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HYDRAZINE SAFETY REPORT

John G. Guidero
Aerospace Corporation

Frank H. Johnson
Captain USAF

TECHNICAL REPORT NO. AFWL-TR-73-50

July 1973

AIR FORCE WEAPONS LABORATORY
Air Force Systems Command
Kirtland Air Force Base
New Mexico

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FOREWORD

This report was prepared by the Aerospace Corporation, Albuquerque Field Location, Kirtland AFB, New Mexico, and the Air Force Weapons Laboratory under Contract F04701-72-C-0073. The research was performed under Program Element 63605F, Project 317J, Task 15.

Inclusive dates of research were March 1972 through July 1972. The report was submitted 7 May 1973 by the Air Force Weapons Laboratory Project Officer, Captain Frank H. Johnson (LRL).

The authors would like to thank the following personnel for their guidance and assistance in preparing this report: Lt Colonel E. H. Thrush (ASD); Major C. Eggert (AFWL); Dr. K. C. Back (Aerospace Medicine, WPAFB); Mr. W. Studhauter (North American Rockwell Corporation); Mr. P. Gendron (Sundstrand Aviation); Major H. A. Shelton (AFWL); and Mr. L. E. Rackley (General Dynamics).

This technical report has been reviewed and is approved.

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ABSTRACT

(Distribution Limitation Statement B)

The use of large quantities of hydrazine onboard a military aircraft is of major concern because of its toxicity and potential fire hazard. These hazards and their control are emphasized in this special hydrazine report. The experience accumulated over the past several years indicates that with reasonable precautions, trained personnel, and adequate procedures the proper handling of hydrazine should present no serious hazards.

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INTRODUCTION

The use of large quantities of hydrazine onboard a military aircraft is of major concern because of its toxicity and potential fire hazard. These hazards and their control are emphasized in this report. At the present time all known hazards associated with the use of monofuel hydrazine systems are controllable. With reasonable precautions, trained personnel, and adequate procedures the proper handling of hydrazine should present no serious hazards. However, prolonged exposure to high concentrations of hydrazine vapor, contact with the skin, or ingestion will produce harmful effects. The experience accumulated by the chemical and aerospace industries indicates that with suitable and rather simple precautions, which are contained in this report, there should not be any toxicity problem or danger involved in the handling, use, and airborne dumping of hydrazine. Hydrazine has been used for many years in missile and space vehicles. More recently the monofuel M-86, which is a combination of hydrazine and monomethyl-hydrazine, is being used in emergency power units on both military and commercial aircraft.

The proper design of aircraft systems and the training of aircraft crew members, maintenance, and ground support personnel should ensure that no undue hazards will exist with the use of hydrazine within an aircraft.

This report is intended as a ready source of information and as a general guide in planning for minimizing the hazards associated with the handling, storage, and transportation of hydrazine (N_2H_4) when used aboard military aircraft. It also contains the results of a special study prepared by Captain Frank H. Johnson, System Safety Project Officer, Air Force Weapons Laboratory (LRL). This special study is concerned with safe dumping (planned or emergency) and dispersion of hydrazine from an aircraft.

Up to 2000 pounds of hydrazine, N_2H_4, MIL-P-26536C, may be stored onboard an aircraft. It may be used as a monofuel to run other aircraft systems.

This hydrazine safety report was prepared by a special system safety team and describes hydrazine characteristics, hazards, handling, storage, transportation, materials compatibility, safe atmospheric dispersion, and recommended future studies and required safety test programs.

SECTION II

HYDRAZINE

1. GENERAL PROPERTIES AND DESCRIPTION (Ref. 1)

a. Chemical Composition

Propellant-grade hydrazine contains a minimum of 97.5 percent hydrazine, N_2H_4, the remainder being primarily water. Military Specification MIL-P-26536C (USAF) covers this grade.

b. General Appearance

Hydrazine is a clear, oily, water-white liquid with an odor similar to that of ammonia.

c. Chemical Nature

Hydrazine is a strong reducing agent, weakly alkaline, and very hygroscopic. It will react with carbon dioxide and oxygen in air. Exposure of hydrazine to air on a large surface (as on rags) may result in spontaneous ignition from the heat evolved by its oxidation with atmospheric oxygen. A film of hydrazine in contact with metallic oxides or other oxidizing agents may ignite. Hydrazine decomposes on contact with some metals, including iron, copper, molybdenum, and their alloys and oxides.

d. Physical Properties

Boiling point	236°F
Freezing point	35°F
Density of liquid at 68°F	8.4 lb/gal
Specific gravity of vapor relative to normal air	1.1
Critical temperature	716°F
Critical pressure	2120 psig
Critical density	1.9 lb/gal

Vapor pressure	
at 40°F	0.07 psia
at 80°F	0.31 psia
at 120°F	1.04 psia
at 160°F	2.9 psia
Viscosity at 68°F	0.97 centipoises
Flash point	
Open cup	126°F
Closed cup	100°F
Autoignition temperature	518°F
Flammability (or explosive) limits in air at 212°F	
Lower limit	4.7 percent by volume
Upper limit	100 percent by volume

e. Solubility

Hydrazine is miscible with water and soluble in ammonia and alcohol but is insoluble in hydrocarbons.

f. Stability

Hydrazine is a stable liquid under the extremes of heat and cold expected in long-term storage. It will freeze, but upon freezing, it contracts, so there is no danger of rupture or damage to storage vessels. Freezing does not affect the chemical properties of hydrazine. Thermal decomposition begins at about 320°F, but if hydrazine is permitted to remain in contact with catalysts such as copper, molybdenum, or iron oxide, decomposition may occur at room temperatures. Liquid hydrazine is stable to shock. Hydrazine vapor can be exploded by a spark or flame if it is within the flammable limits.

SECTION III

SOURCE AND COST

Anhydrous hydrazine is produced for Air Force and other military applications under Military Specification MIL-P-26536C (USAF). This propellant-grade hydrazine is produced at Kelly Air Force Base (Plant 80), San Antonio, Texas. The current cost of hydrazine as of April 1972 was quoted from Plant 80 as $2.30/lb delivered in all quantities.

SECTION IV

CURRENT AIRCRAFT MONOFUEL SYSTEMS

Several monofuel emergency power systems have been produced in the United States both for commercial and military aircraft use. Four current systems of interest are (three of the systems have been delivered and ground and flight tested) the F-14 Navy Fighter monofuel emergency power unit (MEPU), the F-15 Air Force Fighter MEPU, and the Concorde SST (first commercial aircraft to utilize an MEPU). A similar MEPU is planned for the F-16 light-weight fighter. The systems all use an M-86 monofuel, which is similar in physical characteristics to anhydrous hydrazine. M-86 consists of 86 percent monomethylhydrazine and 14 percent anhydrous hydrazine. Hydrazine has a higher available energy content and has a higher freezing point (+35 versus -68°F) than M-86. In addition to the use in aircraft monofuel systems, there has been many years of experience with the use of hydrazine in rocket propulsion systems. Hydrazine monofuel control systems are currently used on manned and unmanned space vehicles.

SECTION V

HAZARDS AND PREVENTION

1. HYDRAZINE HAZARDS

Hydrazine exhibits three general types of hazards; health hazards from direct exposure to the liquid propellant or its vapor, fire hazards, and explosion hazards.

a. Health Hazards

(1) General

At normal temperatures, hydrazine is a clear, mobile, hygroscopic liquid with moderate volatility. The liquid is mildly alkaline and caustic to human tissue.

(2) Toxicity

If spilled on the skin or in the eyes, liquid hydrazine can cause local damage or burns, if not completely rinsed and diluted with water, and can cause dermatitis. In addition, it can penetrate the skin to cause systemic effects similar to those produced when the compound is swallowed or is inhaled for a prolonged time period. If inhaled, the vapor causes local (irritation of eye and respiratory tract) and systemic effects. On short exposure of high concentrations, systemic effects involve the central nervous system. Resultant symptoms include tremors; on exposure to higher concentrations, convulsions and possibly death may result. Repeated exposures may cause toxic damage to the liver (fatty liver) and kidney (interstitial nephritis), as well as anemia. The threshold exposure limit value (no harmful effects) of hydrazine is 1 ppm 1.3 mg/cu m) for continuous 8-hour exposure. For short exposure times the limits are

<u>Emergency Exposure Limits</u>

30 ppm for 10 minutes exposure limit

20 ppm for 30 minutes exposure limit

10 ppm for 60 minutes exposure limit

(3) Fire

Hydrazine vapor is flammable in all concentrations in air above 4.7 percent. It is hypergolic with some oxidants, such as hydrogen peroxide and fuming nitric acid. When a film of hydrazine comes in contact with metallic oxides, such as iron oxide, copper oxide, lead oxide, manganese oxide, and molybdenum oxide, it may ignite owing to the chemical heat of reaction. Rags, cotton waste, sawdust, excelsior or other materials of a large surface area that have absorbed hydrazine should not be stored under conditions that prevent dissipation of the heat that can evolve by the gradual process of air oxidation and may eventually cause spontaneous ignition.

(4) Explosion

Vapors of hydrazine can be exploded by an electric spark or by an open flame. Liquid hydrazine is stable to shock and friction.

b. Additional Operational Hazards

All propellants present the hazard of flammability. High-energy propellants provide additional hazards due to their unique chemical and physical properties. Hydrazine has the added hazards of (1) spontaneous reaction with certain other propellants, (2) formation of explosive mixtures with air or other chemicals, (3) chemical attack on common materials of construction, and (4) toxicity.

c. Hazard Prevention

All hydrazine storage and transfer areas, as well as surrounding areas that may be reached by leakage or spills, shall be cleared and kept clean of organic matter and possible oxidizers. All electrical sparks and open flames must be strictly prohibited. All leaks and spills shall be immediately flushed away with copious* quantities of water.

Hydrazine must be stored apart from oxidizers and catalytic agents and away from possible sources of ignition such as electric spark or flame. All equipment must be grounded to prevent the generation of any static charge, all electrical equipment shall be of the class and group recommended in the

*Minimum 10-to-1; all areas shall have drainage to a catch basin to prevent entrance of the chemicals into the water table.

National Electrical Code. Hydrazine should be stored and handled under an atmosphere of nitrogen at all times. All confined spaces shall be well ventilated to minimize the buildup of an explosive mixture.

Spontaneous reaction of hydrazine with certain other propellants and the formation of explosive mixtures with air or other chemicals are prevented by storing and handling hydrazine under an atmosphere of gaseous nitrogen (or other inert gas) at all times. Chemical attack on common materials is prevented by prohibiting the use of catalytic materials with hydrazine. Toxicity is prevented by the wearing of protective clothing and use of respirators or self-contained breathing apparatus to ensure against inhalation of the vapor or exposure of the body to the liquid or vapor.

d. Hazard Control

(1) Air-Supported Fire

Water, which acts by cooling and diluting, is the most effective agent for completely extinguishing air-supported hydrazine fires. A mixture of 60 percent water in a hydrazine-water solution is nonflammable. The most efficient means of applying water is in a coarse spray. Water fog and bicarbonate-base (powder) extinguishing agents may be used for combating spill-type hydrazine fores. In large fires, there is a danger of back-flashing with these agents. Hydrazine accelerated the disintegration of foam. The use of vaporizing liquids on hydrazine fires is not recommended because these agents are generally ineffective on this type of fire. Effective use of water minimizes the re-ignition and flashback hazard in hydrazine fires.

(2) Oxidizer-Supported Fire

For oxidizer-supported fires (flare burning) with hydrazine, where acceptable for the specific oxidizer present, water is the most effective extinguishing agent.

SECTION VI

SAFETY

1. SAFETY MEASURES

a. General

All operations involving the handling of hydrazine shall be performed by experienced persons working in a group.

b. Education of Personnel

The following subjects should be explained thoroughly to all persons concerned with the handling, storage, and transfer of hydrazine:

(1) Nature and properties of hydrazine

(2) Compatible materials of construction

(3) Proper personal protective equipment for each operation involving hydrazine and the care of such equipment

(4) Fundamentals of self-aid and first-aid treatment after exposure to hydrazine or its vapors

Trained supervision of all potentially hazardous activities involving anhydrous hydrazine is essential. Each person working with hydrazine must be taught both first-aid and self-aid.

(1) First-Aid and Self-Aid

If hydrazine is spilled on the body, remove contaminated clothing at once and flush affected parts thoroughly with large amounts of water. If spilled in the eyes, flush thoroughly with large amounts of water for at least 15 minutes and get medical help. If necessary to choose between flushing and getting help, flush the eyes for at least 10 minutes and then seek help, then resume flushing. Persons exposed to high concentrations of the vapor for a prolonged period should be removed to an uncontaminated atmosphere and kept as quiet as possible; get medical help as soon as possible. If confulsions occur, quick-acting barbiturates administered only by direction of a physician with due regard for synergistic depression of respiration should help.

(2) Personal Protection

The chief personal hazards associated with the handling of hydrazine are inhalation of the vapor, exposure of the body to the liquid or vapor, and fire.

(a) Head, Face, and Body Protection

Under normal conditions of use a plastic face shield, rubber or plastic wrist and arm protectors, and a rubber-type apron will be worn. Whenever there is a possibility of gross splashing, however, protective clothing covered by Military Specification MIL-C-43063B shall be worn. Also approved are rubber or rubberized items of clothing (including neoprene), fiberglass clothing impregnated with a corrosion-resisting plastic (such as Teflon or Kel-F), and vinyl-coated cotton.

(b) Respiratory Protection

Whenever the vapor concentration of hydrazine exceeds the threshold limit value and if it is necessary to work continuously in that atmosphere, approved respiratory protection must be worn. A person should not depend upon the odor to indicate the need for wearing respiratory protective devices.

The degree of protection afforded by the ammonia canister gas mask has not been firmly established. Until more information on this subject is available, the gas mask should not be relied upon for protection in confined areas or whenever there are potential or actual exposures to moderate or high concentrations of hydrazine vapors. Under such conditions self-contained breathing apparatus shall be used.

(c) Hand and Foot Protection

The selection of a protective glove depends on two factors: (1) protection against the propellant and (2) ease of finger manipulation. Fuel-resistant gloves under Specification MIL-G-43196A will be worn.

Natural rubber, reclaimed rubber, or GR-S rubber safety shoes, or an overboot designed to be worn over regular safety footwear and high enough to fit comfortably under the legs of protective trousers, shall be worn. Contaminating agents will be removed promptly and the footwear inspected frequently.

c. Air Sampling and Detection

A system should be installed to sample the air and to detect and record air pollution in the vicinity of the hydrazine storage area, at the test stand, and during all transfer operations. The gas analyzer produced by Mine Safety Appliance Company (MSA) can be used for this purpose; however, according to Dr. London of AMRL, its effectiveness is questionable at the lower threshold limit value of 1 ppm. It is adaptable for continuous monitoring and alarm and is not considered a portable instrument. Other small portable units are available, but their effectiveness is questionable at the lower limit of 1 ppm for field use in detecting leaks, spot checking, and checking decontamination. All current personnel hydrazine dosimeters developed to date have not proven satisfactory when tested in the field.

d. Emergency Equipment

Safety showers and eyewash fountains should be provided to permit immediate treatment of personnel in case of accidental contact with hydrazine.

An adequate nearby water supply should be available to wash down any accidental spillage. In areas where there is a possibility of spillage, such as unloading and handling points, it is good practice to install a sprinkler system operated by local and remote control. Hoses supplying a heavy stream of water should be provided for flushing down spills or extinguishing fires. Self-contained breathing apparatus should be worn in the event of gross spillage or when in confined areas.

SECTION VII

MATERIALS

1. MATERIALS COMPATIBILITY

a. General

Hydrazine is basically compatible with a wide spectrum of materials of construction. However, considerable care must be exercised in selecting suitable materials due to the hazardous properties of the propellant and the necessity to eliminate propellant spills and leaks.

Hydrazine reacts with metal oxides and oxidizing agents and absorbs water readily. Consequently, the hydrazine transfer and storage systems must be free of air, moisture, rust, and contamination. The lubricants, solvents, and gaskets utilized in these systems must be chemically inert to hydrazine.

b. Compatible Materials

The following materials and lubricants have been found to be compatible with hydrazine:

Aluminum Alloy No. 1100	Stainless Steel 304
Aluminum Alloy No. 2014	Stainless Steel 321
Aluminum Alloy No. 2024	Stainless Steel 347
Aluminum Alloy No. 4043	Stainless Steel AM-350*
Aluminum Alloy No. 5052	Stainless Steel AM-355*
Aluminum Alloy No. 6061	Stainless Steel 17-7 PH
Aluminum Alloy No. 6066	Iron-base Superalloy A-286*
Aluminum Alloy No. 356	Inconel
Aluminum Alloy No. B 356	Inconel-X
Aluminum Alloy Tens 50	Titanium Alloy Ti-6Al-4V
Chromium plating	Graphite*
Kel-P	Dow Corning No. 11*
Teflon	Sinclair L743 (MIL-L-25336)
Teflon 100X	Quigley "Q" seal*
Fluorolube GR-70*	Kel-F grease*

*These alloys contain over 0.5 percent of molybdenum (Mo) and should not be used at temperatures above 160°F.

c. Materials for Limited Service

Copper, nickel, and Johns-Mansville Packing No. 76 are satisfactory for limited service in hydrazine. Since these materials are attacked by hydrazine under some expected conditions or time duration, their use is not recommended.

d. Incompatible Materials

The following materials and lubricants have been found to be incompatible with hydrazine and must not be used.

K-Monel	Copper plating
Brass	Micarta
Bronze	Johns-Mansville Packing No. 60
Silver	Viton A
Zinc	Kel-F Elastomer
Cadmium	Mylar
Hastelloys	Buna-N
Electroless Nickel plating	Hypalon
Cadmium plating	
Magnesium	
Lead	
Iron	

e. Lubricants

A completely satisfactory lubricant has not been developed for use with hydrazine due to its solvent properties; however, these materials have been used.

Neoprene (Oxylube)
Saran (MIL-L-6086)
PVC (Tygon) (MIL-L-25336)
Dow Corning No. 55 (MIL-G-4343)

2. PREPARATION OF MATERIALS

All components of a hydrazine storage and/or transfer system must be prepared properly prior to installation. Preparation procedures consist of rendering the components chemically inert to the propellant.

Items such as valves, pumps, etc., cannot be cleaned in the assembled state since solvents may damage nonmetallic components or residues may be trapped in inaccessible areas. Consequently, the cleaning of these items must be done before the component parts are assembled.

The preparation of materials generally consists of degreasing, descaling, passivating, and drying. The cleaning solutions utilized on these operations shall be applied by immersing, spraying, wiping, circulating, or in any other manner, as long as the surfaces to be cleaned are completely wetted in the solutions. Any component which can trap or retain liquids shall be drained or emptied between applications of different cleaning solutions. All solutions shall be made with distilled, deionized, or clean tap water and all chemicals shall be of chemically pure grade or better. The water shall be filtered through a 40-micron nominal size filter.

SECTION VIII

HANDLING

1. TRANSFER, DELIVERY, AND STORAGE

a. Transfer of Hydrazine

Hydrazine can be transferred by pressurinzing the container with dry nitrogen* gas or by connecting a transfer pump in the discharge line (Ref. 2). Both methods have been used with success. The propellant transfer system must be chemically compatible and in good operating condition before use.

(1) Transfer Equipment

(a) Pipes and Fittings

All pipes and fittings will be of approved materials. The piping system will be identified in accordance with MIL-STD-101A (Ref. 9). The primary warning color shall be brown. The secondary warning color (arrow) shall be yellow.

(b) Gaskets

Gaskets may be of Teflon, polyethylene, and type 304 stainless steel, spiral-wound (Flexitallic, Spirotallic, or equivalent). For valve stems, solid Teflon cylinders, chevron V rings, or braided Teflon equivalent to John Crane 704 or Garlock 5733 may be used.

Braided asbestos impregnated with Teflon may be used for rotating shafts, but mechanical seals for pumps are preferred.

(c) Valves

Valves recommended by the supply source and made of compatible metals shall be used in hydrazine service. Valve packing shall be as noted in section VI.2 and VI.4.

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*Any inert gas is suitable for pressurization of hydrazine; however, carbon dioxide and atmospheric air are not inert with hydrazine. Normally, nitrogen is employed. Adequate filters should be employed in the pressurizing lines to keep contaminating materials (such as rust from the gas bottles) from coming in contact with the hydrazine.

(d) Pumps and Hose

Conventional centrifugal pumps with graphite-impregnated asbestos or braided Teflon packing are satisfactory. Sealless pumps are also recommended because no shaft is involved.

The type of hose recommended depends on the specific service intended. Flexible hoses fabricated from stainless steel, polyethylene, Teflon, or unplasticized Kel-F encased in stainless steel braiding are recommended.

(e) Pressure Gages

Standard-type pressure gages, made of compatible materials, shall be used in hydrazine service. To minimize operator reading errors, all pressure gages used for a common purpose should have identical scales.

(f) Venting Systems and Safety Relief

All vents and pressure-relief systems will be extended to the atmosphere. Each system's termination will be at a height and location that will give adequate protection for personnel.

(2) Transfer Operation

In preparing for a transfer operation, all personnel not directly concerned with the operation shall evacuate the hazard area. Appropriate warning lignts and signs shall be displayed to keep out unauthorized personnel and to warn of hazardous operations in progress. Personnel performing the transfer operation shall wear the fully protective equipment described in the safety measures section (V.1). If the operations are performed remotely, at least two operating personnel shall be fully dressed to facilitate proper spill and fire control. Sufficient safety equipment shall be available for all personnel allowed to remain in the hazard area. Supervisory and emergency support personnel shall be notified prior to executing any hazardous operations in the storage area.

(3) Transfer Procedure

The propellant transfer procedures are dependent upon numerous factors such as transfer system design, type of propellant containers, training of personnel, prevailing weather conditions, etc. Establishing proper operating procedures for each specific situation in a single document is practically impossible. Therefore, the procedures presented are general in nature.

b. Hydrazine Delivery

Hydrazine is classified by the ICC as a corrosive liquid and requires a white label during shipment. It may be shipped in 55-gallon stainless steel (type 304 or 347) drums with openings not exceeding 2.3 inches in diameter, in aluminum or stainless steel tank cars, or in aluminum or stainless steel tank trucks which require a special permit from the ICC. Vapor space in tanks must be filled with nitrogen gas at slightly above atmospheric pressure.

(1) Drums

Normal procedures for unloading drums from vehicles will apply. Drums and containers will be electrically bonded and grounded. Drums may be emptied by use of an eductor, which is a self-priming pump (hand or motor drive) or by gravity flow. Empty drums will be filled completely with water and drained and the bung replaced before being set aside (away from direct sunlight) for storage or for return to the manufacturer. Nitrogen pressure should be maintained on partially empty drums.

(2) Tank Trucks and Tank Cars

In general, normal acceptable practices for unloading tank cars of combustible liquids are applicable. Tank cars loaded with hydrazine are equipped with a standpipe through which contents are removed. The car's contents can be discharged by pressurization with nitrogen or by pumping; if pumping is used, nitrogen must be bled into the top of the tank car to prevent any atmospheric oxygen from entering. The tank shall be electrically grounded at all times. After being emptied, the tank car must be thoroughly flooded with nitrogen, capped, and returned.

(3) Spills, Leaks, and Decontamination

If a leak results from a damaged container, flush the spilled hydrazine away with water and transfer the remaining hydrazine to another container by acceptable techniques. Flush areas and equipment contaminated with hydrazine immediately with large quantities of water. In addition, ventilate the area completely and thoroughly. Excess hydrazine may be disposed of by burning, preferably in an open metal pan completely isolated from any inhabited area or storage site.

(4) Rules for Transferring Hydrazine

In transferring hydrazine from the shipping container to the main storage tank, the following rules will be observed:

(a) Assign at least two persons to any operation involving the handling, transfer, and storage of hydrazine.

(b) Use approved protective clothing.

(c) Maintain an atmosphere of nitrogen over the hydrazine at all times. Purge transfer lines and the container receiving the hydrazine with nitrogen prior to transfer.

(d) Make the transfer where spillage will not come into contact with organic matter or oxidizers.

(e) Have safety showers and eye-wash fountains available, as well as an adequate supply of water for flushing and decontamination.

(5) Accident Procedure

If a shipping incident occurs involving a motor vehicle transporting hydrazine (container or tank spill or leak), (a) all precautions prescribed for flammable liquids, e.g., removing flames, no smoking, etc., and precautions against inhaling the vapors and spilling liquid on skin or eyes should be observed; (b) the vehicle should be stopped, the motor turned off, and large quantities of water should be used to dilute spillage; (c) leaking drums must be removed from the truck before it may proceed; (d) the contents of leaking containers must be transferred to safe containers or safely disposed of; (e) if a cargo tank is involved, transport the vehicle to the nearest place where the contents of the tank can be disposed of with safety, meanwhile employing every available means to prevent any liquid from spilling or leaking onto the highway; and (f) if the character of the leak makes further transport of the tank unsafe, remove the vehicle from the highway. Flush the leakage with large quantities of water and dilute the tank's contents with fresh water (10-to-1 or more) before or while draining the contents into ditches or nonoxidizing absorbent materials. This is a reasonable practice if the operating personnel are wearing complete protective clothing and the accident occurs in an uninhabited area. Otherwise, flush the leakage with water and devise some means of transferring the contents of the tank into safe containers by suitably protected personnel. In any event, as soon as immediate measures have been taken, local authorities should be notified of the fire, vapor, explosion, and toxicity hazards.

Truck drivers and trainmen must be educated to the nature of hydrazine and to the recommended means of handling emergency situations such as spills, leaks, and fires.

c. Hydrazine Storage

Hydrazine may be stored in drums, tank trucks, tank cars, or permanent tanks. Hydrazine can be stored in the drums in which it is received. The drums shall be stored bung side up on a concrete pad, preferably raised from the pad on racks to allow for the drainage of flush water. This also prevents collecting of pockets of hydrazine (from leaks) under drums and minimizes rusting of chimes. Combustible dunnage shall not be used. Good practice in hydrazine storage is to maintain temperatures below 120°F. Large quantities should be stored in comparatively isolated areas. Strong oxidizing agents should be kept out of the immediate storage area. Horizontal cylindrical tanks are preferred for bulk storage. Tanks must be electrically grounded. On the top of each tank there should be a fluid inlet-outlet (sump and dip leg), a level gage (bubbler type), a nitrogen inlet, a rupture disc, and a relief valve. Storage tanks should be maintained in a nitrogen atmosphere at a pressure equivalent to about 9 inches of water. It is good practice to install an automatic sprinkling system over the storage tanks. Locate the hydrazine storage area so that under the worst probable meteorological conditions any release of toxic gases resulting from an accidental propellant spill of any conceivable magnitude will be reduced to relatively harmless concentrations by the time it reaches off-site population.

(1) Storage Tank Sizing

Storage tanks should be sized to receive at least twice the expected individual shipments, with at least 10 percent volumetric allowance for ullage. All storage tanks and associated valves and piping should be located above ground to facilitate detection of leaks. Tank supports and foundations should be designed with a minimum safety factor of 4 with due regard for local seismic conditions. Each tank should be located within a separate retaining wall, dike, or revetment sized to contain at least 1.5 times the tank capacity. Each tank should be electrically grounded and equipped with an adequately sized, remotely controlled "fail safe" vent valve. Storage tanks may be located as close as 8 feet to each other, provided that adequate water spray coverage is available. Main tank connections should be made through the top portion of the tanks to reduce the possibilities of propellant spill.

(2) Prevention of Freezing

The best method of preventing hydrazine from freezing in the transfer lines appears to be that of insulating plus tracing with heating elements. A well must be provided at the bottom of the storage tanks to permit almost complete propellant drainage. The well may, in turn, be completely drained for cleaning purposes by providing an adequate tank connection. The vent and relief gases should be piped to a vent stack and released at least 60 feet higher than the highest working point in the area. The vent stack should be equipped with an appropriate flame arrestor.

(3) Quantity Distance Relationships

Liquid hydrazine is classified by AFM 127-100, Explosive Safety Manual, as a group III hazard for determination of quantity distance relationships. A 20,000-gallon storage facility would require a barricaded distance of 405 feet to inhabited buildings and an intraline distance of 150 feet. It would required an unbarricaded distance of 1800 feet to inhabited buildings, passenger railroads, public highways, and incompatible storage groups.

(4) Storage Facility

Buildings shall be fire resistant. Open-shed construction is desirable to provide adequate shade and weather protection with maximum ventilation. Buildings shall be electrically grounded and shall have approved protection against lightning. The following shall be installed in all storage buildings: (a) fire extinguishers of a type approved for use in combating hydrocarbon-fuel fires; and (b) soap or soap solutions, safety showers, and eye baths.

All electrical fixtures in the storage and transfer area shall be explosion-proof and all wiring shall be enclosed in rigid metal conduit.

Oxidizers, open flames, sparks, and static electricity cannot be tolerated in or near fuel-storage areas. Care must be taken to avoid spillage. A constant vigilance shall be exercised over maintenance of facilities to prevent leakage. All spills and leaks must be immediately flushed away with large quantities of water or soaked up in sand or dirt which is to be burned off elsewhere. Frequent inspections shall be made by operational and supervisory personnel to ensure the continuance of good housekeeping habits.

(a) Electrical Equipment

The electrical installation in transfer and storage areas shall conform to the National Electrical Code requirements for class I, group D, division 1. At least two access roads to transfer and storage sites shall be provided that are wide enough at each site to give adequate space for turning. Facilities shall be provided for storing protective clothing and related equipment. Safety showers, fire blankets, and eye-wash fountains shall be provided and properly located for easy access. There shall be adequate water for dilution and flushing down. Drainage shall be arranged to prevent the mixing of hydrazine with oxidizing materials. The workroom or operational area may have a general ventilation ssytem, but special mechanical exhaust ventilation of the down-draft type should also be supplied. It is more important that the ventilation system ensure a substantial air flow away from the work area. A forced-draft ventilating system should be arranged so that a fire in the building will automatically shut it down. There should be remote manual controls for the ventilation system. Combustible materials and other extraneous materials will not be stored in a facility or area in which hydrazine is stored. All such items will be removed from the area for proper storage or disposal. Good housekeeping is essential to minimize fire hazards and to provide a safe work area.

(b) Storage Area Fire Control

The hydrazine storage area should be provided with a firewater loop system of ample and adequate size with strategically located hydrants. A sprinkler system must be included to provide remote controlled water coverage to the storage tanks and unloading docks. An adequate supply of water for fire fighting and washdown is imperative. For a single 20,000-gallon storage tank approximately 80,000 gallons of water are required. Provisions should be made for replenishment of the total stored water within 12 hours or less without the use of portable or emergency equipment.

Sprinkler systems must be protected from freezing. The spraying system should be fabricated of pipes not less than 1 inch in diameter and provided with a nozzle pressure of at least 50 psig. The storage area should also be provided with portable, chemical-type fire extinguishers. The carbon-dioxide extinguisher is recommended for general use throughout the area. The storage area should be fenced and equipped with appropriate warning signs, safety placards, and other equipment and techniques typical of good industrial practice.

The diking or retainment system around the storage tank should be designed so that it will gravity-drain into a burn basin, a collection basin, and a reclamation sump. These facilities can be interconnected by means of concrete channels and isolated as required by means of valves.

(c) Hydrazine Disposal

The hydrazine storage area must be provided with facilities for the safe disposal of hydrazine and contaminated hydrazine solutions. Hydrazine disposal can be accomplished by burning, reacting, or diluting. The burning operation can be performed in a rectangular, flat-bed type burn basin. Hydrazine and hydrazine acqueous solutions containing over 40 percent hydrazine are combustible. For hydrazine concentrations below 40 percent, a miscible solvent or fuel can be added to render the solution combustible.

Hydrazine solutions, especially those containing less than 40 percent hydrazine, can be easily disposed of by reacting them with hydrogen peroxide. This operation can be performed in the collection basin. Hydrazine solutions can be also disposed of by diluting with water until the hydrazine concentration falls below that locally permitted. This technique is particularly applicable when the hydrazine concentration is below 10 percent.

(d) Storage Area Lighting

The storage area should be floodlighted. Electrical power distribution within the area should be made through appropriate ducts, preferably underground. Adequate electrical receptacles should be conveniently located for maintenance purposes. Storage tanks, pumps, loading points, electrical equipment, and propellant transfer lines must be grounded and bonded electrically in accordance with national, state, and local codes. Vent stacks, storage tanks, and steel structures must have integrally mounted lightning protection systems.

SECTION IX

SERVICING

1. AIRCRAFT SERVICING

a. Servicing Vehicle/Aircraft Quantity Distance Requirements

The hydrazine servicing vehicle used to transport the propellant from the storage area to the aircraft and back should have just enough capacity to fill the tank in the aircraft because of the quantity-distance relationships of AFM 127-100 (Ref. 11). Amounts in excess of need will increase the magnitude of the hazards and necessitate greater distances from inhabited areas for servicing the aircraft with hydrazine. If the aircraft is required to take on 300 gallons (2500 pounds) of hydrazine, it should be located no closer than 600 feet from the nearest public highway, the nearest inhabited building or passenger railroad as a precaution in case of fire or explosion.

b. Servicing Trailer Design

The hydrazine servicing vehicle should be a four-wheel trailer towable at 25 miles per hour. It should have a capacity for one aircraft filling of hydrazine plus 10 percent ullage. The transfer tank must be of the sump and dip leg design with the opening at the top. Loading and unloading operations must be via the dip leg. Bubbler-type (using nitrogen gas), liquid-level gages should be used to eliminate the possibility of hydrazine spillage. The transfer tank must be designed to withstand pressure up to 35 psig. The transfer system must be checked under hydrostatic test before being used.

The servicing vehicle should be equipped with a high-pressure, gaseous nitrogen bottle which (through a filter, pressure regulator, and isolation valves) can provide clean, low-pressure (9 to 15 inches H_2O), gaseous nitrogen for a vapor blanket over the liquid and for purging the receiver system before filling. The gaseous nitrogen at a higher pressure (up to 35 psig) can be used to force the liquid from the servicing vehicle into storage tanks in the aircraft.

The servicing vehicle hydrazine tank will have three penetrations along the top of the tank which will be protected by a cover when the tank is not being loaded or unloaded. One penetration will mount the dip tube which will be used for filling and emptying the tank. The bottom of the dip tube will extend into a sump on the bottom of the tank. The second penetration will mount a relief valve set for 45 psig. The third penetration will mount a vent nozzle for venting during filling operations, for blanketing the liquid with gaseous nitrogen during transit or storage operations, and for pressuring the tank during unloading operations.

The service vehicle tank should be constructed of type 304L or 347 stainless steel or equivalent compatible material to contain a pressure of 35 psig with a safety factor of 4, thus preventing accidental rupture. Pipe and fittings should be made from 304L stainless steel or equivalent compatible material. Flanges with stainless steel bolts and nuts should be used instead of threaded connections. Flange gaskets may be made from Teflon or polyethylene. The piping system will be identified in accordance with MIL-STD-101A. The primary warning color will be brown. The secondary warning color (arrow) will be yellow. Shut-off valves should be stainless steel split-body type globe or angle globe with Teflon seat and chevron packing.

SECTION X

SAFETY STUDIES AND TESTS

During this study several areas of concern were revealed which require future study and reporting. These areas are listed below as recommended safety studies and tests to be performed.

1. Hydrazine airborne dispersion study

2. Recommended design specifications for hydrazine systems onboard the aircraft

3. Determine the content and hazards of hydrazine turbine exhaust products (toxicity, fire, explosion)

4. Conduct hydrazine dispersion tests from the aircraft at various altitudes and speeds (planned and simulated emergency dumps)

5. Provide emergency aircraft safety procedures for inadvertent spillage, leakage, fire, explosion, and vapor exposure

6. Conduct a hydrazine dispersion study for use in a ground handling procedure

7. Provide a hydrazine environmental impact study with recommendations

APPENDIX I

POSTED SAFETY INSTRUCTIONS FORMAT

The recommended format for safety instructions to be posted at the operations site is as follows:

SAFETY INSTRUCTIONS
FOR
HYDRAZINE

HAZARDS

1. Contact with liquid may cause burns, severe eye damage and general vomiting.
2. Breathing of vapor may cause lung damage and irritation of the eyes, nose, and throat.
3. Spills represent an immediate fire and explosion hazard.
4. Contact with acid causes fire and possibly explosion.

FIRST AID

1. Remove casualties from contaminated area and keep them quiet. Apply artificial respiration if breathing has stopped. Call for medical aid.
2. If hydrazine splashes into the eyes, flush them immediately with water, and continue flushing for 15 minutes, holding the eyes open. If it is necessary to choose between treating the eyes and summoning medical attention, flush for 10 minutes, seek medical help, and resume eye flushing. Do not put anything but water in the eyes.
3. If hydrazine is spilled on the skin, immediately flush the affected area with large amounts of water.

SAFETY PRECAUTIONS

1. All personnel must be familiar with the nature and characteristics of hydrazine.

2. Persons handling hydrazine must wear fuel-resistant gloves, shoes or overboots, a face shield, wrist and arm protectors, and a rubber-type apron. Where there is a chance of gross splashing, an approved protective suit must be worn.

3. Respiratory protection must be available when working in hydrazine-contaminated atmospheres. Under emergency conditions or in confined spaces, approved self-contained respirators must be used.

4. Storage, transfer, and operating areas shall be kept clean of organic matter and oxidizers. No electrical sparks or open flames shall be permitted.

5. Leaks and spills must be immediately flushed away with large amounts of water.

6. Transfer, handling, and storage must be performed by at least two persons.

7. An atmosphere of nitrogen must be maintained over the hydrazine.

8. An adequate supply of water must be available for flushing and decontamination, as well as for safety showers and eye-wash fountains.

9. Drums and containers shall be grounded.

APPENDIX II

HYDRAZINE AIRBORNE DISPERSION STUDY

1. HYDRAZINE DISPERSION WHEN DUMPED FROM LARGE AIRCRAFT--SUMMARY

By using dispersion estimates, it has been determined that 2300 pounds of hydrazine can safely be dumped from an aircraft under certain conditions. In a situation where the aircraft is flyable, but an emergency condition exists upon landing (for example, the landing gear will not extend), hydrazine can be dumped under the following conditions:

a. Temperature $\geq$ 35°F

b. Altitude $\geq$ 2000 feet AGL

c. Dump time $\geq$ 90 seconds

d. Airspeed $\geq$ 200 mph

If the above conditions cannot be met, then the pilot must use his judgment in deciding whether or not to dump the hydrazine. In general, hydrazine should not be dumped over populated areas or at low altitudes over waterways.

The values presented in this appendix are highly approximate because many assumptions were made. It is believed that they are within an order of magnitude of the actual values because the dispersion will occur very rapidly in the turbulent wake behind the aircraft.

2. AIRBORNE HYDRAZINE DISPERSION

a. Problem

Dumping of hydrazine from an aircraft presents a problem in toxicity. However, if the hydrazine can be diffused to about 1 ppm in air, then hydrazine can be safely dumped. Safe dumping conditions, therefore, must be determined, i.e., what speeds, altitudes, and dumping times are necessary to safely dump the hydrazine.

b. Assumptions

The assumptions for dumping hydrazine from large aircraft are

(1) That the hydrazine vaporizes as soon as it leaves the aircraft

(2) That the turbulent wake and the vortex sheet are the influencing factors on the vapors until wake and vortex sheet break up

(3) That the length of the volume of vapor is defined by the dump time D_t

(4) That the width and depth of the volume is defined by the vortex sheet and the wake (as shown in figure 1)

(5) The volume is treated as a line source after vortex sheet and wake break up

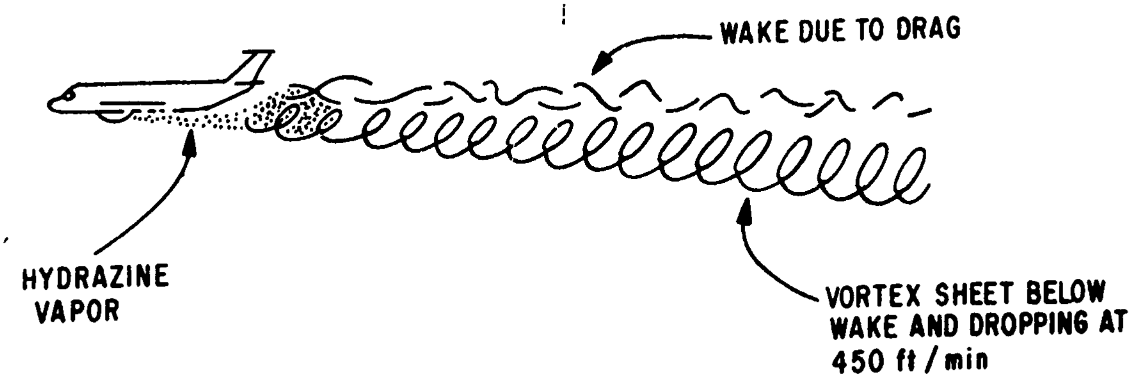

Figure 1. Hydrazine Dump Model

After 2 minutes the wake and vortex have dissipated (Refs. 15, 16, 17). The wake and vortex describes the volume as shown in figure 2. The hydrazine is assumed to expand evenly into this volume. The volume is treated as a line source (figure 3). The line source of vapor is treated as a diffusion problem with average diffusion coefficient.

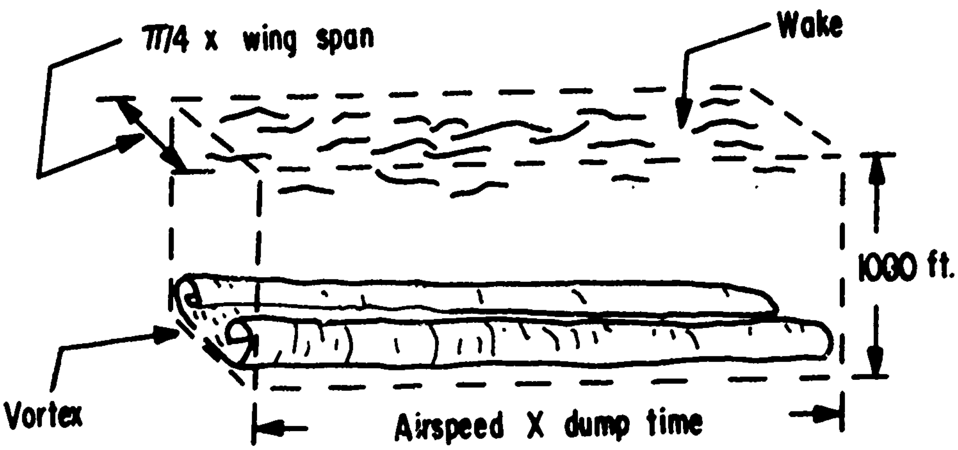

Figure 2. Volume Described by Wake and Vortex

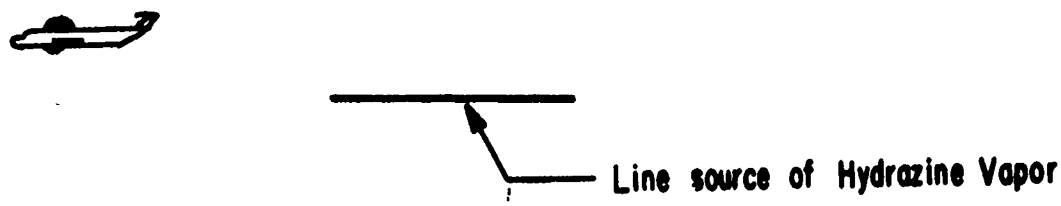

Figure 3. Line Source Model

4. SOLUTION

The solution for the expansion of hydrazine is outlined below. An amount of 2300 pounds has been used as an example.

a. Variables--airspeed and time

b. Output--concentration, i.e., toxicity in ppm

(1) Expand 2300 pounds of hydrazine into volume

(2) Determine concentration

(3) Use diffusion to get down to 1 ppm

(4) Determine sink rate of vapors

5. PROGRAM FOR EXPANSION

The details of the program input are

a. W_{tH} = weight of hydrazine = 1.04×10^6 gm

b. W_v = width of wake = 3.32×10^3 cm

c. h_v = height of volume = 3.048×10^4 cm

d. ℓ_v = length of volume = airspeed x dump time

$= V \times D_t$

e. v goes from 8.94×10^3 cm/sec (200 mph) to 2.68×10^4 cm/sec (600 mph)

at 2.23×10^3 cm/sec interval (50 mph)

f. D_t goes from 10 to 310 seconds at 20-second intervals for each airspeed

g. Calculate concentration for each combination of airspeed and dump time

h. N = concentration = W_{tH}/volume

i. Volume = $W_V \times h_V \times \ell_V$

Output or plot values of constant dump times against concentration and airspeed

Units:

Concentration (gm/cm^3)

Airspeed (mph) (1 mph = 44.7 cm/sec)

Dump time (sec)

Plots for this program are shown in figures 4 and 5.

6. DISPERSION ESTIMATES

Assuming an instantaneous infinite crosswind line source and using equation (7) from references 13 and 14,

$$C = \frac{Q_L}{\pi \sigma_{X1} \sigma_{Z1}} \exp \left\{ - \left[\frac{(x - \bar{u}t)^2}{2 \sigma_{X1}^2} + \frac{h^2}{2 \sigma_{Z1}^2} \right] \right\} \qquad (1)$$

If we assume the vapors are swept along at the wind velocity u and in the same direction, we have $(x - \bar{u}t)^2 = 0$. Also we are interested in the concentration at the peak or maximum concentration, so our reference is the line source at all times, i.e., h = 0, therefore we have

$$C = \frac{Q_L}{\pi \sigma_{X1} \sigma_{Z1}} \exp [0] \qquad (2)$$

$$C = \frac{Q_L}{\pi \sigma_{X1} \sigma_{Z1}} \qquad (3)$$

We can assume that the standard deviation $\sigma_{X1} = \sigma_{Z1}$, thus we have σ^2. The standard deviation can be approximated by $\sigma = ax^b$, where for the neutral condition $a \simeq 0.15$ and b = 0.75 between 3800 to 200,000 meters. The initial concentration is

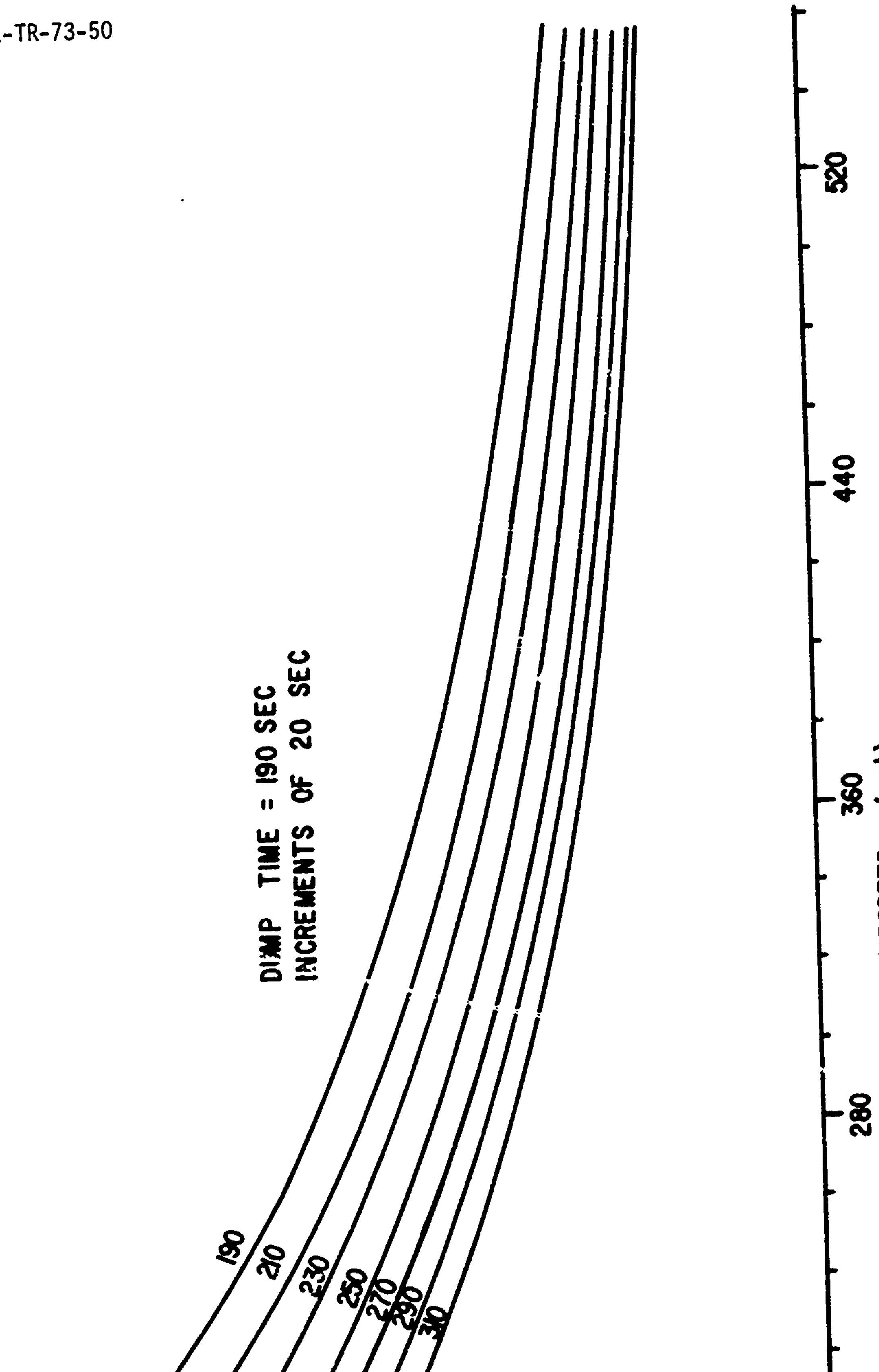

Figure 4. Hydrazine Dispersion Due to Expansion of Vapors; Dump Time 190 Seconds

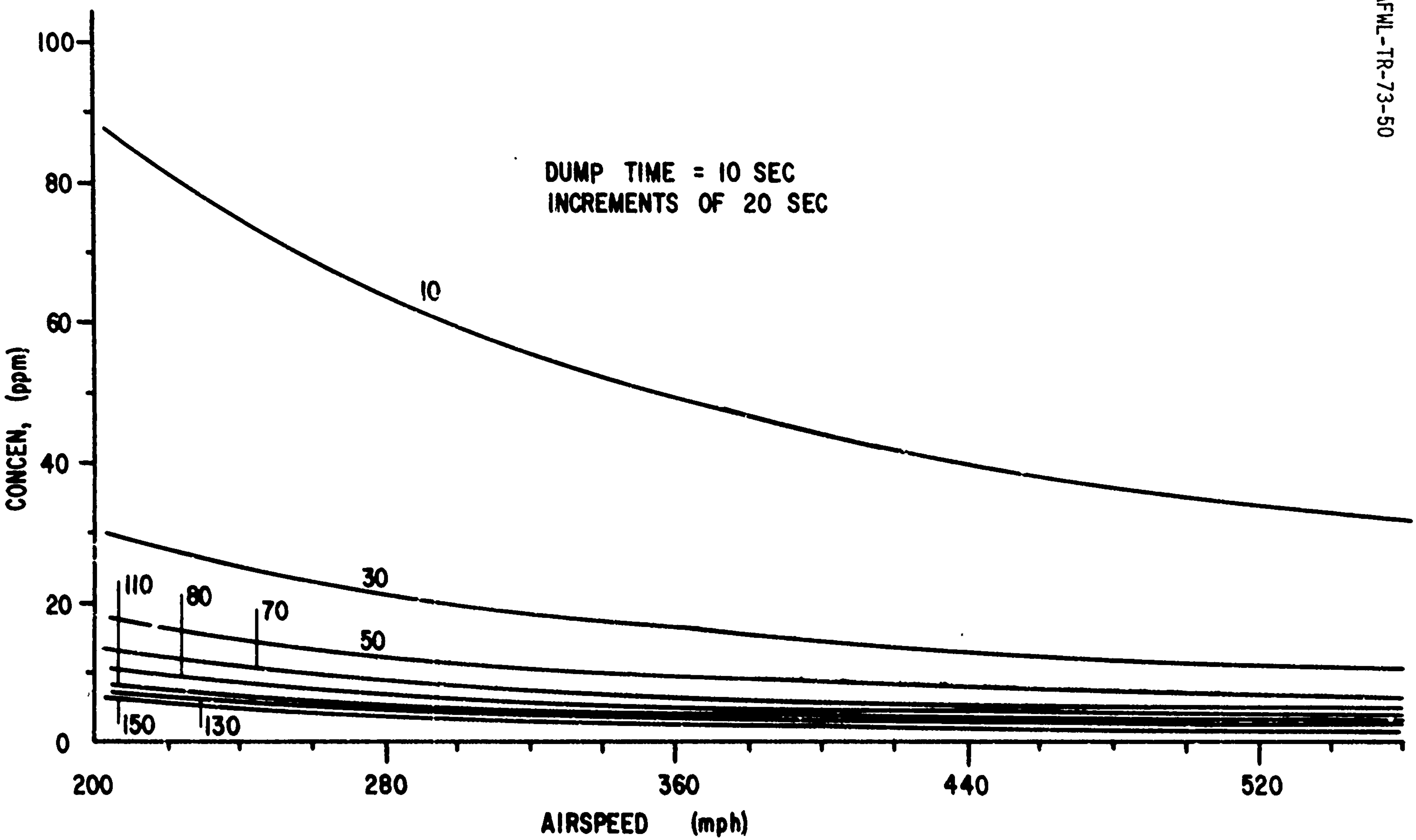

Figure 5. Hydrazine Dispersion Due to Expansion of Vapors; Dump Time 10 Seconds

$$C_o = \frac{Q_L}{\pi a^2 x_o^{2b}} \tag{4}$$

where

$$x_o = f\left(C_o, Q_L\right) \tag{5}$$

X_o and Q_L (shown in figure 6) are known values for given aircraft speeds and dump times. So we have

$$X_o^{2b} = \frac{Q_L}{\pi a^2 C_o} \tag{6}$$

$$X_o = \left[\frac{Q_L}{\pi a^2 C_o}\right]^{1/2b} \tag{7}$$

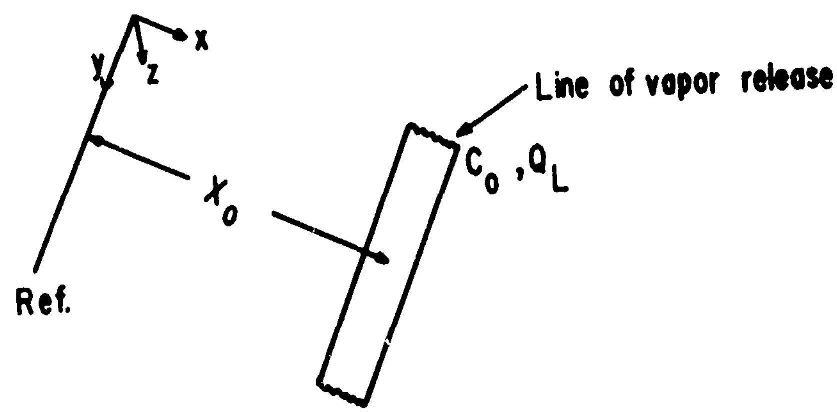

Figure 6. Line of Release Model

Because of the nature of the equations, we have to use an imaginary reference line which is some distance, X_o, from the line of release. Equation (3) now becomes

$$C = \frac{Q_L}{\pi a^2 \left(X - X_o\right)^{2b}} \tag{8}$$

where X now is measured from the reference line. It is possible now to calculate the concentration of the vapor at various distances from the line of vapor release. However, it will be of interest to know the concentration as a function of time only.

We have from equation (8) and equation (3)

$$\sigma^2 = a^2 \left(x - x_o\right)^{2b} \tag{9}$$

and from Heffter's relation,*

$$K_h = \frac{\sigma^2}{2\left(t + t_o\right)} \tag{10}$$

solving for σ^2, we have

$$\sigma^2 = K_h\, 2\left(t + t_o\right) \tag{11}$$

where an average dispersion coefficient of $K_h = 10^6$ cm²/sec is used. The time required to expand into the volume after release is $t_o = 2$ minutes. Now equation (8) becomes

$$C = \frac{Q_L}{\pi K_h\, 2\left(t + t_o\right)} \qquad \text{for } t \geq 10^{-8} \text{ sec}$$

where Q_L is known, and values of time are selected.

7. PROGRAM FOR DISPERSION ESTIMATES

The program for expansion can be used as an input and then change concentration to concentration per unit length by multiplying width and depth to the concentration per unit volume.

$$Q_L = \text{concentration (gm/cm}^3\text{)} \times (3.32 \times 10^3 \text{ cm}) \times (3.04 \times 10^4 \text{ cm})$$

*This equation is for lateral-dispersion, but since the wind direction and source orientation is not known, this is used as an approximation.

where

Q_L = concentration/unit length

C = concentration/unit volume

$$C = \frac{Q_L}{\pi K_h (2) \left(t + t_o\right)}$$

$$K_h = 10^6 \text{ cm}^2/\text{sec}$$

Let t go from 30 to 1030 seconds at 100-second intervals

Plot C versus time for various dump times

$$D_t = 10, 90, 210, \text{ and } 310 \text{ sec}$$

Change gm/cm² to ppm for both programs

$$1 \text{ ppm} = 1.3 \times 10^{-9} \text{ gm/cm}^3$$

Plots for this program are shown in figures 7, 8, and 9.

8. CONCLUSIONS

From a standpoint of planned emergency dumps, hydrazine can be dumped under certain conditions as follows:

1. It can be dumped only at altitudes between 2000 and 8000 feet because hydrazine freezes at 34°F. At higher altitudes the temperature is normally below this value. The lower limit is established from physical characteristics of the vortex wake, i.e., it drops to a level of 100 feet below the aircraft and remains at this level. This allows for a 1000-foot margin of safety.

2. The dump time, other than emergencies, should be longer than 60 seconds, preferably 90 seconds or longer.

3. Airspeed must be above or equal to 200 mph.

In summary, dumping is allowable when temperature $\geq$ 35°F; altitude $\geq$ 2000 feet; dump time $\geq$ 90 seconds; and airspeed $\geq$ 200 mph. Under these minimum conditions the hydrazine concentration will be at 1.00 ppm 165 seconds after dumping begins.

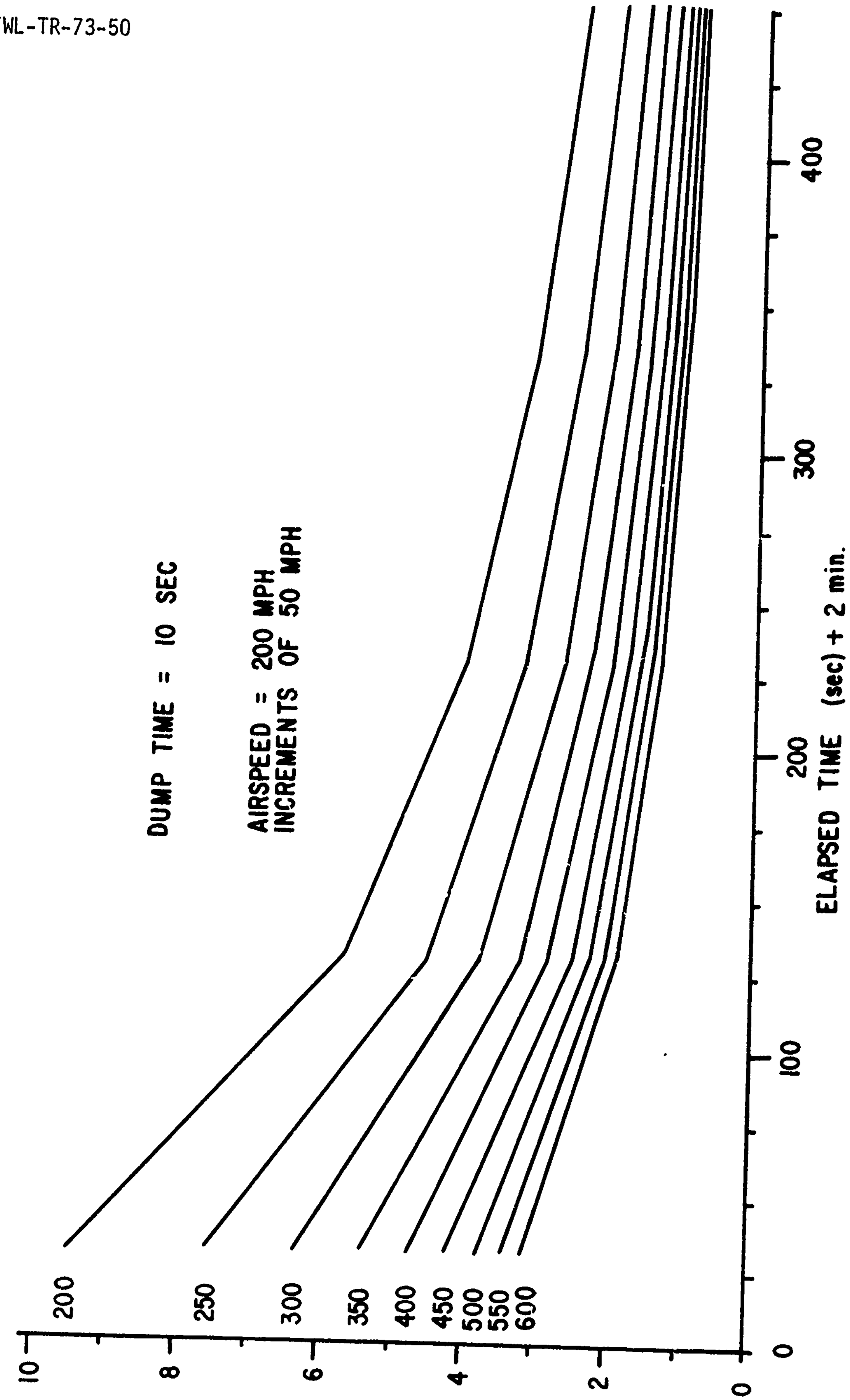

Figure 7. Hydrazine Dispersion over Time; Dump Time 10 Seconds

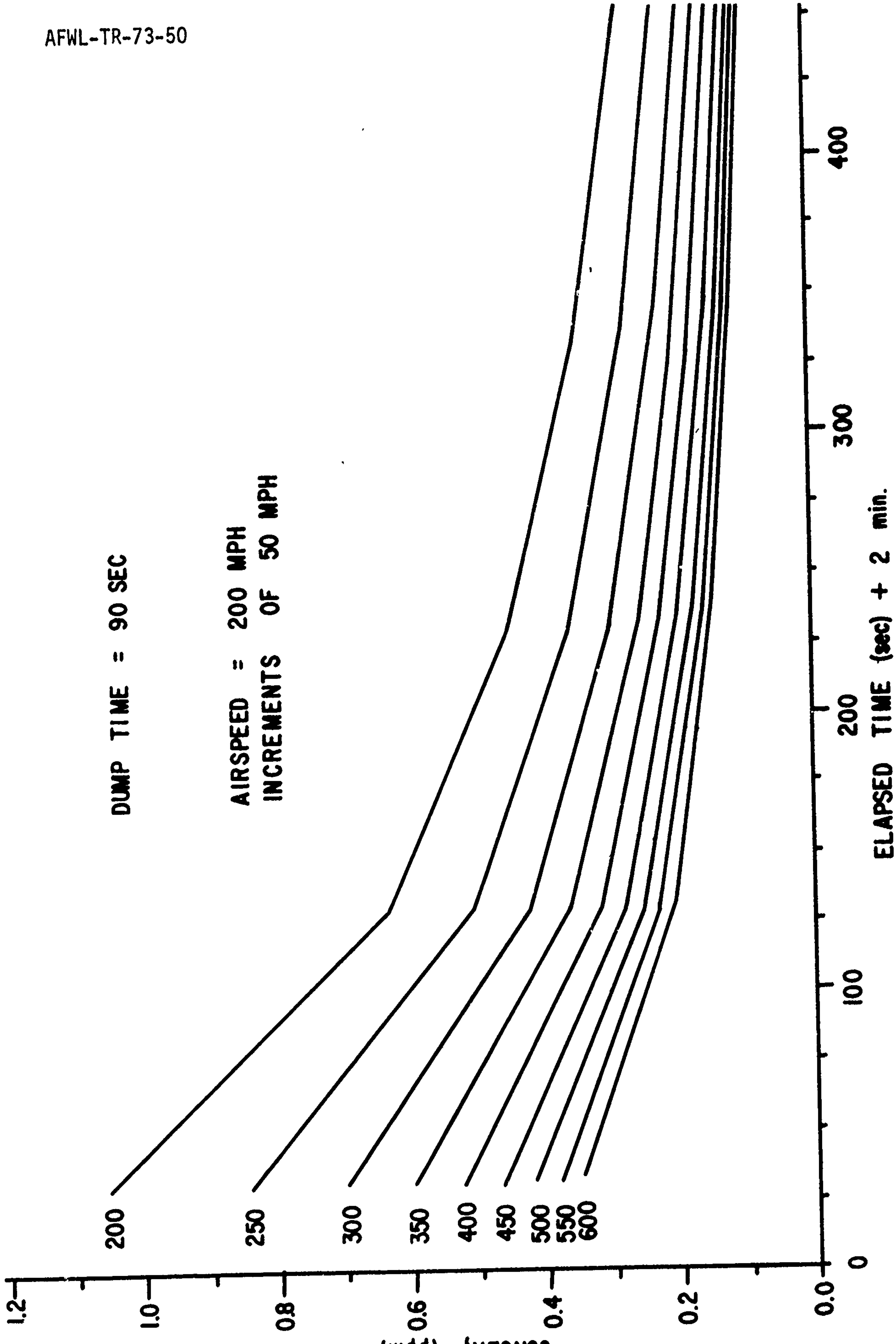

Figure 8. Hydrazine Dispersion over Time; Dump Time 90 Seconds

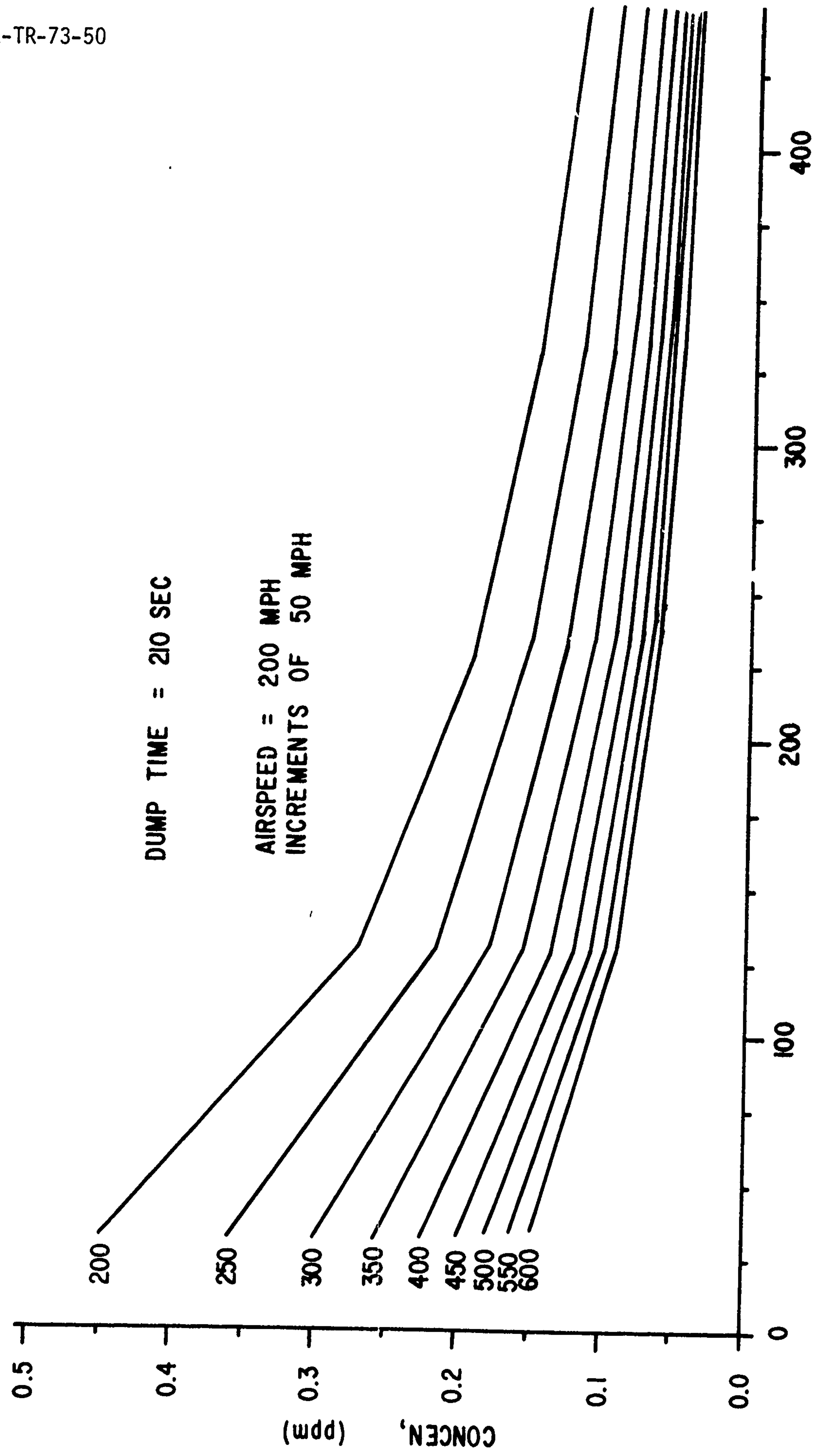

Figure 9. Hydrazine Dispersion over Time; Dump Time 210 Seconds

During an emergency the pilot may not be able to meet the above conditions for dumping hydrazine. In this case the pilot must use his own judgment. A guideline or rule of thumb is "DO NOT dump hydrazine over populated areas." The sink rate for the vapor is negligible since the specific gravity of hydrazine vapor in air is 1.10.

9. RECOMMENDATIONS

For planned emergency dumps it is more advantageous to have a long dump time, i.e., 5 minutes. For emergency dumps it is necessary to have a very short dump time, i.e., less than 1 minute. These requirements could be solved by having two dump times, one short and one long dump time.

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13. ABSTRACT

(Distribution Limitation Statement B)

The use of large quantities of hydrazine onboard a military aircraft is of major concern because of its toxicity and potential fire hazard. These hazards and their control are emphasized in this special hydrazine report. The experience accumulated over the past several years indicates that with reasonable precautions, trained personnel, and adequate procedures the proper handling of hydrazine should present no serious hazards.

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