueling stand specifically developed for this purpose is illustrated in Figure 3) has minimized the potential exposure. Prior to improvements in the venting system of the fuel stand, potential TWA exposures up to 0.19 ppm were noted. In servicing of aircraft, the increased use of hydrazine as an EPU fuel may involve increased risk of exposure from contact with residues on aircraft whose EPUs have been fired or from spills that may occur in flight line servicing of EPUs.

5. Hydrazine is widely used as an oxygen scavenger in boiler systems. The quantities used during each addition are rather small, and exposure data submitted by a utility in the course of this study indicated relatively low exposure. Short-term exposures (5 to 37 minutes) did not exceed 0.23 ppm. Long-term area samples indicated concentrations below 0.1 ppm. However, the potential for exposure exists if spills occur during transfers and, therefore, use of protective equipment (gloves, mask, shield) is appropriate in handling the hydrazine formulations. Hydrazine manufacturers recommend automated hydrazine transfer procedures in larger boiler systems.

In summary, data obtained in the course of this study (data submitted by companies, obtained from companies during site visits, or collected as part of an in-depth industrial hygiene survey) have shown that time-weighted average exposures to hydrazines are relatively low (generally below 0.1

ppm). The number of exposed workers is also small; only a few workers are involved in hydrazines manufacture and the routine use of hydrazines as propellants and fuels. The current manufacturing methods are relatively new and large scale propellant and emergency power unit usage is also fairly recent. Because of these factors, the accumulated person-years of exposure are relatively low, and it is unlikely that suitable cohorts exist for retrospective exposure studies.

RECOMMENDATIONS

1. Exposures to hydrazine and hydrazine compounds may occur during spills or other non-routine situations. Generally, where the potential for such exposures is in any way predictable, employees have been well protected (air-supplied protective suits), and the potential exposure areas have not been re-entered until it has been determined that hydrazine concentrations have adequately abated. There is a need for direct-reading devices to rapidly characterize the potential for exposure in such situations, especially where hydrazines are used as propellants and fuels (loading and off-loading, engine testing, and the bottle refilling and aircraft decontamination activities associated with servicing aircraft emergency power units).

   However, existing sampling and analytical methods for hydrazine generally are suitable only for reliably determining TWA exposures. The direct-reading instruments presently available lack specificity (i.e., the instruments are cross-sensitive to other materials) or provide indications that are affected by humidity. Colorimetric tubes are being widely used in the interim, but reliable direct-reading instruments are needed for rapid characterization of exposure potential in such applications as establishing safety zones around known or suspected spills or "clearing" an area for entry by unprotected workers. Research on such instruments is currently being done, primarily to satisfy government requirements.

2. The increased use of hydrazine as a military aircraft emergency power unit fuel will undoubtedly entail a greater frequency of spills and leaks, due to increased servicing and refueling requirements. Refueling should be done only in well-ventilated facilities. Temperature control may be necessary to allow the use of protective devices (gloves, mask, apron) without causing skin exposure as a result of concentration of hydrazine against the skin as vapors dissolve in perspiration.

3. Hydrazine and hydrazine derivatives are manufactured and processed in closed systems. In such systems, the greatest risk of routine exposure occurs when the pressurized system is accessed for process and quality control sampling. Control of exposure during sampling may be improved through the use of closed loop sampling systems and the more cautious disposal of excess samples.

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