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ESL-TR-84-18

AD-A150 699

# ATMOSPHERIC DISPERSION OF HYPERGOLIC LIQUID ROCKET FUELS, (VOLUME II of II)

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NOVEMBER 1984

FINAL REPORT  
JUNE 1982 - DECEMBER 1983

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## REPORT DOCUMENTATION PAGE

1a. REPORT SECURITY CLASSIFICATION UNCLASSIFIED			1b. RESTRICTIVE MARKINGS			
2a. SECURITY CLASSIFICATION AUTHORITY			3. DISTRIBUTION/AVAILABILITY OF REPORT Approved for public release; distribution unlimited.			
2b. DECLASSIFICATION/DOWNGRADING SCHEDULE						
4. PERFORMING ORGANIZATION REPORT NUMBER(S)			5. MONITORING ORGANIZATION REPORT NUMBER(S) ESL-TR- 84-18			
6a. NAME OF PERFORMING ORGANIZATION Martin Marietta Aerospace		6b. OFFICE SYMBOL (If applicable)	7a. NAME OF MONITORING ORGANIZATION HQ AFESC/RDV			
6c. ADDRESS (City, State and ZIP Code) Denver, Colorado 80201			7b. ADDRESS (City, State and ZIP Code) Tyndall AFB, Florida 32403			
8a. NAME OF FUNDING/SPONSORING ORGANIZATION		8b. OFFICE SYMBOL (If applicable)	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER F42600-81-D-1379			
8c. ADDRESS (City, State and ZIP Code)			10. SOURCE OF FUNDING NOS.			
			PROGRAM ELEMENT NO. 62601F	PROJECT NO. 1900	TASK NO. 90	WORK UNIT NO. 13
11. TITLE (Include Security Classification) ATMOSPHERIC DISPERSION OF HYPERGOLIC LIQUID						
12. PERSONAL AUTHOR(S) ROCKET FUELS, (VOLUME II OF II) Williard R. Haas; Stephen Prince						
13a. TYPE OF REPORT Final		13b. TIME COVERED FROM Jun 82 TO Dec 83		14. DATE OF REPORT (Yr., Mo., Day) 1984 November		15. PAGE COUNT
16. SUPPLEMENTARY NOTATION Availability of this report is specified on reverse of front cover.						
17. COSATI CODES			18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)			
FIELD	GROUP	SUB. GR.	Atmospheric Dispersion Modeling)		Nitrogen Tetroxide	
21	09	01	Hydrazine)		Toxic Hazard Corridor,	
09	02		Hypergolic Fuels,			
19. ABSTRACT (Continue on reverse if necessary and identify by block number) Titan II weapons systems are charged with hypergolic liquid rocket propellants (hydrazine fuel and nitrogen tetroxide oxidizer). These same propellants are used in support of other systems, including the MX missile and the space shuttle. This effort was designed to characterize the interactions of hypergolic liquid rocket propellants and to provide information pertinent to the development of a model to describe the transport and diffusion of airborne combustion products and unreacted vapors from an accident involving these propellants.  This report is prepared in two volumes. Volume I addresses the reactions between nitrogen tetroxide and hydrazine, including the reaction products and the heat released. This information was used to determine the combustion time and the height of the resulting fireball before it cools and disperses with the air. Volume II discusses the chemical and physical interactions of the combustion products with air, and the dispersion of these products in the environment. <i>Of interest to suppliers to military aircraft.</i>						
20. DISTRIBUTION/AVAILABILITY OF ABSTRACT UNCLASSIFIED/UNLIMITED <input type="checkbox"/> SAME AS RPT <input type="checkbox"/> DTIC USERS <input type="checkbox"/>			21. ABSTRACT SECURITY CLASSIFICATION UNCLASSIFIED			
22a. NAME OF RESPONSIBLE INDIVIDUAL 2Lt Glenn D. Seitchek			22b. TELEPHONE NUMBER (Include Area Code) (904) 283-4234		22c. OFFICE SYMBOL RDV	

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## SECTION I

### INTRODUCTION

Hypergolic liquid rocket propellants are toxic, and accidental releases during handling and storage may endanger the civilian population. The U.S. Air Force developed procedures to predict toxic hazard corridors that would result from the release of any individual propellant material. These corridors result from the evaporation and subsequent dispersion of the vapors.

A different situation arises when fuel and oxidizer come into contact as the result of an accidental release. In this case, a violent explosion can occur that will send the combustion products and, possibly, some of the unreacted propellants high into the air. When this occurs, the atmospheric dispersion begins at the high elevation and cannot be determined using the same calculation method as that for a ground release.

Phase I of this program (Source Characterization), addressed the reactions between nitrogen tetroxide and hydrazines. The reaction products and the heat released by the reaction were quantified during that work. That information was used to determine the combustion time and the height the resulting fireball achieves before it cools and passively disperses with the air.

Phase II of the project (Atmospheric Dispersion Modeling), which is described in this report, investigated the chemical and physical interactions of the combustion products with air and the dispersion of these products in the environment.

The chemical interaction of reaction products of nitrogen tetroxide combined with a hydrazine was determined by evaluating the literature on the topic and by laboratory experimental work. This information showed which products, both toxic and nontoxic, could be expected to form and dissipate as the cloud moves away from the accident location. Furthermore, the chemical kinetics of these reactions were determined so the rate of appearance and disappearance of each constituent could be assessed.

The atmospheric dispersion of the products was described by considering the coupled affects of convection, dispersion, and chemical reaction. A mathematical description of this transport process, a Hypergolic Accidental Release Model (HARM), was developed by H.E. Cramer Co. during this project. They combined the source characterization algorithm developed at Martin Marietta (Prince 1982 , 1983) , the bouyant cloud models by Briggs (1970), and the dispersion model for rocket launches by Bjorklund (1982) to describe this phenomenon.

This report summarizes two interim reports: "Atmospheric Dispersion of Hypergolic Liquid Rocket Fuels, Phase II: Atmospheric Dispersion Modeling" by Stephen Prince and "User's Manual for the Hypergolic Accidental Release Model (HARM) Computer Program" by C.R. Rowman, W.R. Hargraves, J.R. Bjorklund, R.K. Dumbauld, and J.F. Rafferty. Complete copies of these reports are included as Appendices A and B respectively.

## SECTION II INTERACTIONS, REACTIONS AND ANALYSES

### PLUME/ATMOSPHERE INTERACTIONS

The hypergolic rocket propellants and the products of combustion formed after an accidental release of these materials can be toxic. The results of work done during this portion of the project provide chemical reaction rate data for the interaction of hydrazine ( $N_2H_4$ ), unsymmetrical dimethylhydrazine (UDMH), nitrogen tetroxide ( $NO_2$ ), and combustion products with air and the reactive components in the air which include ozone, oxygen, water vapor, and carbon dioxide. These reaction rate data, when coupled with the dispersion characteristics of the effluent plume, can be used to assess the environmental impact of the vapors and the control necessary to avoid injuries to personnel in the area of the hypergolic release. A summary of the important reactions that can take place in this situation will be given here. A more thorough discussion of the chemistry is presented in the Phase I report and a more extensive discussion of the chemical reaction rates is presented in the Interim Report: Task 1 "Plume/Atmospheric Interaction" included as Appendix A.

### $N_2H_4$ REACTIONS

At high  $N_2H_4$  concentrations in air, the major reaction pathway for its depletion is with molecular oxygen,

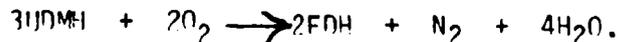


As the concentration decreases to the part per million level the major reactions are with the atmospheric pollution contaminants; hydroxide radical ( $OH$ ), ozone ( $O_3$ ), and nitrogen dioxide ( $NO_2$ ). These reactions are about an order of magnitude faster than the ones with oxygen and prevail as long as the rate of photooxidation in the atmosphere is great enough to replenish the reactants.

The products of these reactions, in general, have low toxicity. These products are  $N_2$ ,  $H_2O$ ,  $NH_3$ ,  $N_2H_3$ .

## UDMH REACTIONS

UDMH is reactive with the same atmospheric components as is  $N_2H_4$ . At high UDMH concentration, the reaction occurs with molecular oxygen and forms formaldehyde dimethylhydrazone (FDH) as a major product,



At lower UDMH concentrations when the atmospheric contaminants' concentrations are approaching those of the hydrazines, they again are the major contributor to the decomposition. The products of these reactions include nitrosodimethylamine (NDMA, a known carcinogen) and other substituted tetrazines and nitramine products that are toxic. The known products from air oxidization of UDMH are formaldehyde dimethylhydrazone (FDH), ammonia, dimethylamine, NDMA, diazomethane, nitrous oxide, methane, carbon dioxide, formaldehyde, formaldehyde monomethyl hydrazone (FHM), and tetramethyltetrazine (TMT).

## NITROGEN DIOXIDE REACTIONS

Nitrogen dioxide ( $NO_2$ ) reacts in two major ways in the atmosphere. Atmospheric water vapor combines with  $NO_2$  to produce nitric acid ( $HNO_3$ ) vapor and at the reaction site the concentration of these materials may exceed the vapor pressure of the water solution and form liquid nucleation sites which will lead to a mist. Nitrogen dioxide is also photochemically active and enters into the photolysis reaction train that produces ozone ( $O_3$ ). This series of chemical reactions results in other oxidized nitrogen species including  $NO$ ,  $NO_2$ ,  $NO_3$ , and  $N_2O_5$  and upon interaction with other atmospheric contaminants, photochemical smog is produced.

## REACTION EXPERIMENTS

Supplemental chemical rate data were obtained at Martin Marietta on reactions between the reactive components in air (oxygen, carbon dioxide, and water vapor) and vaporized propellant species. These data were used, along with published information, to develop rate expressions compatible with the dispersion modeling theory. The propellant-atmospheric reaction experimental test condition matrix used for this work is shown in Table 1.

TABLE 1. TEST MATRIX ATMOSPHERIC REACTION OF HYPERGOLS

Test No.	Propellant Species	Prop. Conc.	Reactant Gas* Composition	Sampling Time, Hrs
1	Hvdrazine	0.5%	Helium	0,0.5,1,2,4
2	Hvdrazine	0.5%	21% O <sub>2</sub> in He	0,0.25
3	Hydrazine	0.5%	21% O <sub>2</sub> + 1% H <sub>2</sub> O in He	0,0.25
4	Hvdrazine	0.5%	21% O <sub>2</sub> + 0.05% CO <sub>2</sub> in He	0,0.25
5	Hydrazine	0.5%	21% O <sub>2</sub> + 0.05% CO <sub>2</sub> + 1% H <sub>2</sub> O in He	0,0.25
6	UJDMH	0.5%	Helium	0,5,12,21,45,70
7	UJDMH	0.5%	21% O <sub>2</sub> in He	0,5,12,21,45,70
8	UJDMH	0.5%	21% O <sub>2</sub> + 1% H <sub>2</sub> O in He	0,5,12,21,45,70
9	UJDMH	0.5%	21% O <sub>2</sub> + 0.05% CO <sub>2</sub> in He	0,5,12,21,45,70
10	UJDMH	0.5%	21% O <sub>2</sub> + 0.05% CO <sub>2</sub> + 1% H <sub>2</sub> O in He	0,5,12,21,45,70
11	NO <sub>2</sub>	0.25%	Helium	0,1,3,7,24
12	NO <sub>2</sub>	0.25%	21% O <sub>2</sub> in He	0,1,3,7,24
13	NO <sub>2</sub>	0.25%	21% O <sub>2</sub> + 1% H <sub>2</sub> O in He	0,1,3,7,24
14	NO <sub>2</sub>	0.25%	21% O <sub>2</sub> + 0.05% CO <sub>2</sub> in He	0,1,3,7,24

\* 1% H<sub>2</sub>O in Helium Corresponds to 50 Percent Relative Humid Air at 25°C (77°F)

Test temperature were ambient (21-23°C) for amine fuel tests and elevated (35°C) for nitrogen dioxide tests.

RATE STUDY SUMMARY

A summary of the chemical rate constant information assembled during this study is presented in Table 2. This information was used to formulate the rate of chemical consumption in the HARM model for accidental releases of propellant.

TABLE 2. ATMOSPHERIC REACTION RATE CONSTANTS FOR  
FIREBALL DISPERSION MODELING

Fireball Species	Concentration in Atmosphere	Meteorological Condition	Rate Constant	Half-Life	Major Reaction Products	Percent Yield
Hydrazine	0-1 ppm	Dry or Humid Air	0.2 ppm <sup>-1</sup> Min <sup>-1</sup>	2 Hr*	H <sub>2</sub> O <sub>2</sub>	NA
Hydrazine	Above 1 ppm	Dry Air	0.064 Hr <sup>-1</sup>	10.8 Hr	N <sub>2</sub> , H <sub>2</sub> O	100
Hydrazine	Above 1 ppm	Humid Air	0.141 Hr <sup>-1</sup>	4.9 Hr	N <sub>2</sub> , H <sub>2</sub> O	100
UDMH	0-1 ppm	Dry or Humid Air	0.15 ppm <sup>-1</sup> Min <sup>-1</sup>	0.2 Hr*	NDMA	60
UDMH	Above 1 ppm	Dry Air	0.0007 Hr <sup>-1</sup>	990 Hr	FDH**	67
UDMH	Above 1 ppm	Humid Air	0.015 Hr <sup>-1</sup>	46 Hr	FDH**	67
NO <sub>2</sub>	10 ppm	Humid Air	5.5x10 <sup>4</sup> l <sup>2</sup> mole <sup>-2</sup> sec <sup>-1</sup>	5 Hr	HNO <sub>3</sub> (a)	100
NO <sub>2</sub>	50 ppm	Humid Air	5.5x10 <sup>4</sup> l <sup>2</sup> mole <sup>-2</sup> sec <sup>-1</sup>	0.2 Hr	HNO <sub>3</sub> (a)	100
NO <sub>2</sub>	Above 50 ppm	Humid Air	5.5x10 <sup>4</sup> l <sup>2</sup> mole <sup>-2</sup> sec <sup>-1</sup>	0.2 Hr	HNO <sub>3</sub> (a)	100
NO <sub>2</sub>	All Conc.	Dry Air	NO REACTION			

\* Clean, Unpolluted Atmosphere

\*\* NDMA Formed in 0.2 Percent Yield (.002 Moles NDMA Found Per 1 Mole UDMH Reacted)

NO = Not Available

## OVERALL ENERGY CONSIDERATIONS

The combustion products contained in the "fireball" that leave a hypergolic accident are cooled by air entrainment and heat transfer to the environment. The assumption was made that the major cooling affect after the effluent cloud has stabilized is caused by air entrainment. On cooling, the temperature cloud can fall below the saturation point of some of the constituents at high concentrations.

The calculations necessary to determine if there is a possibility for condensation are shown in the report in Appendix A. The results of these calculations revealed that even when there is excess fuel (a situation that creates the most likely chance for condensation to occur because the concentration of the low vapor pressure material is highest and the temperature is lowest), no possibility for condensation exists.

The overall results obtained during this part of the project furnished the data needed to incorporate the effects of chemical reactions in the environment into the overall dispersion model for propellant releases.

### SECTION III HYPERGOLIC ACCIDENTAL RELEASE MODEL (HARM)

The Hypergolic Accidental Release Model (HARM) was developed to predict the transport and dispersion of the products downwind of a hypergolic reaction between fuel and oxidizer. This model is an improvement over the existing method used to assess the hazard of propellant releases (Ocean Breeze/Dry Gulch Model) because it can compute results for elevated sources, thermally buoyant clouds, and considers the effect of chemical reactions taking place in the cloud. The HARM model can predict ground level concentration of toxic materials that result from a catastrophic reaction of hypergolic propellants.

A summary of the model is presented here and Appendix II is a copy of the User's Manual for the Hypergolic Accident Release Model (HARM) Computer Program by C.R. Bowman, W.R. Hargraves, J.R. Bjorklund, R.K. Dumbauld, and J.F. Rafferty.

The HARM model is currently constructed to evaluate the environmental impact that would result from the accidental release and subsequent reaction of the propellants in a Titan II ICBM vehicle. The thermal energy released from the reaction of A-50 and NTO heats the combustion products and unreacted propellants to form a buoyant cloud. The model uses basic information about the cloud and its environment to determine the concentration and dosage of the constituents at ground level as a function of time and distance downwind from the reaction site. Based on information from Phase I of this project, Source Characterization, and specific information about the accident (quantities of propellant spilled and location of the accident), the program calculates the temperature, buoyancy, and composition of the fireball at lift-off.

An instantaneous cloud rise model that has been adapted to rocket launches is incorporated into HARM to determine the stabilization height and rise time for the buoyant cloud that has resulted from the combustion. The results of these calculations determine the initial conditions for the next phase of the computation. These conditions are very important because they fix the region in the atmosphere where dispersion begins and, based on the local conditions, will determine the transport process.

The dispersion of the stabilized cloud is determined by dividing the atmosphere into sections that comply with rawinsonde measurements made at prescribed times to give the wind direction and speed and temperature profile for the atmosphere. The dispersion model is derived assuming that the source of material to be transported can be represented by a finite vertical line source in each of the rawinsonde-defined layers. The diameter of the cloud at the stabilized height is equal to the diameter used in the cloud-rise model. The concentration of source material in each layer is uniform in the vertical direction and Gaussian along the wind. The assumption is also made that the concentration at one cloud radius from the center line of the cloud is 0.1 times the maximum concentration. The concentration variation in the vertical direction is uniform in each layer but Gaussian, layer by layer, over the height of the cloud.

The mixing and expansion of the cloud, as the material moves downwind are calculated, based on the standard deviation of the vertical and horizontal wind direction over a 10-minute time interval. Standard, tested correlations are available to determine the degree of mixing that results and are given in the report in Appendix B.

The computer program that calculates the concentration and dosage (time-integrated concentration) uses a rectangular coordinate system with the origin at ground level under the cloud center at the time of stabilization with the x axis directed along the mean wind velocity vector and the y axis orthogonal to the wind vector. All points on the ground are then related back to the point of the accident and expressed in a polar coordinate system through a coordinate transformation.

The calculation routine in the model also accounts for the consumption of chemical species and the generation of others using the reaction rate data presented earlier. Standard quantitative parameters for alteration of the constituents by precipitation are also included.

Section 5 of the HARM report (Appendix B) gives complete execution and data preparation instructions for the HARM computer program. It also describes the format available to plot the meteorological data and the output concentration and dosage data. Format information for the input rawinsonde data is also described.

ATMOSPHERIC DISPERSION OF HYPERGOLIC LIQUID ROCKET FUELS

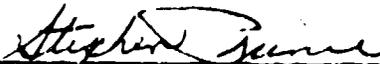
PHASE II: ATMOSPHERIC DISPERSION MODELING

INTERIM REPORT

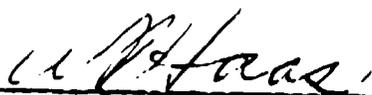
Task 1 Plume/Atmosphere Interaction

18 May 1983

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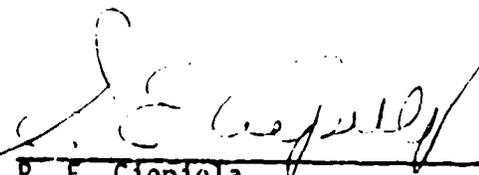
  
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## 1.0 INTRODUCTION

This document and the experimental work described herein is intended to provide time dependent gas phase reaction rate data between hypergolic rocket propellants (hydrazine, unsymmetrical dimethylhydrazine or UDMH and nitrogen tetroxide or NTO) with the reactive atmospheric components of air (which include ozone, oxygen, water vapor, and carbon dioxide). This reaction rate (kinetic) data will be used to modify an existing atmospheric plume dispersion model to incorporate time-dependent atmospheric reactions into the dispersion pattern of an instant release source of a hypergolic fireball. A computer program will be developed to model this instant release/continuously reacting hypergolic plume which uses atmospheric meteorological data and predicts the ground level concentrations of toxic materials that result from a catastrophic reaction of hypergolic propellants. Additional information on the identification of the gas-phase reaction products between the hypergolic propellants and air were obtained during this task period. The purpose of defining atmospheric reaction rates is to assess the potential environmental impact of vaporized propellants and the corresponding degree of control required on their releases into the atmosphere following a hypergolic fireball explosion.

## 2.0 COMPILATION OF EXISTING ATMOSPHERIC REACTION DATA

### 2.1 Hydrazine-Air Reaction

Since hydrazines do not photolyze in the actinic region ( $\lambda < 290$  nm)<sup>2</sup> the major atmospheric sinks for hydrazine decomposition include hydroxide radical, ozone, and nitrogen dioxide, all of which are produced in the NO<sub>x</sub> photooxidation system in polluted and urban atmospheres, and by molecular oxygen in clean unpolluted air. In general, the decay of hydrazine by OH, O<sub>3</sub>, or NO<sub>2</sub> is an order of magnitude more rapid than the decay by molecular oxygen and these processes are thought to be more prevalent when the concentration of hydrazine in the atmosphere is at or near the part-per-million (ppm) level. At higher hydrazine concentrations it is believed that the concentration of these reactive photooxidation products is rapidly depleted by hydrazine reaction and the reaction of hydrazines by molecular oxygen becomes the major atmospheric reaction pathway.

The nominal concentrations of these reactive species in the clean lower troposphere is  $1 \times 10^6$  molecule cm<sup>-3</sup> hydroxide radical, 40 ppb ozone<sup>1</sup>, and between 10 and 50 ppb NO<sub>x</sub> (NO<sub>2</sub> and NO). Polluted industrial atmospheres, however, will exhibit substantially higher concentrations of these atmospheric reactants. Low-level hydrazine concentrations are very reactive in these polluted urban atmospheric systems.

The reaction between hydrazine and hydroxide radical is second-order according to Equation (1).



$$k_1 = 6.1 \pm 1.0 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1} \\ (9.0 \times 10^4 \text{ ppm}^{-1} \text{ min}^{-1})$$

and the rate constant  $k_1$  is relatively independent of temperature between 300 and 425°K.<sup>2</sup> Assuming an average hydroxide concentration of  $1 \times 10^6 \text{ cm}^{-3}$  in the lower troposphere, the half-life for hydrazine in the ppm concentration range can vary between less than one hour in polluted atmospheric environments up to six hours in clean environments.

The reaction between hydrazine and atmospheric ozone is also second order and its reported rate constant is temperature dependent. Tuazon et. al. report a rate constant of  $1.3 \pm 0.1 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$  at 24°C ( $0.2 \text{ ppm}^{-1} \text{ min}^{-1}$ ) with an activation energy of 3.5 to 5 kilocalories per mole. Hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) was the major product in this oxidation reaction, and nitrous oxide ( $\text{N}_2\text{O}$ ) was a minor product. The remaining gas-phase decomposition products were postulated to be nitrogen, water vapor, and hydrogen gas. The tropospheric half-life for ppm concentration of hydrazine vapor were estimated by Tuazon to be about 10 minutes during ozone pollution episodes to less than two hours in an unpolluted atmosphere.

The reaction between ppm levels of hydrazine vapors and atmosphere  $\text{NO}_x$  concentrations also at ppm levels produced no observable change in the initial  $\text{NO}_x$  reactant when performed in the dark, but proceeded rapidly under photolytic conditions.<sup>2</sup> In the later case, hydrazine is rapidly consumed, NO is converted to  $\text{NO}_2$  at a rate approximately equal to that of the hydrazine decay, and  $\text{O}_3$  is formed following NO consumption. The only nitrogen-containing product observed was  $\text{N}_2\text{O}$  in trace amounts. When a 1.3 ppm hydrazine sample was sunlight irradiated with 0.9 ppm NO and 0.12 ppm  $\text{NO}_2$  the hydrazine was completely depleted in 30 minutes. Later studies by Tuazon et. al. indicated that none of the hydrazines studied, which included hydrazine, MMH, and UDMH, reacted with NO alone at measureable rates, but did react significantly with  $\text{NO}_2$ . The rate constant for the dark reaction between  $\text{NO}_2$  and hydrazine reported by Tuazon was approximately  $2.5 \times 10^{-19} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$  ( $3.7 \times 10^{-4} \text{ ppm}^{-1} \text{ min}^{-1}$ ). The reaction of  $\text{NO}_2$  with  $\text{N}_2\text{H}_4$  resulted in the formation of high yields of nitrous

acid (HONO), hydrazinium nitrate, diazine (in excess hydrazine only), and traces of  $N_2O$  and  $NH_3$ . Results of these reported experiments indicate that hydrazine undergoes reactions at significant rates with hydroxide radical, ozone, and nitrogen dioxide when present at ppm levels in air, and Pitts et. al.<sup>2</sup> has suggested that under most conditions, reaction with ozone will be the major fate of ppm levels of hydrazines released into the atmosphere.

The reaction between hydrazine and molecular oxygen is believed to be the major atmospheric reaction pathway when fuel concentrations greatly exceed the part-per-million level. The reaction between hydrazine vapor and molecular oxygen is somewhat complex, and proceeds at a rate which is strongly dependent upon reaction cell geometry and surface composition.

Stone<sup>5</sup> has reported that the main oxidation reaction of hydrazine by molecular oxygen is expressed by equation 2:



In addition to the main reaction which produces nitrogen and water vapor, there are side reactions which produce ammonia and are largely heterogeneous in nature. The oxidation half-lives studied by Stone depended on both the surface area and composition of the reaction vessel and ranged from 25 minutes for a five liter flask (surface area = 1600  $cm^2$ ) to two and a half hours for a specially constructed 44 x 2 -cm cell (surface area = 300  $cm^2$ ). The decay rate for each of these reactions, however, was determined to be first order with respect to initial hydrazine concentration. The rate of ammonia production, and thus the total amount produced was also a function of the surface-to-volume ratio of the reaction vessel. The 5-liter flask had produced approximately 0.2 torr ammonia (.03% v/v) from an initial hydrazine concentrations of 5.0 torr (.66% v/v) in an 80% nitrogen -20% oxygen gas mixture in which the total pressure was 760 torr. The

half-life for ammonia production appeared to be approximately 40 minutes. The 44 x 2 - cm cell had produced approximately 0.3 torr ammonia (.04% v/v) from an initial hydrazine concentration of 3.5 torr (.46% v/v) in an 80% nitrogen - 20% oxygen gas mixture in which the total pressure was 760 torr. In this latter case, the half-life for ammonia production was approximately 160 minutes. The surface-to-volume ratio for the 5-liter flask and 44 x 2 - cm cell was  $0.3 \text{ cm}^{-1}$  and  $2 \text{ cm}^{-1}$ , respectively.

Tuazon et. al. measured the dark decay of hydrazine at low concentration (5-12 ppm) in a purified air environment, i.e. ozone and  $\text{NO}_2$  concentration were negligible. The study was conducted in a 3800 liter chamber fabricated from 50 micron (2-mil) thick Teflon sheeting. The calculated surface-to-volume ratio of this chamber was ca.  $0.06 \text{ cm}^{-1}$ , a factor of five lower than the reaction vessels used by Stone. The reported half-life for hydrazine decay at  $22^\circ\text{C}$  and 12% relative humidity was 10.8 hours, and at 55% relative humidity was 4.9 hours. Ammonia was also observed as a reaction product in these tests, but only account for 5-10% of the hydrazine lost during reaction.

The decay of hydrazine in air therefore was seen to be highly dependent on the geometry of the gas reaction vessel as well as the amount of humidity in the air, showing an approximately two-fold faster oxidation rate in humid air than in dry air. Actual atmospheric oxidation rates, in which a typical ambient surface-to-volume ratio of  $9 \times 10^{-6} \text{ cm}^{-1}$  is taken,<sup>5</sup> is unknown at present but will most likely approximate those values performed in the larger reaction chambers.

## 2.2 Unsymmetrical Dimethylhydrazine-Air Reaction

In general, the same atmospheric components which were found to be reactive with hydrazine vapors are also reactive with substituted hydrazine vapors, which include both unsymmetrical dimethyl hydrazine (UDMH) and monomethylhydrazine (MMH). The substituted hydrazines did exhibit different reaction rates with the reactive atmospheric species and the reaction products were more diverse in nature.

The rate constant for the reaction between hydroxide radical and UDMH was estimated by Tuazon et. al.<sup>1</sup> to be approximately  $5 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$  ( $7.4 \times 10^4 \text{ ppm}^{-1} \text{ min}^{-1}$ ). The rate constant was assumed to be second order and relatively temperature independent between 300 and 425<sup>0</sup>K. The half-life for UDMH decay by atmospheric hydroxide radical was estimated to be approximately 3 hours, but could be two to five times larger in pristine atmospheres and less than one hour in polluted urban atmospheres.

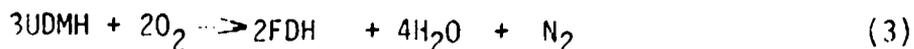
When UDMH vapors were reacted with ozone in ppm concentration levels, the fuel reacted at a rate which was too rapid to accurately measure. The half-life for substituted hydrazines due to ozone oxidation was estimated by Tuazon<sup>6</sup> to be a factor of 10 shorter than that of unsubstituted hydrazine. This would place the window for ppm UDMH decay by atmospheric ozone between 1 minute during ozone pollution episodes to .2 hr (12 minutes) in clean atmospheres. The overall apparent rate constant for UDMH + O<sub>3</sub> reaction therefore must be greater than  $10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$  ( $1.5 \text{ ppm}^{-1} \text{ min}^{-1}$ ). In these reactions, Nitrosodimethylamine (NDMA, a known carcinogen) was formed in high yields (60%) and the observed O<sub>3</sub>/UDMH stoichiometry was 1.5/1. Tuazon<sup>1</sup> also performed studies on atmospheric destruction mechanisms for the NDMA formed from the UDMH/ozone reaction. He determined that the major atmospheric sink for NDMA destruction is the photolysis by ambient sunlight. The reaction displayed a quantum yield of 1.0, and no appreciable decay of NDMA by air or ozone was observed under atmospheric conditions. The photolysis reaction has a half-life of ca. 30 minutes and results in the formation of dimethylnitramine as well as other minor products.

The reaction between UDMH and NO<sub>2</sub> produced tetramethyltetrazine (TMT) as the major organic reaction product and displayed an apparent second-order rate constant of  $2 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$  ( $.03 \text{ ppm}^{-1} \text{ min}^{-1}$ ), with a half-life of about 5 minutes. Nitrous acid (HONO) was also a product in the UDMH/NO<sub>2</sub> reaction. In these three cases for low-level UDMH decay by atmospheric species, the oxidation by

ozone was assumed to be the major fate of UDMH vapors released into the atmosphere. The main reaction product from this reaction is NDMA which displays unacceptable personnel exposure hazards at any measurable concentration.

The reaction between UDMH and molecular oxygen is believed to be the major environmental fate for elevated fuel concentrations in the atmosphere. The vapor-phase reaction between UDMH and molecular oxygen is very complex and may involve free-radical processes.<sup>3</sup> Free radical reactions are greatly influenced by the geometry and surface composition of the reaction vessel, as rate determining intermediates are presumed to occur on the surface of the reaction vessel. Additionally, different reaction mechanisms (and thus reaction rates) appear to be prevalent at higher fuel concentrations (0.2-1.0 percent) than at lower fuel concentrations (2-10 ppm).<sup>4</sup> Stone<sup>4</sup> reported an atmospheric half-life of approximately 175 hours for an initial UDMH concentration of 0.7%, which was identical for reaction with dry nitrogen, 20% oxygen in dry nitrogen, and 80% oxygen in dry nitrogen. Tuazon reported a half-life for 12-13 ppm UDMH in "dry" air of  $341 \pm 384$  hours in a 6400 liter environmental chamber and  $341 \pm 64$  hours in a 3800 liter chamber. When the air was humidified to 50% R.H., this half-life was decreased to  $70.9 \pm 9.6$  hours. These results substantiate the effect of vessel geometry and perhaps reactant fuel concentration on the determination of kinetic rate constants and half lives for UDMH decay by atmospheric air. Perhaps more importantly, they indicate that the reaction between UDMH and dry air is relatively insignificant under the conditions studied, and the driving force in the air oxidation of UDMH becomes the degree of humidity.

The reaction between UDMH and molecular oxygen is first order (zero order with respect to oxygen), and thus the reaction rate is directly proportional to the UDMH concentration. The main reaction as proposed by Loper<sup>3</sup> proceeds according to Equation 3.



Thus the major product in the air oxidation of UDMH is formaldehyde dimethylhydrazone (FDH) and it is produced in a reaction stoichiometry of 1 mole FDH formed per 1.5 mole UDMH reacted. Other minor products in the UDMH air reaction include ammonia ( $\text{NH}_3$ ), dimethylamine, NDMA, diazomethane, nitrous oxide, methane, carbon dioxide, formaldehyde, formaldehyde monomethyl hydrazone (FMH) and TMT.

## 2.3 Nitrogen Dioxide-Air Reactions

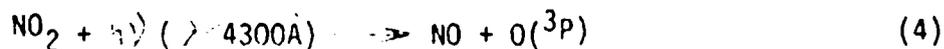
Nitrogen dioxide ( $\text{NO}_2$ ) reacts with atmospheric air by two main pathways: (1) it interacts with sunlight to produce photochemical smog which is representative of polluted urban atmosphere such as Los Angeles<sup>8</sup>; and (2) it reacts with atmospheric water vapor to produce both vapor phase and condensed-phase nitric acid. These atmospheric reactions of nitrogen dioxide and the implications for dispersion modeling of released  $\text{NO}_2$  vapors are discussed in the sections that follow.

### 2.3.1 Photochemical Reactions of Nitrogen Dioxide.

The photolysis of nitrogen dioxide by ambient sunlight is the major reaction resulting in the formation of ozone in the troposphere<sup>8,19</sup>. The ozone produced by the photolysis reaction can react with nitric oxide to reform the nitrogen dioxide, with nitrogen dioxide to form symmetrical nitrogen trioxide ( $\text{NO}_3$ ), or with hydrocarbon pollutants in the atmosphere to produce oxidized carbon species.

In general, photochemical reactions producing tropospheric (or stratospheric) ozone as well as the transient nitrogen trioxide species and dinitrogen pentoxide ( $\text{N}_2\text{O}_5$ ) has been extensively studied by atmospheric and meteorological scientists<sup>11,12,15</sup>.

The major photolysis reactions of  $\text{NO}_2$  can be expressed by the following series of equations.



In equations (4) - (6), nitrogen dioxide is regenerated by the action of ozone on the nitric oxide formed by reaction (4). In equation (7) and (8) which represent an alternate reaction pathway for the ozone formed, dinitrogen pentoxide ( $\text{N}_2\text{O}_5$ ) is formed through the transitory and unstable nitrogen trioxide molecule ( $\text{NO}_3$ ). The equilibrium composition of the final mixture and the kinetics are complex since the reaction mechanisms are competitive for the reactive ozone molecule. The reaction rates for each of the individual reactions have been elucidated and are described as follows.

The photolysis of nitrogen dioxide (Eq. 4) is the preliminary step in the production of photochemical smog. This reaction provides both nitric oxide and photochemically excited triplet oxygen atom ( $\text{O}(^3\text{P})$ ). This process was observed to have a quantum yield of 1.0 (one excited oxygen atom produced per photon absorbed) when irradiated with sunlight of wavelength 295 - 398 nm<sup>12</sup>. The first-order rate constant was determined to be 0.43 min<sup>-1</sup> under ambient conditions<sup>8</sup>. The actual photolytic kinetic rate constant,  $k_4$ , however, was determined by Sickles et. al.<sup>19</sup> to be highly dependent on the latitude, solar zenith angle, and cloud cover. Other factors influencing the transparency of the atmosphere to sunlight irradiation, including aerosol loading and particulate count, were also found to preclude the accurate prediction of  $k_4$  during the sunlight portion of the day. Sickles did observe an apex of the of the rate constant value during solar noon (.46 for a sunny - 0% sky cover day) which was reduced to ca. .25 (clear day) and .14 (cloudy day) at early morning hours and late afternoon hours, respectively.

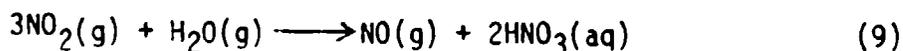
The highly reactive triplet P-oxygen formed in air collides with oxygen molecules forming ozone by Equation (5). In this case, M represents a 3rd molecular species (nitrogen, oxygen, water vapor, etc) that removes a fraction of the energy released during the interaction of the oxygen atom with the oxygen molecule. This energy removal stabilizes the ozone product. Typically, reaction (5) is very rapid and Garvin<sup>12</sup> reports a third order rate constant of  $5.8 \times 10^{-34} \text{ cm}^6 \text{ molecule}^{-2} \text{ sec}^{-1}$  at 25°C and for  $M = \text{N}_2$ . A steady state concentration of ozone is quickly reached by the reaction pathways (6) and (7). Reaction (6) is very rapid as is reaction (7). Graham and Johnston<sup>9</sup> report a second-order rate constant for reaction (7) of  $3.4 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$  at 25°C ( $5 \times 10^{-2} \text{ ppm}^{-1} \text{ min}^{-1}$ ). Reaction (8) which combines the transient nitrogen trioxide with nitrogen dioxide to form dinitrogen pentoxide is also very rapid.

Nitrogen dioxide destruction by photolysis is a complex phenomenon and the subsequent reformation by reaction with nitric oxide and ozone can lead to a net decrease in the atmospheric nitrogen dioxide equal to the steady-state ozone level developed. The calculation of steady-state ozone production (and nitrogen dioxide decay) for an atmospheric release of hypergolic fireball components is difficult at best, and a qualitative description of these photochemical reactions of nitrogen dioxide will suffice for the present task effort.

### 2.3.2 Gas-Phase Reaction Between Nitrogen Dioxide and Water Vapor

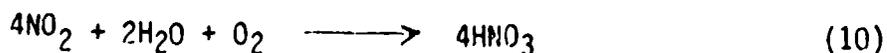
The kinetics of the gas-phase reaction between nitrogen dioxide and water vapor was studied by England and Corcoran<sup>14</sup>. Under normal atmospheric conditions (in which  $\text{NO}_2$  gas is present at ppm levels in polluted urban atmospheres), the reaction with water vapor was very slow and formation of nitric acid aerosols did not form. This observation has been contrasted to the atmospheric nucleation, hydration, and misting of sulfuric acid from the reaction of sulfur dioxide with moist air<sup>8</sup>. The apparent difference in the acid rain effect for sulfur dioxide and that for nitrogen dioxide was accounted for by the high vapor pressure of

nitric acid compared to the low vapor pressure ( $10^{-8}$  to  $10^{-10}$  torr) of sulfuric acid. The vapor pressure of pure nitric acid was 51 torr (7.2% at one atmosphere) at  $20^{\circ}\text{C}$ . The vapor pressure of a 50% nitric acid-water solution was ca. 470 ppm nitric acid and 1.02% water vapor also at  $20^{\circ}\text{C}$ . The gas-phase reaction between nitrogen dioxide and water vapor supplies nitric acid nuclei when partial pressure of acid exceeds the vapor pressure. Water vapor readily condenses on each nucleus to form strong nitric acid droplets. England and Corcoran suggest that the threshold for the two-phase region of nitric acid occurs at about 50 ppm  $\text{HNO}_3$  at one atmosphere pressure and  $25^{\circ}\text{C}$ . Above this concentration, mists or condensation of nitric acid were observed to form. The overall reaction



is favored thermodynamically at ambient conditions.

When gas-phase reactions were performed at concentrations low enough to prevent the formation of a two-phase system, the rate of disappearance of  $\text{NO}_2$  was first-order with respect to nitrogen dioxide. The overall reaction in the presence of oxygen



goes to completion in the gas phase and the third order rate constant is represented by equation (11)

$$R_{\text{NO}_2}^{\circ} = -k (\text{NO}_2)^2 (\text{H}_2\text{O}) \quad (11)$$

$$k = 5.5 \times 10^4 \text{ l}^2 \text{ mole}^{-2} \text{ sec}^{-1} \text{ at } 25^{\circ}\text{C}.$$

This rate constant indicates that the initial rate of reaction increases as the square of the nitrogen dioxide concentrations and therefore would be very slow at low  $\text{NO}_2$  concentrations and very fast at higher concentrations.

For a 1% concentration of water vapor and an initial concentration of 10 ppm of nitrogen dioxide, the half-life for reaction would be about 5 hr. If the initial concentration of nitrogen dioxide was 50 ppm (the maximum level of  $\text{NO}_2$  before misting or condensation occurs); the reaction half-life would be 12 minutes.

Therefore, in cases where nitrogen dioxide vapors are released into the atmosphere from a hypergolic explosion, misting and condensation is expected to form where the concentration is elevated above 50 ppm  $\text{NO}_2$ , at which time the residual  $\text{NO}_2$  vapor will quickly react to form vapor-phase nitric acid.

### 3.0 PROPELLANT-ATMOSPHERE REACTION EXPERIMENTS

Chemical reactions between the reactive molecular components of air (oxygen, carbon dioxide, and water vapor) and vaporized propellant species (hydrazine, UDMH, and nitrogen dioxide) were performed in order to supplement the reaction rate data obtained in current literature sources and to provide information on the gas-phase reaction products between vaporized hypergolic propellants and air. Results of these experiments will be correlated with previously reported atmospheric reaction data and incorporated into an existing atmospheric plume model to incorporate time-dependent atmospheric reactions into the dispersion pattern of an instant release source of a hypergolic fireball. The test matrix for the propellant-atmospheric reaction experiments is included in Table 1.

#### 3.1 Experimental Methods

##### 3.1.1 Hydrazine-Atmospheric Reactions

Gas phase mixtures of 0.5% hydrazine vapor were prepared by injecting a known amount of anhydrous hydrazine liquid (5.2 microliters) into a one liter gas sampling bulb (Ace Glass Inc.) which was previously purged with pure helium, a 21% oxygen helium mixture, or a 21% oxygen .05% carbon dioxide in helium mixture as detailed in Table I. Atmospheric gases were obtained in the ultra-pure grade from Linde Specialty Gases and mixed using appropriate flowraters to give the desired oxygen and carbon dioxide composition. Water vapor was added to the sampling bulbs Nos. 8 and 10 by injection of 6.0 microliters of liquid distilled water. This corresponds to 1% water vapor under Denver barometric conditions (25°C, 0.806 atmospheres). Vaporization of the liquid components and gas mixing was accomplished using 1/4-inch teflon beads. Gas samples were removed from the bulbs at the time increments detailed in Table I and analyzed for hydrazine by the paradimethylaminobenzaldehyde (PDAB) colorimetric method and for gaseous reaction products (nitrogen, oxygen, water vapor, and ammonia) using gas chromatographic techniques. The PDAB colorimetric analysis method for hydrazine is summarized below.

Table I Test Matrix Atmospheric Reaction of Hypergols

Test No.	Propellant Species	Prop. Conc.	Reactant Gas* Composition	Sampling Time, Hrs
1	Hydrazine	0.5%	Helium	0,0.5,1,2,4
2	Hydrazine	0.5%	21% O <sub>2</sub> in He	0,0.25
3	Hydrazine	0.5%	21% O <sub>2</sub> + 1% H <sub>2</sub> O in He	0,0.25
4	Hydrazine	0.5%	21% O <sub>2</sub> + 0.05% CO <sub>2</sub> in He	0,0.25
5	Hydrazine	0.5%	21% O <sub>2</sub> + 0.05% CO <sub>2</sub> + 1% H <sub>2</sub> O in He	0,0.25
6	UDMH	0.5%	Helium	0,5,12,21,45,70
7	UDMH	0.5%	21% O <sub>2</sub> in He	0,5,12,21,45,70
8	UDMH	0.5%	21% O <sub>2</sub> + 1% H <sub>2</sub> O in He	0,5,12,21,45,70
9	UDMH	0.5%	21% O <sub>2</sub> + 0.05% CO <sub>2</sub> in He	0,5,12,21,45,70
10	UDMH	0.5%	21% O <sub>2</sub> + 0.05% CO <sub>2</sub> + 1% H <sub>2</sub> O in He	0,5,12,21,45,70
11	NO <sub>2</sub>	0.25%	Helium	0,1,3,7,24
12	NO <sub>2</sub>	0.25%	21% O <sub>2</sub> in He	0,1,3,7,24
13	NO <sub>2</sub>	0.25%	21% O <sub>2</sub> + 1% H <sub>2</sub> O in He	0,1,3,7,24
14	NO <sub>2</sub>	0.25%	21% O <sub>2</sub> + 0.05% CO <sub>2</sub> in He	0,1,3,7,24

\* 1% H<sub>2</sub>O in Helium Corresponds to 50% Relative Humid Air at 25°C (77°F)

Test temperatures were ambient (21-23°C) for amine fuel tests and elevated (35°C) for nitrogen dioxide tests.

### Reagents

1. PDAB Stock Solution - Dissolve 10.0 grams PDAB in approximately 150 ml methyl alcohol. Add 10 ml concentrated hydrochloric acid and dilute to 250 ml with methyl alcohol.
2. 0.1 N Sulfuric Acid - Dilute 2.78 ml concentrated  $H_2SO_4$  to 1000 ml with distilled water.
3. PDAB Final Solution - Dilute 100 ml of the PDAB stock solution to 500 ml with 0.1 N  $H_2SO_4$ .

### Hydrazine Calibration Curve

A hydrazine calibration curve was prepared by injecting known amounts of hydrazine stock solution into the PDAB stock solution, allowing the yellow color to fully develop for 10 minutes, and reading the absorbance of the resulting solution at a wavelength of 455 nm in a Spectronic 20 Colorimeter.

The resulting calibration curve for anhydrous hydrazine is depicted in Figure 1.

### Sample Analysis

1. Pipet 10.0 ml PDAB final solution into a stoppered 30 ml sample vial.
2. Inject 1.0 ml of the gas mixture contained in the gas sampling bulb through the septum in the 30 ml sample vial using a gas tight syringe. The gas sample to be analyzed is added to the gas ullage above the PDAB solution contained in the vial.

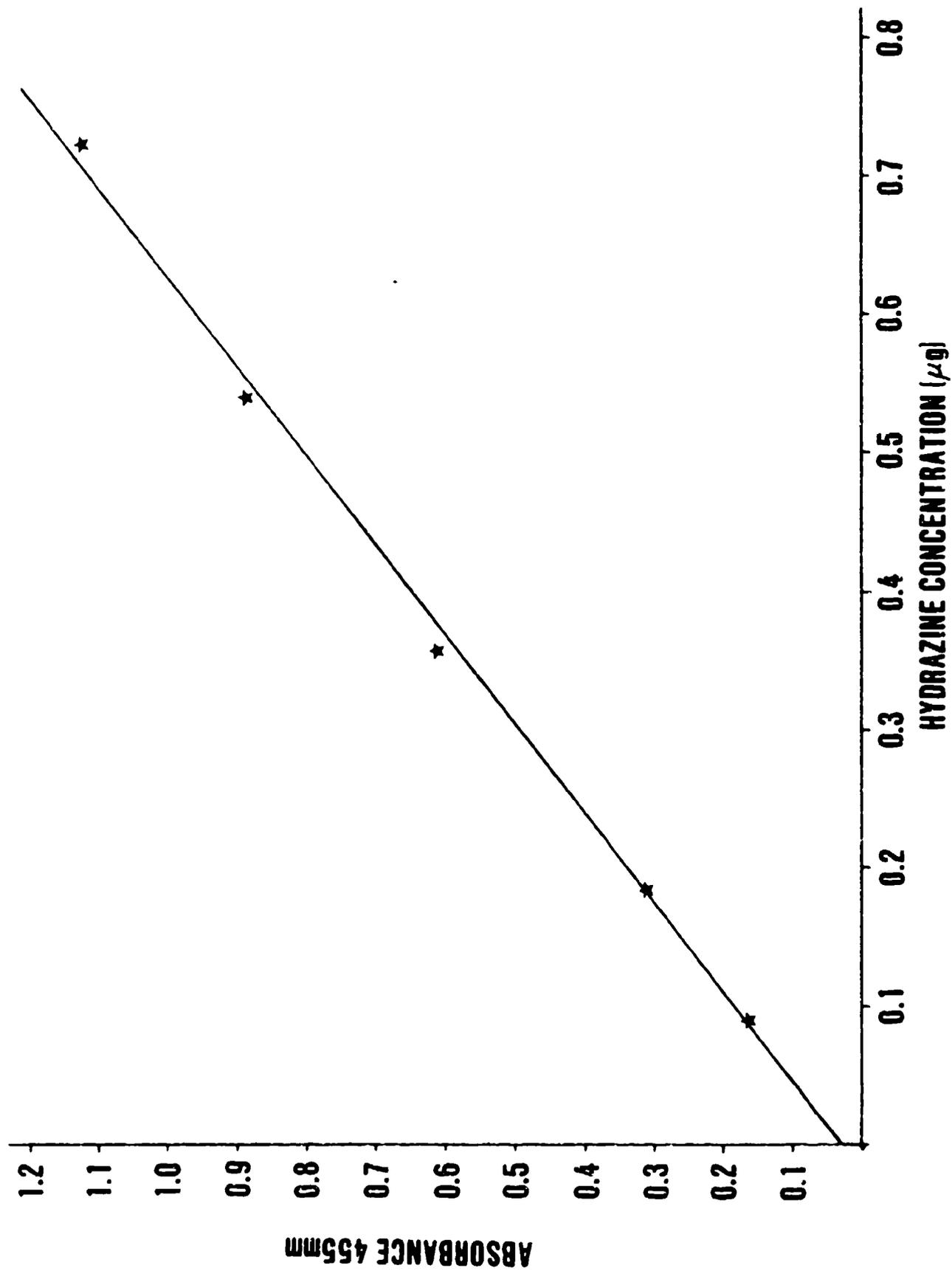
Analysis of Hydrazine Vapor Composition by the  
Paradimethylaminobenzaldehyde Method (PDAB)  
(Continued)

3. Shake the vial vigorously for 30 seconds to ensure complete hydrazine reaction by the PDAB solution.
4. After 10 minutes color development time, read the absorbance of the solution at 455 nm.
5. Compare the absorbance of the analyzed sample with the absorbance of the calibration standards and report the hydrazine vapor concentration in the sample.

Interference Studies

Because ammonia was observed by some researchers to be a side-product in the hydrazine-air reaction,<sup>5</sup> the PDAB colorimetric reagent was tested for its reaction and color development with ammonia gas. The interference ratio for ammonia with the PDAB reagent was approximately 100:1 (100 ppm NH<sub>3</sub> corresponded to 1 ppm N<sub>2</sub>H<sub>4</sub>).

Figure 1. PDAB Calibration Curve Hydrazine



### 3.1.2 UDMH-Atmospheric Reactions

Gas mixtures containing 0.5% UDMH vapor (Test Nos. 6-10 in Table I) were prepared by injecting 12.6 microliter of high purity 1, 1-dimethylhydrazine liquid ( 0.2% FDH by volume) into a 1-liter gas sampling bulb (Ace Glass Inc.) which was previously purged with the desired reactant gases as described in Section 3.1.1. To the UDMH-atmospheric mixtures contained in the gas sampling bulb, 1.0 ml of pure ethane gas (Scott Calibration Gases) was added as an internal standard.

Water vapor was added to the appropriate sample bulbs by injection of 6.0 microliters of liquid distilled water and vaporization and mixing of the liquid component was accomplished using the 1/4-inch teflon beads as previously described. Aliquots of the gas reaction mixture were removed from sample bulb at the reaction time intervals indicated in Table 1, and the bulbs were stored in the dark at ambient temperatures (21-23°C) between sampling intervals. Oxygen, water vapor and UDMH reactant gas composition as well as FDH, NDMA, and nitrogen reaction products were quantitated using the gas chromatographic techniques to be subsequently described. The gas chromatographic analysis of hydrazine-air mixture is also included in this section.

#### Preparation of Standards for GC Calibration

Gas calibration standards were prepared in 1-liter gas sampling bulbs using nitrogen as the matrix gas. The 0.5% UDMH standard was prepared by injecting 12.6 microliters of purified UDMH liquid into the 1-liter bulb which had been previously purged with dry nitrogen gas. To this mixture, 1.0 ml of ethane was added as an internal standard. The 0.5% FDH standard was prepared in the identical manner, using 14.6 microliters of purified formaldehyde dimethylhydrazine to give the final desired composition. The calibration of the vapor-phase concentration of nitrosodimethylamine (NDMA) was accomplished by injection of a liquid NDMA standard in methanol such that 1.0 microliter of the liquid standard corresponds to the same amount of NDMA which would be present in 0.5 milliliters of a 0.008% NDMA gas standard. Additional NDMA standards in methanol were prepared to give equivalent responses of 0.004%, 0.0016%, and 0.0008% NDMA in the gas phase.

The 1% water vapor standard was prepared by adding 6 microliters of liquid water to a 1-liter gas sampling bulb previously purged with dry nitrogen.

A 0.1% ammonia standard was prepared by injecting 1.0 milliliter of high purity ammonia gas into a 1-liter gas bulb purged with nitrogen.

#### Analysis of Standards by Gas Chromatography

The method for analyzing the UDMH, FDH, and NDMA standards employed a 2 meter long glass column packed with Tenax GC 60/80 mesh connected to a flame ionization detector. The GC conditions were: column initial temperature 100°C for 1.0 minute, temperature ramp to 250°C at 15°C/min, injection port temperature 120°C, detector base 300°C, carrier gas helium at 30 ml/min. Due to the high concentrations of UDMH and FDH used, the detector range was initially set at  $10^{-11}$  and then changed to  $10^{-12}$  (most sensitive) during the elution of the NDMA peak. The injection volume used in this analyses was 0.50 milliliters for the gas standards and 1.0 microliter for the NDMA standard in methanol.

The method used for analyzing water vapor, oxygen, and nitrogen for the UDMH-atmospheric tests used a four foot, 1/8-inch stainless steel column packed with Tenax GC 60/80 mesh connected in series with a 9 foot 1/8-inch stainless steel column packed with molecular sieve 5A 30/60 mesh.

The GC conditions were: column initial temperature, 40°C for 1.0 minute, temperature ramp to 140°C at 15°C/min, injection port temperature 100°C, carrier gas helium at 30 ml/min, detector oven 200°C, filament temperature 230°C. The injection volume used was 1.0 milliliter.

The method for analyzing ammonia and water standards for the hydrazine atmospheric tests utilized a four foot, 1/8-inch stainless steel column packed with Tenax GC 60/80 mesh and a thermal conductivity detector. The GC conditions were: column 40°C for 1.0 minute, ramp to 140°C at 15°C/min, injection port 100°C, carrier gas helium at 30 ml/min, detector oven 200°C filament temperature 250°C. The injection volume used was 1.0 milliliter.

## Calibration

Calibration curves for NDMA, water, and ammonia were prepared from the gas-chromatographic results of standards prepared from these commodities. These calibration curves are presented in Figures 2 through 5, respectively. Response factors for oxygen and nitrogen were calculated using room air as the calibration gas (21% oxygen, 79% nitrogen nominal composition). Calibration for UDMH and FDH were performed using propane as an internal standard and were calculated on a Varian Vista 6000 gas chromatography data system in volume percent of UDMH and FDH, respectively.

The GC retention time and detector responses for the analyzed gas commodities using the instrument parameters described above are included in Table II.

The GC retention time and detector responses for the analyzed gas commodities using the instrument parameters described above are included in Table II.

Table II Gas Chromatography Results  
Atmospheric Gas Standards

Commodity	Concentration	Retention Time (min.)	Detector Response (Counts)
Propane	1% (int. std.)	0.316	$3.01 \times 10^5$
UDMH	0.5%	2.995	$9.925 \times 10^5$
FDH	0.5%	4.531	$1.838 \times 10^6$
NDMA	0.005%	6.609	$1.057 \times 10^{5*}$
Water Vapor <sup>1</sup>	1.0%	0.769	$5.82 \times 10^4$
Oxygen	21% (nom.)	10.946	$3.43 \times 10^6$
Nitrogen	79% (nom.)	12.534	$1.166 \times 10^7$
Ammonia <sup>2</sup>	0.1%	0.487	$4.0 \times 10^3$
Water Vapor <sup>2</sup>	1.0%	0.737	$1.85 \times 10^5$

<sup>1</sup> UDMH Tests

<sup>2</sup> Hydrazine Tests

\* Attenuation Change on Detector  $\times 10^1$

Figure 2. Ammonia Calibration Curve Gas Chromatography

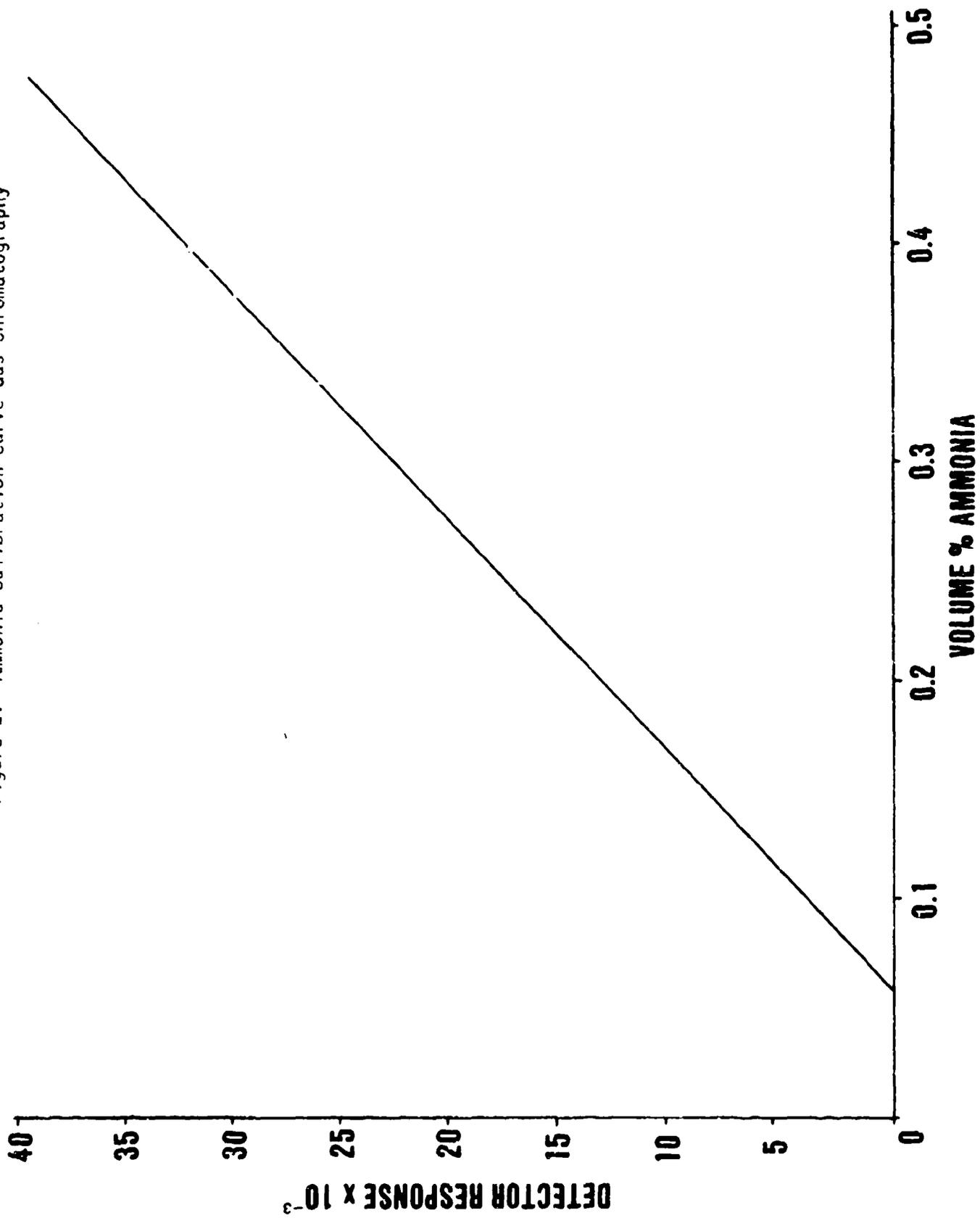


Figure 3. NDMA Calibration Curve Gas Chromatography

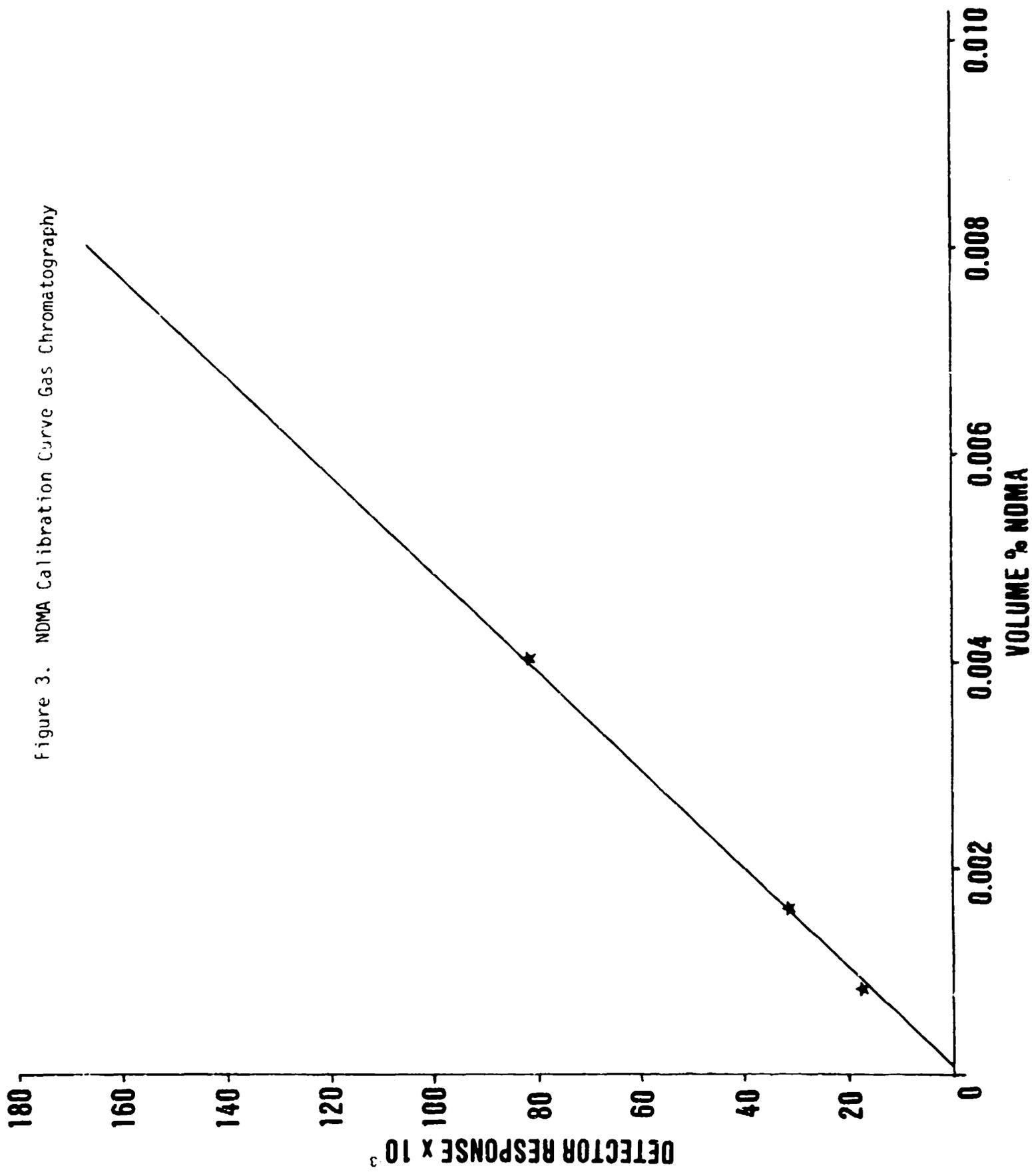


Figure 4. Water Calibration Curve (UDMH) Gas Chromatography

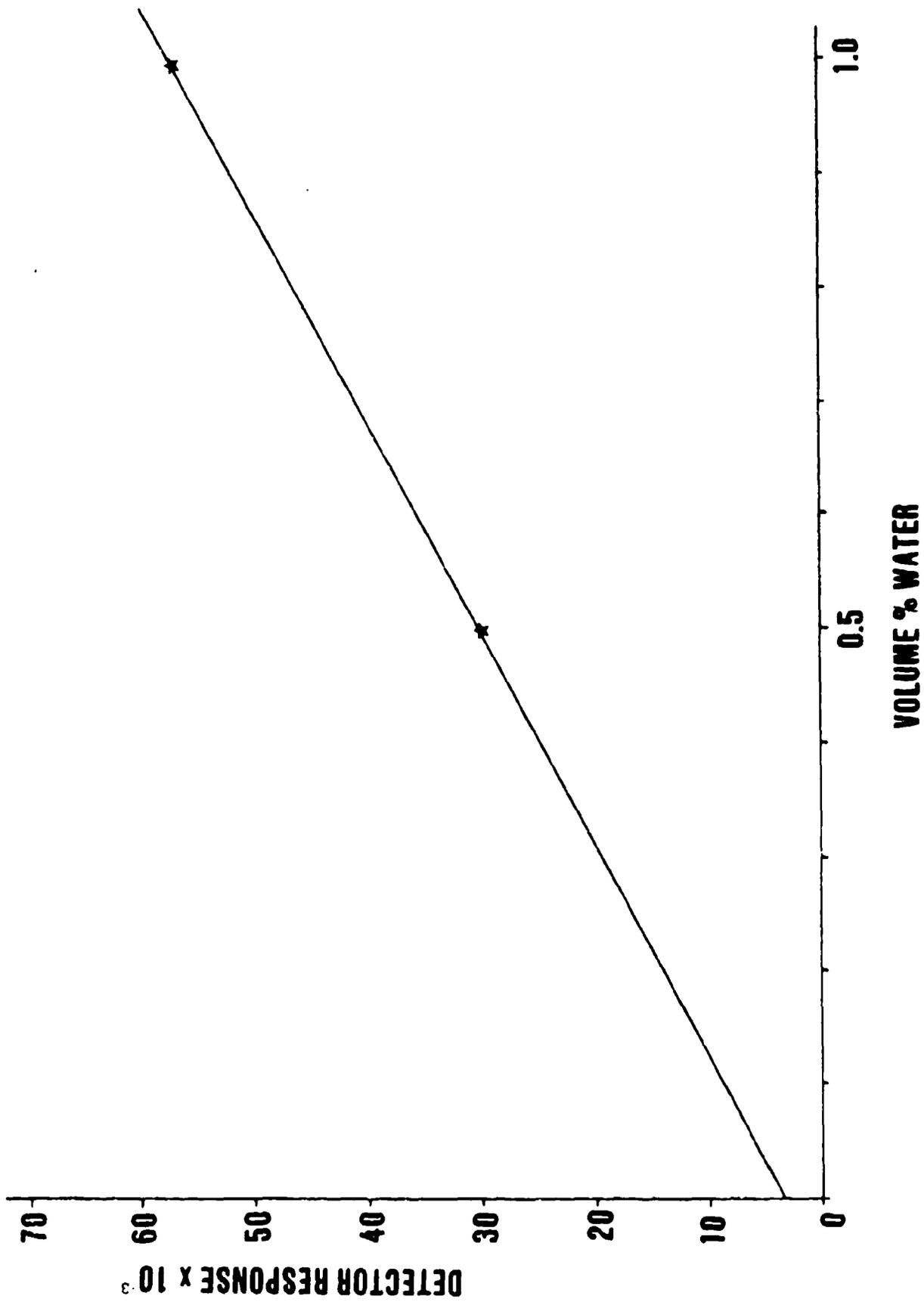
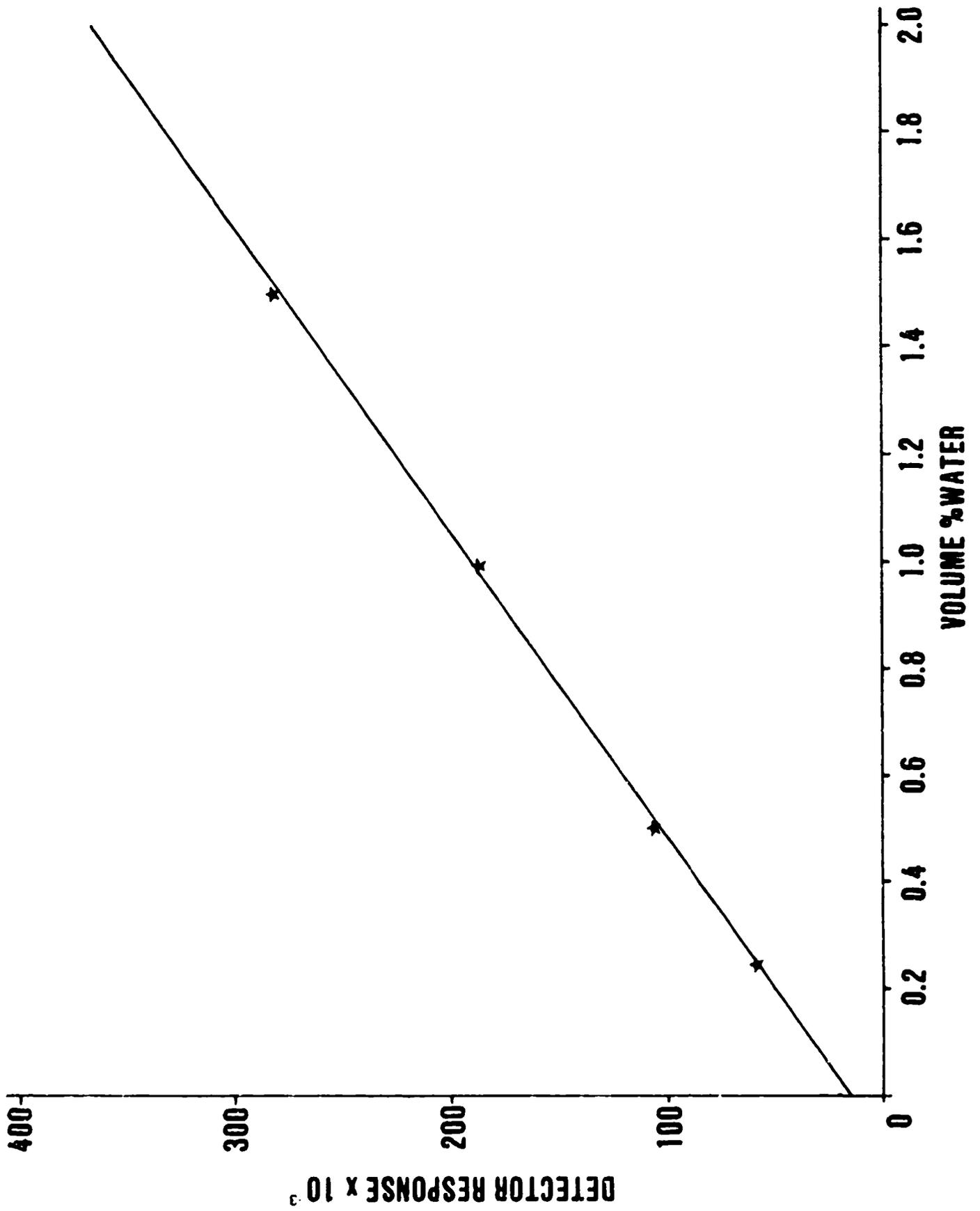


Figure 5. Water Calibration Curve (Hydrazine Tests) Gas Chromatography



### 3.1.3 Nitrogen Dioxide-Atmospheric Reactions

Gas-phase mixtures of NO<sub>2</sub> in helium, 21% oxygen in helium, and 21% oxygen + 0.05% carbon dioxide in helium were prepared by mixing ultra pure gas mixtures provided by Linde Specialty Gases. Sample No. 13 (21% oxygen + 1% water vapor in helium) was prepared by humidifying the 21% oxygen-helium mixture by bubbling the gas through a gas washing bottle filled with distilled water (flow rate 0.5 lpm) prior to mixing with the nitrogen dioxide gas. Gas reaction mixtures were then fed into large (15-liter) gas sample bags (Calibration Instruments, Inc.) which were equilibrated at an elevated temperature (35°C) by a mechanical convection oven. The large sample bags were required for the NO<sub>x</sub>-NO sample analysis to be described below.

#### Sample Analysis

Gas aliquots from Test Nos. 11 through 14 were sampled at the time intervals detailed in Table I and analyzed for NO<sub>x</sub> and NO concentrations using a chemiluminescent analyzer (Thermoelectron Corp.). The instrument was calibrated using a 440 ppm NO standard prior to each series of analysis. Chemiluminescent readings were accomplished by attaching a teflon line connecting each of the four sample bags to a five-port switching valve, the outlet (port 5) of which was connected to the NO<sub>x</sub> analyzer. Readings could be quickly taken from all four sample bags by sequentially switching the five-port valve. The sampling flow rate from the chemiluminescent NO<sub>x</sub> analyzer was 0.5 lpm, which accounted for the need of a large reaction container.

## 3.2 Results

### 3.2.1 Hydrazine-Atmospheric Reactions

Hydrazine decay results in the 1-liter gas sampling bulb as measured by the PDAB colorimetric method are presented in Table III. Hydrazine did not decay in the pure helium mixture, indicating that very little autodecomposition occurred on the glass surface. All samples exposed to 21% oxygen decayed completely within 15 minutes. The addition of 0.05% carbon dioxide seemed to slow or inhibit the reaction. The very rapid decay of the

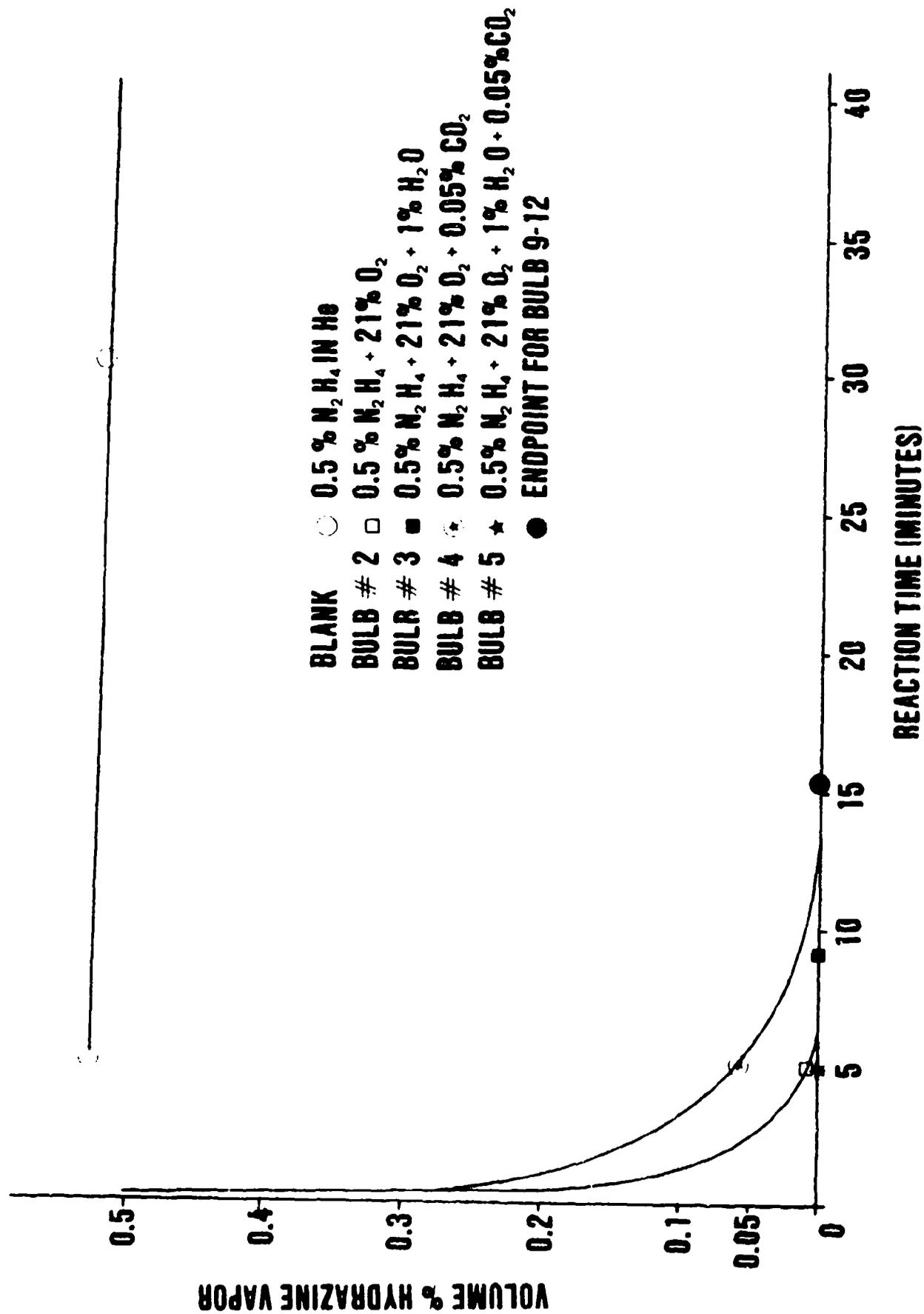
hydrazine vapor in oxygenated atmosphere is most certainly heterogeneous, and is probably due to the large surface-to-volume ratio of the 1-liter gas bulbs used in these tests.

Table III PDAB Colorimetric Analysis Hydrazine Atmospheric Reaction

Test No.	Initial Gas Composition	Reaction Time Minutes	Absorbance 455 nm	Percent Hydrazine Vapor
1	0.5% N <sub>2</sub> H <sub>4</sub> in He	5	0.90	0.52
		30	0.90	0.52
		60	0.89	0.51
		120	0.90	0.52
		240	0.86	0.49
2	0.5% N <sub>2</sub> H <sub>4</sub> + 21% O <sub>2</sub> in He	5	0.015	0.003
		15	0.010	0.002
3	0.5% N <sub>2</sub> H <sub>4</sub> + 21% O <sub>2</sub> + 1% H <sub>2</sub> O in He	8	0.005	0.002
		15	0.009	0.002
4	0.5% N <sub>2</sub> H <sub>4</sub> + 21% O <sub>2</sub> + .05% CO <sub>2</sub> in He	2	0.08	0.037
		5	0.108	0.049
		15	0.001	0.002
5	0.5% N <sub>2</sub> H <sub>4</sub> + 21% O <sub>2</sub> + 1% H <sub>2</sub> O + 0.05% CO <sub>2</sub> in He	5	0.004	0.002
		15	0.000	0.002

A graph of the hydrazine concentration for the five sample bulbs versus time is shown in Figure 6.

Figure 6. Hydrazine Atmospheric Reactions



Results of the water vapor/nitrogen/oxygen gas analysis for the hydrazine atmosphere reaction mixtures are presented in Table IV and indicate that both nitrogen and water vapor are formed in these reactions and that ammonia formation reported by Stone<sup>5</sup> was well below detectable limits in the present study. Water vapor was formed in the ratio 2 moles H<sub>2</sub>O formed per 1 mole N<sub>2</sub>H<sub>4</sub> reacted which is in excellent agreement with the results by Stone.

Table IV Gas Chromatography Results Hydrazine Atmospheric Reaction

Test No.	Initial Gas Composition	% Water	% Oxygen	% Nitrogen	% Ammonia
1	0.5% N <sub>2</sub> H <sub>4</sub> in He	< 0.01	0.07	0.21	< .05
2	0.5% N <sub>2</sub> H <sub>4</sub> + 21% O <sub>2</sub> in He	0.89	21.9	1.05	< .05
3	0.5% N <sub>2</sub> H <sub>4</sub> + 21% O <sub>2</sub> + 1% H <sub>2</sub> O in He	1.91	26.0	0.71	< .05
4	0.5% N <sub>2</sub> H <sub>4</sub> + 21% O <sub>2</sub> + 0.05% CO <sub>2</sub> in He	0.82	18.0	0.66	< .05
5	0.5% N <sub>2</sub> H <sub>4</sub> + 21% O <sub>2</sub> + 1% H <sub>2</sub> O + 0.05% CO <sub>2</sub> in He	1.96	21.6	1.45	< .05

### 3.2.2 UDMH-Atmospheric Reaction

Results of the unsymmetrical dimethylhydrazine atmospheric reactions as analyzed by gas chromatographic techniques are included in Tables V through IX. The UDMH decay was fitted logarithmically to a pseudo-first order reaction, and the correlation, slope, and rate constant of the plot of the logarithm of the UDMH concentration versus reaction time are also included in these figures. The mathematical development and determination of the pseudo-first order rate constant for UDMH decay are presented in Section 3.3.

The reaction of UDMH with dry CO<sub>2</sub>-free air is very slow under the conditions studied, exhibiting a reaction half-life of approximately 257 hours. When the UDMH-oxygen mixture is humidified with 1% H<sub>2</sub>O, the decay of UDMH is accelerated, with a reaction half-life of 24 hours and a concomitant increase in both FDH and NDMA reaction products. The addition of 0.05% carbon dioxide to both the dry and humidified oxygen mixture seems to inhibit the oxidation of UDMH to FDH. The half-life for these reactions increased to approximately 990 hours for the dry reaction and 46 hours for the humid reaction. This result was unexpected and not easily explained on mechanistic grounds; however, the hydrazine decay also appeared to be retarded by carbon dioxide addition in less than stoichiometric amounts.

Table V

Gas Chromatographic Analysis UDMH + He Reaction  
(Test No. 6)

Reaction Time (hr)	% UDMH	% FDH	% NDMA	% O <sub>2</sub>	% N <sub>2</sub>	% H <sub>2</sub> O
0	0.50	---	---	0.02	0.096	---
4.9	0.49	0.0013	< 0.0001	---	---	---
12.6	0.50	0.0008	< 0.0001	---	---	---
21.8	0.49	0.0008	< 0.0001	---	---	---
68.5	0.46	0.0011	< 0.0001	0.05	0.149	0.04

first order kinetic fit: Correlation .949  
 slope -.0005  
 k 0.001 hr<sup>-1</sup>  
 half-life 693 hr

Table VI

Gas Chromatographic Analysis UDMH + 21% Oxygen in Helium Reaction  
(Test No. 7)

Reaction Time (hr)	% UDMH	% FDH	% NDMA	% O <sub>2</sub>	% N <sub>2</sub>	% H <sub>2</sub> O
0	0.54	0.002	0.0001	22.59	0.152	0.022
5.2	0.48	0.010	0.0001	---	---	---
11.9	0.44	0.017	0.0002	---	---	---
21.3	0.45	0.030	0.0003	22.22	0.170	0.085
45.0	0.41	0.040	0.0004	21.10	0.509	0.116
69.2	0.43	0.102	0.0004	22.05	1.212	0.158

first order kinetic fit: Correlation 0.73  
 slope -.0012  
 k 0.0026 hr<sup>-1</sup>  
 half-life 257 hr

Table VII

Gas Chromatographic Analysis UDMH + 21% Oxygen + 1% Water Vapor  
in Helium Reaction  
(Test No. 8)

Reaction Time (hr)	% UDMH	% FDH	% NDMA	% O <sub>2</sub>	% N <sub>2</sub>	% H <sub>2</sub> O
0	0.49	0.003	0.0001	21.14	0.134	1.08
6.1	0.42	0.097	0.0006	---	---	---
11.8	0.31	0.066	0.0008	---	---	---
21.1	0.28	0.122	0.0009	21.31	0.218	1.38
44.9	0.13	0.128	0.0011	20.71	0.428	1.50
69.1	0.11	0.219	0.0012	22.05	1.193	1.35

first order kinetic fit: Correlation 0.992  
slope -.0126  
k 0.029 hr<sup>-1</sup>  
half-life 24 hr

Table VIII

Gas Chromatographic Analysis  
UDMH + 21% Oxygen + 0.05% Carbon Dioxide  
in Helium Reaction  
(Test No. 9)

Reaction Time (hr)	% UDMH	% FDH	% NDMA	% O <sub>2</sub>	% N <sub>2</sub>	% H <sub>2</sub> O
0	0.50	---	---	21.95	0.135	---
2.8	0.50	0.002	<0.0001	---	---	---
10.5	0.51	0.004	0.0002	---	---	---
19.7	0.49	0.005	0.0001	---	---	---
67.6	0.48	0.006	0.0001	23.35	0.158	0.11

first order kinetic fit: Correlation 0.83  
slope -.0003  
k 0.0007 hr<sup>-1</sup>  
half-life 990 hr

Table IX

Gas Chromatographic Analysis UDMH + 21% Oxygen + 1% Water Vapor  
 + 0.05% Carbon Dioxide in Helium Reaction  
 (Test No. 10)

Reaction Time (hr)	% UDMH	% FDH	% NDMA	% O <sub>2</sub>	% N <sub>2</sub>	% H <sub>2</sub> O
0	0.52	0.002	< 0.0001	21.7	0.21	1.19
5.5	0.43	0.022	0.0003	---	---	---
12.9	0.40	0.038	0.0004	---	---	---
21.4	0.39	0.103	0.0004	21.3	0.22	1.19
45.1	0.26	0.125	0.0006	20.4	0.24	1.14
69.3	0.17	0.172	0.0005	21.1	0.55	1.02

first order kinetic fit: Correlation 0.991  
 slope -.0066  
 k 0.0152 hr<sup>-1</sup>  
 half-life 46 hr

In the 0.5% UDMH reaction with 21% oxygen, 1% water vapor, and 0.05% carbon dioxide (Test No. 10) 0.49 moles of FDH were formed per mole of UDMH reacted. This result is in conflict with the stoichiometry expressed in Equation (3). In this case 0.67 moles of FDH were formed per mole UDMH reacted. These results indicate that the reaction between UDMH vapor and humid air may react in a different stoichiometry ratio than the dry air reaction. These results also indicate that 0.002 to 0.003 moles of NDMA are formed per mole of UDMH oxidized, under the conditions studied.

### 3.2.3 Nitrogen Dioxide Atmospheric Reactions

The  $\text{NO}_x$  concentrations of Test Nos. 11 through 14 as a function of reaction time at 35°C are recorded in Table X. The decrease in  $\text{NO}_2$  concentration as a function of time is pictured in Figure 7 and is most likely attributed to the reaction of nitrogen dioxide with the walls of gas sampling bag. It is also interesting to note that the nitric oxide concentration decreases in the presence of oxygen, forming nitrogen dioxide.

Figure 7. Nitrogen Dioxide Atmospheric Reactions

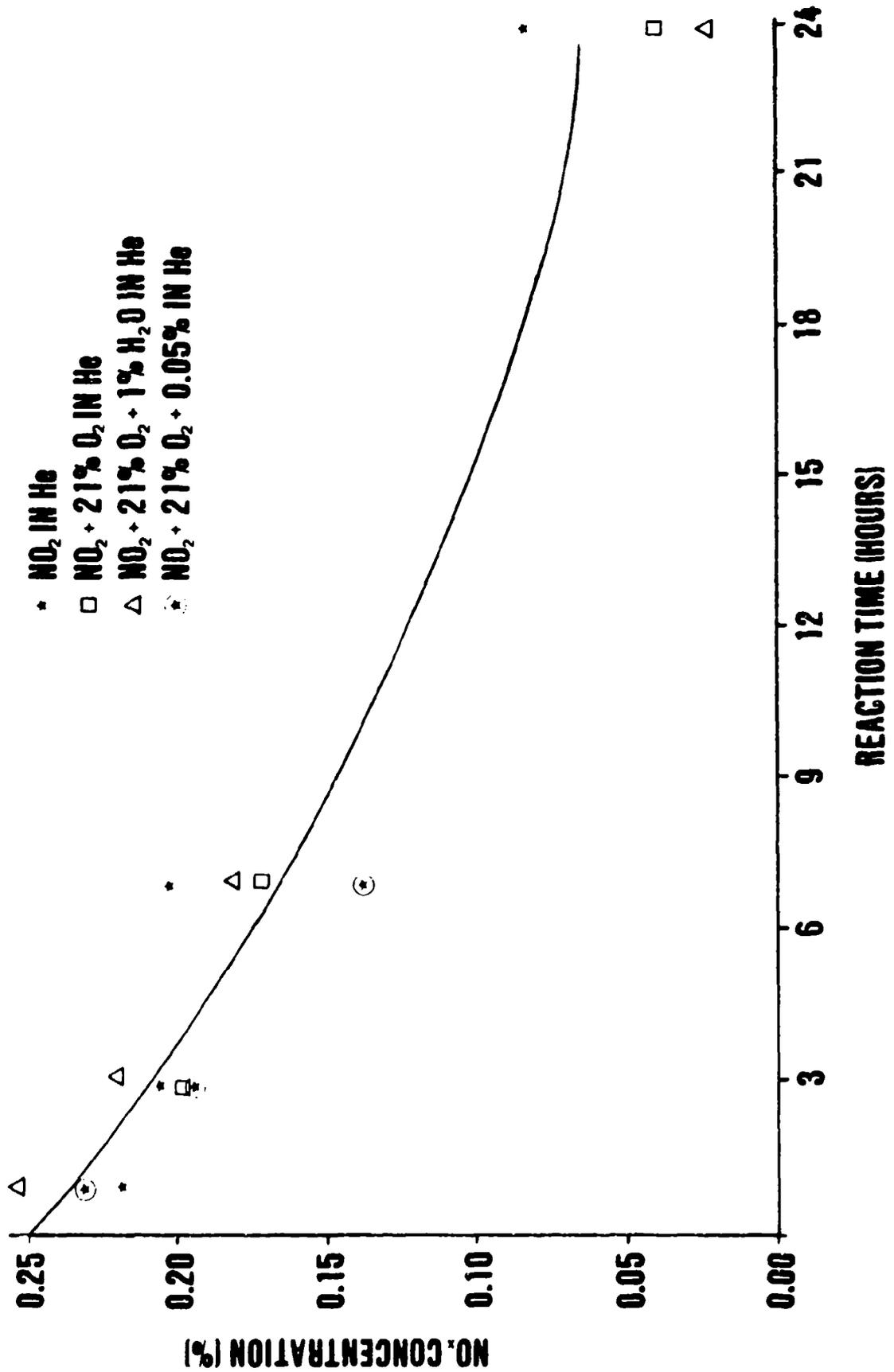


Table X Nitrogen Dioxide - Atmospheric Reaction Analysis

Test No.	Initial Gas Composition	Reaction Time (Hours)	NO <sub>x</sub> Percent	NO ppm
11	0.25% NO <sub>2</sub> in He	1	0.22	113
		3	0.20	118
		7	0.20	138
		24	0.08	100
12	0.25% NO <sub>2</sub> + 21% O <sub>2</sub> in He	1	0.22	107
		3	0.20	105
		7	0.17	42
		24	0.04	8
13	0.25% NO <sub>2</sub> + 21% O <sub>2</sub> + 1% H <sub>2</sub> O in He	1	0.25	115
		3	0.22	95
		7	0.18	45
		24	0.02	5
14	0.25% NO <sub>2</sub> + 21% O <sub>2</sub> + 0.05% CO <sub>2</sub> in He	1	0.23	107
		3	0.20	90
		7	0.14	29
		24	---	7

### 3.3 Rate Constant Evaluation

First order rate constants for the UDMH atmospheric reactions were calculated as follows: If the UDMH oxidation rate with excess oxygen (21% O<sub>2</sub> in air) is first order with respect to the UDMH concentrations, then

let  $[UDMH]_0$  = Initial propellant concentration at t=0.

$[UDMH]$  = Propellant concentration at later time t.

the rate of propellant decay with reaction time is directly proportional to the propellant concentration:

$$-d[UDMH]/dt = k[UDMH] \quad K = \text{1st order reaction rate constant}$$

$$-d[UDMH] = k[UDMH]dt$$

$$-\int_{[UDMH]_0}^{[UDMH]} \frac{d[UDMH]}{[UDMH]} = k \int_0^t dt$$

Upon Intergration:

$$-\ln([UDMH]/[UDMH]_0) = \ln([UDMH]_0/[UDMH]) = kt$$

$$\log([UDMH]_0/[UDMH]) = (k/2.303)t$$

$$\log[UDMH] = [-kt/2.303] + \log[UDMH]_0$$

Therefore a plot of the log of the UDMH concentration versus time will give a slope of  $-k/2.303$ .

The rate constant can also be determined by reaction half-life which is the time required for the reactant species (UDMH) to decrease to half its initial value.

For a first order reaction, the half-life ( $t_{1/2}$ ) is defined

$$\text{at } t = t_{1/2}; \quad c = 1/2[\text{UDMH}]_0$$

then:

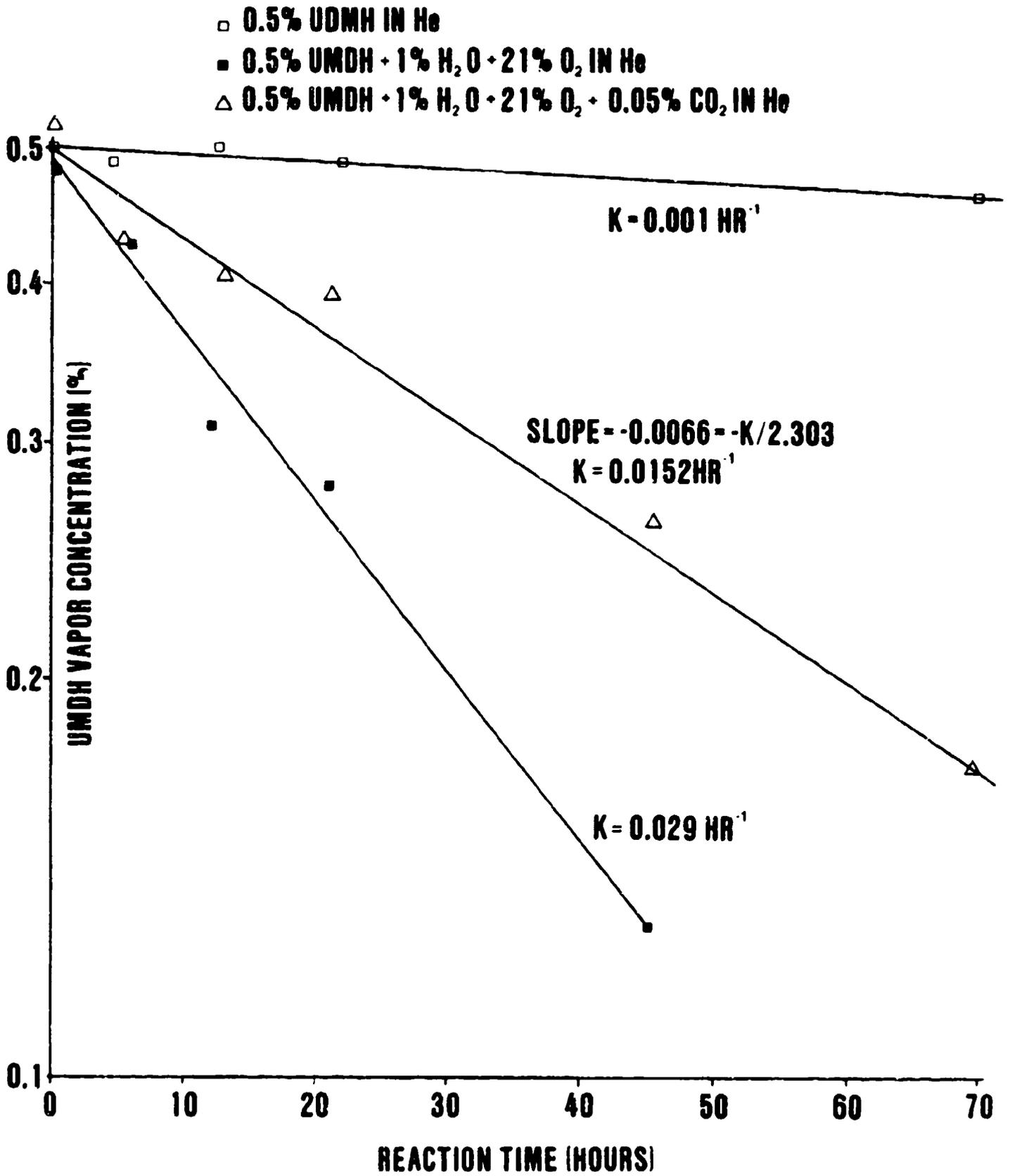
$$\log([\text{UDMH}]_0/0.5[\text{UDMH}]_0) = (k/2.303)t_{1/2}$$

$$t_{1/2} = 0.693/k$$

Figure 8 shows a plot of the log of UDMH concentration vs reaction time for three conditions (pure helium, 21% oxygen + 1% water vapor, and 21% oxygen + 1% water vapor + 0.05% carbon dioxide). It is interesting to note that the oxidation reaction is retarded in the presence of carbon dioxide. In this latter case, a rate constant of  $0.0152 \text{ hr}^{-1}$ , with a reaction half-life of 46 hours is reported (as compared to a half life of 24 hours in the absence of carbon dioxide).

Using the stoichiometry expressed in Equation (3), for every mole (or liter) of UDMH decreased during the oxidation reaction,  $2/3$  mole (0.67) of FDH is formed. In addition, 0.003 mole of NDMA is formed from every mole UDMH oxidized, under the conditions studied in our tests.

Figure 8. Atmospheric Reaction Rates of UDMH



#### 4.0 Condensation of Fireball Components

Since the combustion products in the fireball are cooled by the entrainment of ambient temperature air upon fireball liftoff from ground zero, there is a possibility that certain components will condense out of the cloud. The mathematical method used to determine whether condensation occurs compares the vapor pressure of the component as a pure liquid to its partial pressure in the fireball. If the partial pressure of the component ever meets or exceeds its vapor pressure as a pure liquid, condensation will occur. These condensed materials will coalesce and be deposited on the ground below the approximate point of condensation.

The calculations require the input of the following data:

- 1) Atmospheric pressure
- 2) Atmospheric temperature
- 3) Fireball temperature
- 4) Volume and molar composition of fireball
- 5) Heat capacities and Enthalpies of fireball components

With this data input, the calculations can be performed for either  $N_2O_4$  or  $N_2H_4$ . These chemicals were singled out because of their potential for high concentrations and their hazardous nature. Hydrazine was tested for condensation in an A-50 vapor mixture because it has a lower vapor pressure at ambient temperature than UDMH, and is therefore more likely to condense.

The first calculation necessary is to find the temperature of the fireball as a function of the amount of air entrained. (eq. 12)

$$T(^{\circ}K) = (H_{FB} + H_{air}N_{air}) / (C_{PF}N_F + C_{P_{air}}N_{air}) \quad (12)$$

where:

$T (^{\circ}\text{K})$  = Temperature of fireball in degrees Kelvin

$H_{\text{FB}}$  = Total heat content of original fireball in calories

$$(13) \quad H_{\text{air}} = 6.76T + 1/2 (0.606 \times 10^{-3})T^2 - 2044 + 1/3 (0.13 \times 10^{-6})T^3$$

where T is in degrees Kelvin

$$(14) \quad N_{\text{air}} = (PV/RT) \times 1000$$

$P$  = atmospheric pressure in atm  
 $V$  = volume of air entrained in  $\text{m}^3$   
 $R$  =  $0.0821 \text{ m}^3\text{atm/kg } ^{\circ}\text{K}$   
 $T$  = atmospheric temperature,  $^{\circ}\text{K}$

$$(15) \quad C_{\text{PF}} = \sum_{n=1}^i N_n \% C_{\text{pn}}$$

$C_{\text{PF}}$  = Average heat capacity of fireball  
 $\eta_n \%$  = mole percent of component n  
 $C_{\text{pn}}$  = heat capacity of component n

$$(16) \quad N_i = (PV_1/RT_1) \times 1000$$

$V_1$  = Volume of fireball at liftoff ( $\text{m}^3$ )  
 $T_1$  = Temperature of fireball at liftoff  $^{\circ}\text{K}$

$$(17) \quad C_{\text{p air}} = 6.76 + (0.606 \times 10^{-3})T + (0.13 \times 10^{-6})T^2 \text{ cal/}^{\circ}\text{K},$$

where T is temperature of air in degrees kelvin

After the temperature of the fireball as a function of the amount of air entrained is determined, both the vapor pressure of the pure liquid component, (a function of temperature), and the partial pressure of the component, (a function of concentration), can be calculated.

Vapor Pressure Equation for  $\text{N}_2\text{H}_4$ :

$$P_{v_1} (\text{mm Hg}) = \log^{-1}[-6.508 - (653.88/T (^{\circ}\text{K})) + 0.0479T (^{\circ}\text{K}) - 4.989 \times 10^{-5}T^2 (^{\circ}\text{K}^2)] \quad (18)$$

where  $P_{v_1}$  = vapor pressure of pure  $\text{N}_2\text{H}_4$  in mmHg

$T (^{\circ}\text{K})$  = Fireball temperature as per eq. 12

Vapor Pressure Equation for  $N_2O_4$ :

$$P_{V_2} = \log^{-1}\{9.824 - 2332/T(^{\circ}K) - 84567/T^2(^{\circ}K^2)\} \quad (19)$$

where  $P_{V_2}$  = Vapor pressure of pure  $N_2O_4$  in mmHg

$T(^{\circ}K)$  = Fireball temperature as per eq. 12

Partial pressure for either component:

$$P_i = [N_i/(N_i + N_{air})] \times P \quad (20)$$

where:  $P_i$  = partial pressure of component of interest

$N_i$  = total moles of component of interest

$N_{air}$  = total moles of air entrained

$P$  = atmospheric pressure (mm Hg)

The equations for vapor pressure are only valid for temperatures at or below the normal boiling point of the chemical species in question. This poses no problem because condensation cannot occur above the boiling point. The equation for partial pressure is valid for all situations.

With these equations, it can be determined whether or not condensation will occur. This is done by plotting both the vapor pressure and the partial pressure of the component of interest as a function of the number of moles of air entrained. If the two lines ever intersect, condensation will occur at that point. In the following section two example calculations, one for an excess oxidizer case and the other for an excess fuel case, are carried out.

Data: Fireball radius at ground zero = 35.35<sup>1</sup>m

composition <sup>1</sup> :	CO	= 0.020 mole %	N <sub>2</sub>	= 0.1387 mole %
	CO <sub>2</sub>	= 0.027 "	OH	= 0.022 "
	H <sub>2</sub>	= 0.025 "	O <sub>2</sub>	= 0.041 "
	H <sub>2</sub> O	= 0.144 "	NO <sub>2</sub>	= 0.565 "
	NO	= 0.005 "	H	= 0.012 "

Cloud radius at stabilization<sup>2</sup> 650 m

Total heat content (H<sub>FB</sub>) = 1.40 x 10<sup>10</sup> calories<sup>1</sup>

Initial temperature of fireball = 810<sup>0</sup>K<sup>1</sup>

Assume ambient conditions to be 1 atm & 20<sup>0</sup>C (298<sup>0</sup>K)

1. S. Prince. Atmospheric Dispersion of Hypergolic Liquid Rocket Fuels, Phase I: Source Characterization, Final Report 30 September 1982.
2. H.E. Cramer Co. Report on Cloud Growth and Dispersion Model for Hypergolic Fuels. Personal Communication, 8 April 1983.

Calculations:

$$\begin{aligned}\text{Volume of fireball at ground zero} &= 4/3\pi (35.35\text{m})^3 \\ V &= 185.05 \times 10^3\text{m}^3\end{aligned}$$

From eq. 16,  $N_F = [1\text{atm} \cdot 185.05 \times 10^3\text{m}^3 / (0.0821 \cdot 810^\circ\text{K})] \times 1000 = 2.78 \times 10^6$

From eq. 13,  $H_{\text{air}} = 6.76(298) + 1/2 (0.606 \times 10^{-3})(298)^2 + 1/3 (0.13 \times 10^{-6})(298)^3 - 2044 = -1.466 \text{ cal/g } \eta$

From eq. 15,  $C_{p_F} = 9.8 \text{ cal/g } \eta^\circ\text{K}$

From eq. 17,  $C_{p_{\text{air}}} = 6.76 + (0.606 \times 10^{-3})(298) + (0.13 \times 10^{-6})(298)^2 = 6.95 \text{ cal/g } \eta^\circ\text{K}$

With these values, the equation for vapor pressure as a function of the number of moles air entrained is derived using equations 12 and 19.

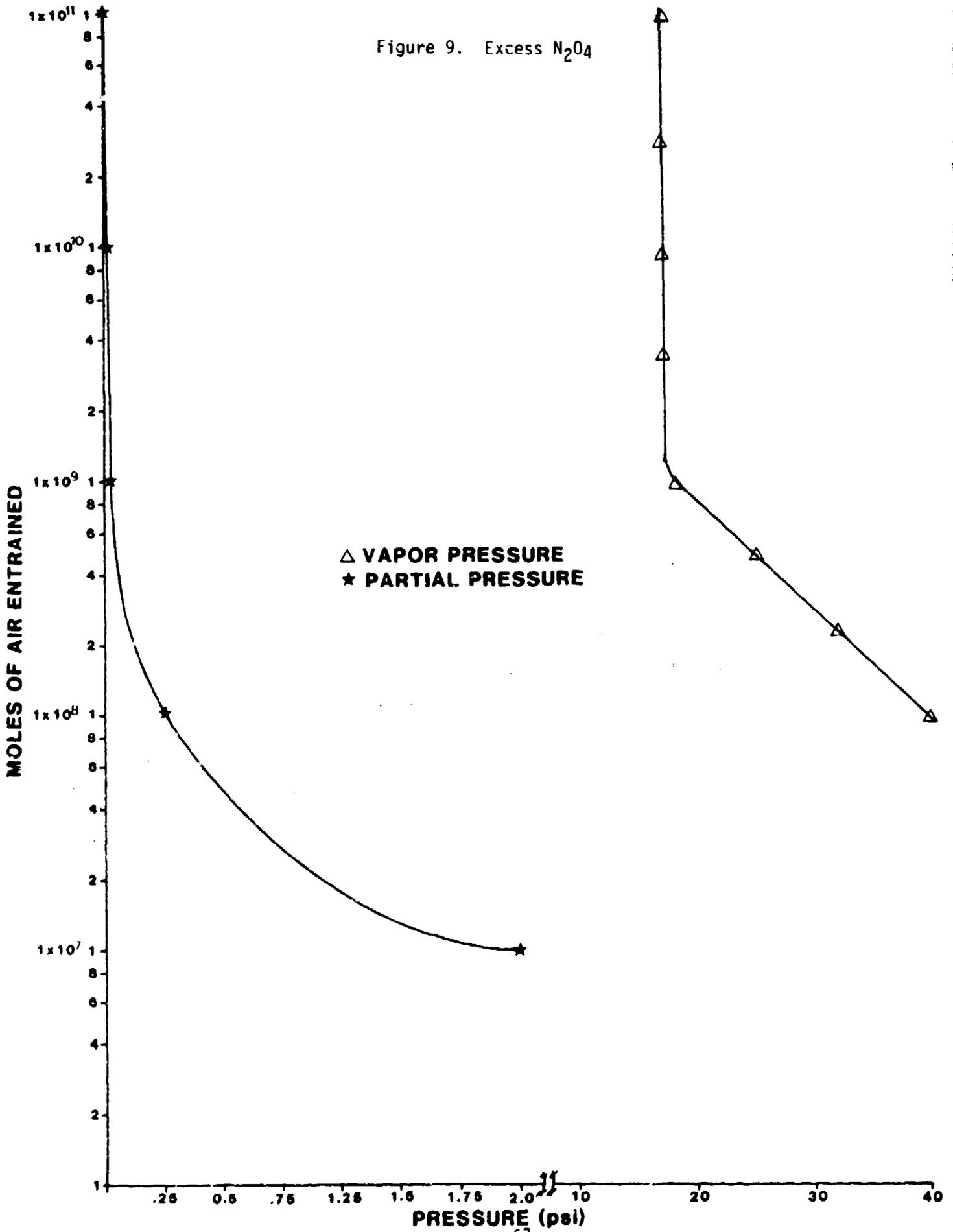
$$\begin{aligned}(21) \quad T(^{\circ}\text{K}) &= [1.4 \times 10^{10} + (-1.466 N_{\text{air}})] / [9.8 \times 2.78 \times 10^6 + 6.95 N_{\text{air}}] \\ P_{v_1} &= \log^{-1} \{ 9.824 - 2332/T(^{\circ}\text{K}) - 84567/T^2(^{\circ}\text{K}^2) \}\end{aligned}$$

The equation for partial pressure as a function of the number of moles air entrained, using equation 20, is:

$$(22) \quad P_{\text{NO}_2} = [(0.565 \times 2.78 \times 10^6) / ((0.565 \times 2.78 \times 10^6) + N_{\text{air}})] \times 760 \text{ (mm Hg)}$$

See Figure 9 for the plots of equations 21 and 22. From the graph, it is obvious that the two lines will never intersect. Note the scale change for the pressure values. There is a difference of approximately three orders of magnitude between the two pressures. For this particular situation there will be no  $N_2O_4$  condensing out of the cloud.

Figure 9. Excess  $N_2O_4$



Data: Fireball radius at ground zero = 34.4m<sup>1</sup>  
Composition<sup>(1)</sup>: CO = 0.037 mole % NO = 0.007 mole %  
CO<sub>2</sub> = 0.031 " N<sub>2</sub> = 0.193 "  
H<sub>2</sub> = 0.035 " OH = 0.032 "  
H = 0.017 " O<sub>2</sub> = 0.057 "  
H<sub>2</sub>O = 0.203 " UDMH = 0.134 "  
N<sub>2</sub>H<sub>4</sub> = 0.254 "  
H<sub>FB</sub> = 2.304 x 10<sup>10</sup>cal(1)  
Temp of Fireball = 1046°K(1)  
Assume ambient temp = 20°C & 1 atm pressure.  
Cloud radius at stabilization = 736 m

Calculations:

$$\begin{aligned} \text{Volume of Fireball at ground zero} &= 4/3 \pi (34.4\text{m})^3 \\ &= 1.705 \times 10^5 \text{m}^3 \end{aligned}$$

From eq 16  $N_F = [(1\text{atm} \times 1.705 \times 10^5 \text{m}^3) / (0.0821 \times 1046^\circ\text{K})] \times 1000 = 1.99 \times 10^6 \text{ moles}$

From eq 13  $H_{air} = -1.466 \text{ cal/gN}$

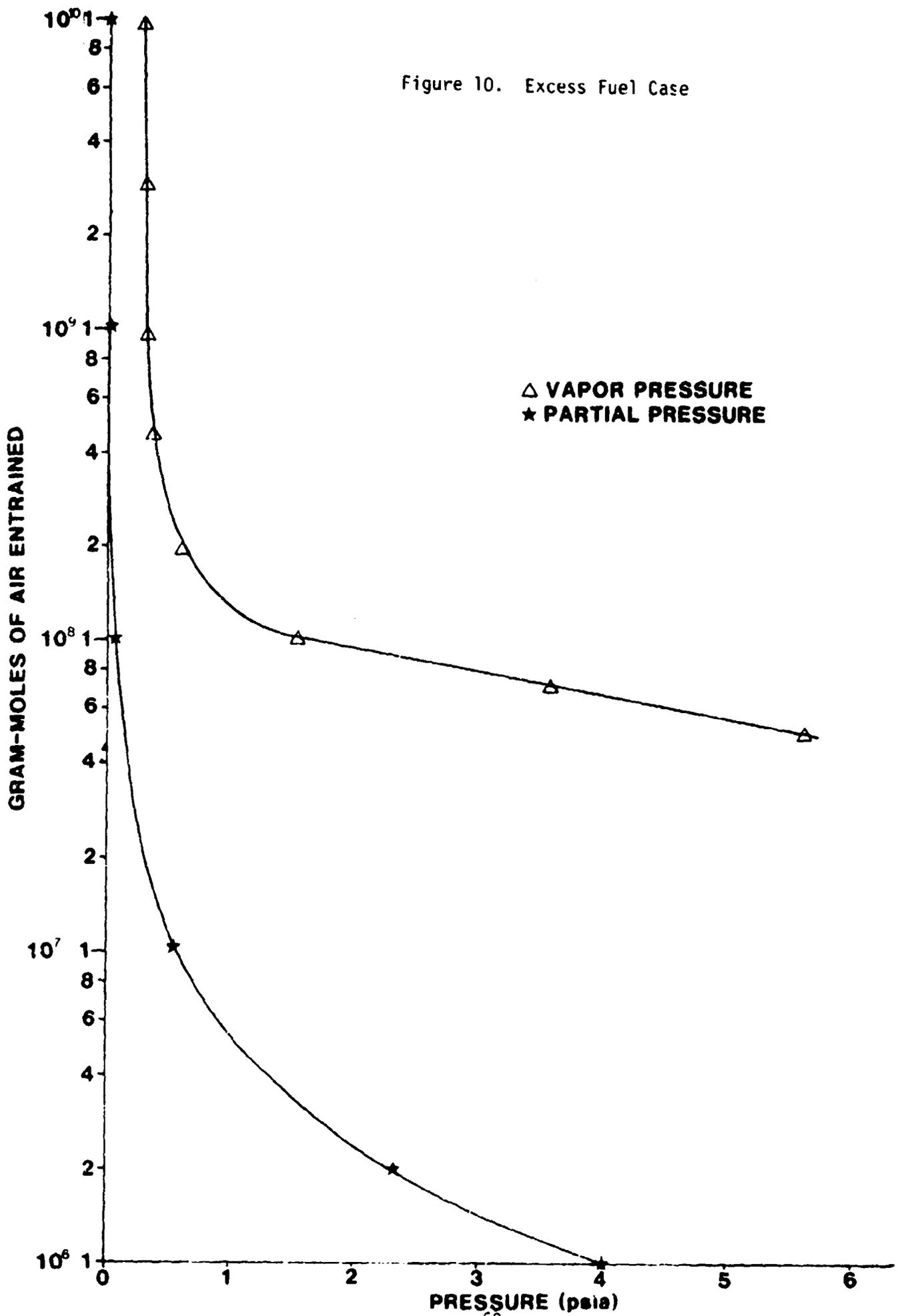
From eq 15  $C_{PF} = 7.97 \text{ cal/gN}^\circ\text{K}$

From eq 17  $C_{P_{air}} = 6.95 \text{ cal/gN}^\circ\text{K}$

Now, using equations 12, 18, 20

and  $T(^{\circ}\text{K}) = (2.304 \times 10^{10} - 1.466 \times N_{air}) / (7.97 \times 1.99 \times 10^6 + 6.95 \times N_{air})$

Figure 10. Excess Fuel Case



$$P_{N_2H_4} = \log^{-1}[-6.506 - 653.88/T(^{\circ}K) + 0.0479T(^{\circ}K) - 4.989 \times 10^{-5}T^2(^{\circ}K^2)] \quad (23)$$

$$P_{N_2H_4} = [(0.254 \times 1.49 \times 10^6)/(0.254 \times 1.49 \times 10^6 + N_{air})] \times 760 \text{ (mm Hg)} \quad (24)$$

See figure 10 for a graph of equations 23 and 24. Equation 23 is only valid for temperatures below 700°R, which is the boiling point of N<sub>2</sub>H<sub>4</sub>. From this graph it is evident that condensation will not occur in this case either. There is about three orders of magnitude difference between the two pressures.

## 5.0 CONCLUSIONS

Atmospheric reaction rate data for reactive fireball species to be incorporated into a computer atmospheric dispersion model are presented in Table XI. The table lists the conditions in which the rate constants and reaction half-lives apply.

Table XI Atmospheric Reaction Rate Constants  
for Fireball Dispersion Modeling

Fireball Species	Concentration in Atmosphere	Meteorological Condition	Rate Constant	Half-Life	Major Reaction Products	% Yield
Hydrazine	0-1 ppm	dry or humid air	0.2 ppm-1 min-1	2 hr*	H <sub>2</sub> O <sub>2</sub>	NA
Hydrazine	Above 1 ppm	dry air	0.064 hr-1	10.8 hr	N <sub>2</sub> , H <sub>2</sub> O	100
Hydrazine	Above 1 ppm	humid air	0.141 hr-1	4.9 hr	N <sub>2</sub> , H <sub>2</sub> O	100
UDMH	0-1 ppm	dry or humid air	0.15 ppm-1 min-1	0.2 hr*	NDMA	60
UDMH	Above 1 ppm	dry air	0.0007 hr-1	990 hr	FDH**	67
UDMH	Above 1 ppm	humid air	0.015 hr-1	46 hr	FDH**	67
NO <sub>2</sub>	10 ppm	humid air	5.5x10 <sup>4</sup> mole-2 sec-1	5 hr	HNO <sub>3</sub> (g)	100
NO <sub>2</sub>	50 ppm	humid air	5.5x10 <sup>4</sup> mole-2 sec-1	0.2 hr	HNO <sub>3</sub> (g)	100
NO <sub>2</sub>	Above 50 ppm	humid air	5.5x10 <sup>4</sup> mole-2 sec-1	<0.2 hr	HNO <sub>3</sub> (l)	100
NO <sub>2</sub>	All Conc.	dry air	NO REACTION			

\* Clean, Unpolluted Atmosphere

\*\* NDMA Formed in 0.2% Yield (.002 Moles NDMA Found Per 1 Mole UDMH Reacted)

NO = Not Available

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APPENDIX B

USER'S MANUAL FOR THE HYPERGOLIC ACCIDENT RELEASE  
MODEL (HARM) COMPUTER PROGRAM

THE REPORT CONTAINED WITHIN THIS APPENDIX  
IS REPRODUCED AS ORIGINALLY PREPARED AND  
SUBMITTED BY THE AUTHORS.

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## SECTION 1 INTRODUCTION

### 1.1 BACKGROUND

The U. S. Air Force, and particularly the Air Force Engineering and Services Center at Tyndall Air Force Base, has pursued the analysis of existing dispersion models and the development of new approaches for modeling dispersion in support of the Titan II safety engineering program. The Hypergolic Accidental Release Model (HARM) is the result of an effort to develop a computer program incorporating source characterization, cloud-rise and dispersion model algorithms appropriate for describing the transport and dispersion downwind from a hypergolic reaction involving the fuel and oxidizer propellants of the Titan II missile. The hypergolic reaction results in the formation of a thermally buoyant cloud which rises vertically to a height related to the amount of heat generated by the reaction, which is a function of the amount of propellant components involved in the accidental release. The existing model (Ocean Breeze/Dry Gulch) used to assess propellant hazards (U. S. Air Force, 1983) is not suited for modeling dispersion downwind from elevated volume sources. The HARM computer program is based on source characterization algorithms for hypergolic reactions developed by Martin Marietta Aerospace (Prince, 1982, 1983), buoyant cloud models developed by Briggs (1970) and dispersion models for rocket launches (Bjorklund, et al., 1982) developed by the H. E. Cramer Company.

### 1.2 PURPOSE

The technical objective of the work described in this report is to provide a computer program that predicts ground-level concentrations of toxic materials resulting from a catastrophic reaction of hypergolic propellants. The purpose of this report is to provide documentation of the following:

- A description of the algorithms used to define the source characteristics of selected catastrophic hypergolic reactions involving Titan II propellants
- A mathematical description of the cloud-rise, dispersion models and other mathematical formulas used in the HARM code
- User's instructions for the HARM computer program

### 1.3 ORGANIZATION OF THE MANUAL

The main body of the manual contains five sections. Section 2 contains a brief overview of the major components of the HARM code, the accident scenarios the code is designed to accommodate, and the meteorological and source model input parameters required to operate the program. The algorithms used in the program to characterize the source, to describe the reaction products and decay/production rates, and to predict the cloud-rise of the thermally buoyant cloud are described in Section 3. Section 4 contains a mathematical description of the atmospheric dispersion models implemented by the computer code. Section 5 provides user instructions for the HARM program.

Appendix A of this manual contains example executions of the HARM program. A program listing and magnetic tape containing the program have been provided to Martin Marietta Aerospace under separate cover.

SECTION 2  
OVERVIEW OF THE HARM COMPUTER PROGRAM

The catastrophic hypergolic reaction of Titan II rocket propellants results in the nearly-instantaneous formation of a relatively large cloud of hot, buoyant reaction products near ground level which subsequently rises and entrains ambient air until the temperature and density of the cloud reach an approximate equilibrium with ambient conditions. Depending on the amount of fuel (A-50) and oxidizer (NTO) involved in an accident and the atmospheric stability, the stabilization height, defined as the point the cloud ceases buoyant rise, can vary from 10's of meters to heights exceeding 1 km. The cloud may contain toxic components of unreacted propellants (hydrazine, unsymmetrical dimethylhydrazine, or UDMH, and nitrogen tetroxide, or NTO) in addition to the products of the reaction. Toxic products of the reaction include dimethylnitrosamine (NDMA), methyl amine, formaldehyde, hydrogen cyanide, ammonia and formaldehyde dimethylhydrazone (FDH). The HARM computer program is designed to calculate peak concentrations and dosages, peak deposition due to precipitation scavenging and isopleths of dosage, concentration and deposition due to precipitation scavenging downwind from catastrophic reactions. The program calculations are automated for considering the five major toxic components of hydrazine, UDMH, NTO, NDMA and FDH. The HARM program is designed to assist the Missile Potential Hazard Team (MPHT) in:

- Planning hazard-safety programs for catastrophic hypergolic accidents involving Titan II propellants
- Real-time support of hazard-safety operations involving Titan II propellants
- Post-accident environmental analyses of hypergolic accidents involving Titan II propellants

While the program is designed for considering hypergolic accidents involving Titan II propellants, it can easily be modified to consider other types of hypergolic reactions.

## 2.1 COMPONENTS OF THE HARM COMPUTER PROGRAM

Figure 2-1 is a schematic diagram showing the major components of the HARM computer program. Requisite meteorological inputs to the computer program are obtained from the vertical profiles of wind direction, wind speed, air temperature, atmospheric pressure and dew point or relative humidity between the earth's surface and 3000 m. This information is obtained primarily from rawinsonde measurements made at selected upper-air stations by the National Oceanic and Atmospheric Administration (NOAA) and by meteorological stations at selected USAF air bases. Rawinsonde measurements are routinely made twice daily at 0000 Greenwich Mean Time (GMT) and 1200 GMT at these stations. The HARM program can be configured to accept the rawinsonde data from tape and disc files or from TTY input devices such as a modem. As shown in Figure 2-1, the rawinsonde data can be manually edited to provide for any changes in the vertical profiles that weather forecasters assigned to the MHPT consider to have occurred between the time the rawinsonde measurements were made and the time of the accident. Similarly, meteorological observations from the accident site can manually be entered to reflect the observed near ground-level conditions at the scene.

The HARM program is controlled by operator input and internal management routines based on the operator's response to plain-language queries displayed on a CRT terminal. In Figure 2-1, this complex interactive function is simply designated by the box labeled CRT Program Control. Provision has been made in the computer program for selection of calculations for the following 5 major accident scenarios:

- Above-ground slow leak

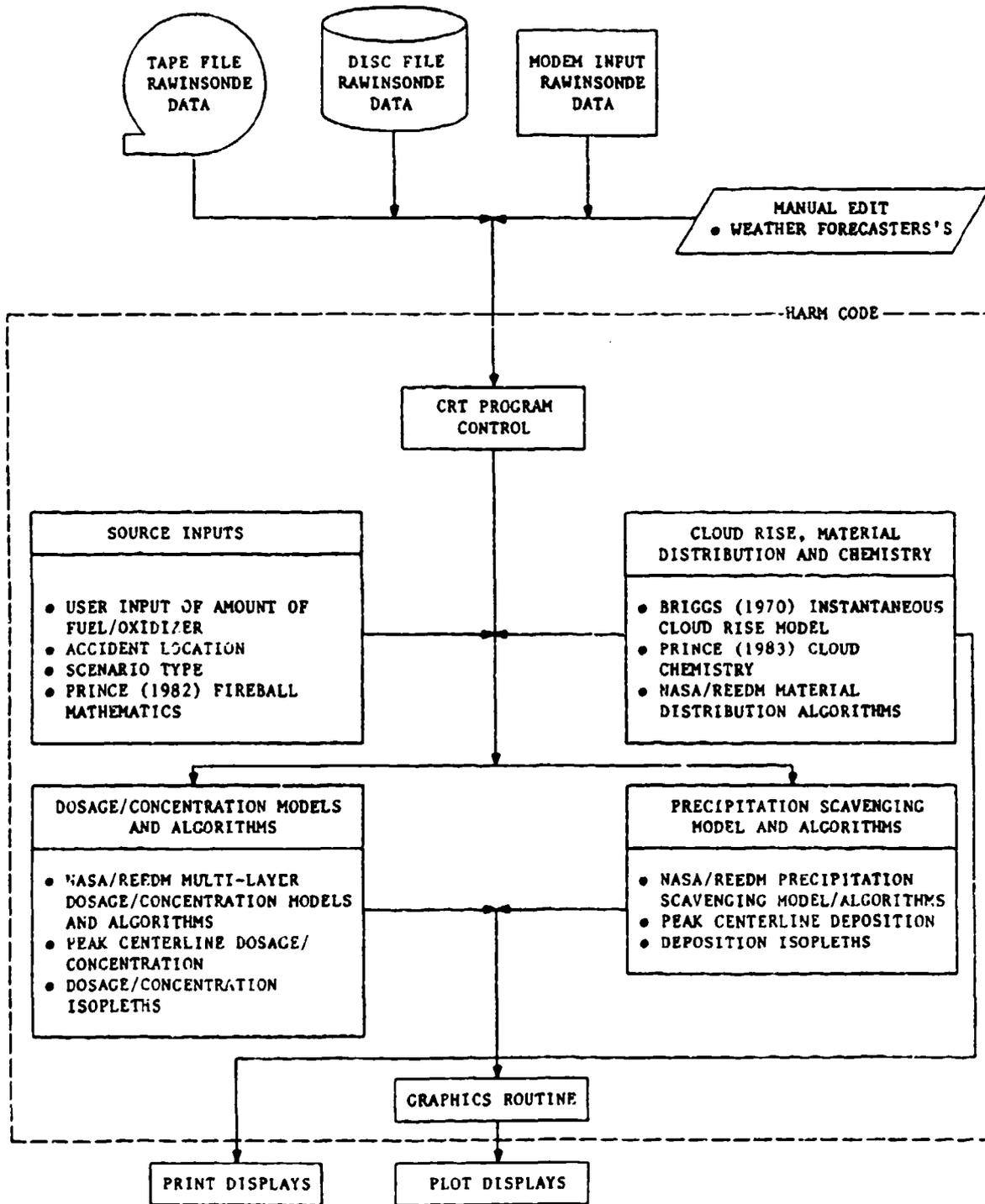


FIGURE 2-1. Schematic diagram illustrating major components of the HARM Computer Program.

- Above-ground major spill (nearly-instantaneous detonation)
- In-silo accident with the silo door closed and either a slow leak ultimately resulting in a hypergolic reaction or an instantaneous hypergolic reaction
- In-silo accident with the silo door open and either a slow leak ultimately resulting in a hypergolic reaction or an instantaneous hypergolic reaction
- Stage ejection with a subsequent explosion at a user specified height

The operator is also asked to supply the amount of fuel (A-50) and oxidizer (NTO) involved in the accident and the specific coordinates of the accident location. After the operator has responded to these queries, the program automatically selects a proper set of source inputs to be used in the calculation of the dimensions of the fireball created by the hypergolic reaction and the heat of the reaction for use in the cloud-rise calculation. The cloud-rise model then calculates the spatial position and dimensions of the cloud as a function of time and distance from the accident until the stabilization height is reached. The vertical distribution of material in the various layers of the atmosphere, where the layer boundaries are given by the heights at which rawinsonde measurements are available, is also automatically calculated. The concentration of material in the cloud is used in an algorithm based on the work of Prince (1983) to determine the half-lives and decay/production constants to be used in the subsequent dispersion calculations. At this point, the rawinsonde meteorological data and the results of the cloud-rise, cloud dimension and material distribution algorithms are output to a printer. The operator also has the option to output a plot display of the vertical profiles of wind direction, wind speed, temperature and virtual potential temperature as well as a simple projection of the stabilized cloud. The operator and/or weather forecaster then have the option of modifying the default values selected and calculated

by the program to represent the major meteorological layer structure parameters (the height of the base and top of an elevated inversion layer, for example) and the turbulence parameters that will be used in the dispersion calculations. After the final selection of model input parameters has been made by the operator, the program performs either the selected dosage/concentration or precipitation scavenging (deposition) calculations using the multi-layer dispersion models described in Section 4. When these calculations are complete, the results are printed and, at the option of the operator, plotted. If the dosage/concentration option was selected, the print output includes peak concentration at 1-km intervals downwind from site of the accident, and the total dosage and time-mean concentration for the period of interest at these points. The operator can request plots of these results for each pollutant versus distance and/or plots of the isopleths of concentration, dosage, and time-mean concentration on maps or map overlays. If the option to calculate deposition due to precipitation scavenging is selected, peak centerline maximum possible or time-dependent peak centerline deposition is printed and, at the user's option, plotted. The user can also request isopleth plots of deposition. Example of the print and plot output produced by the HARM program are included with the example problems described in Appendix A.

Although not shown in Figure 2-1, there are three major modes that the program user can choose for making calculations using the HARM code (operational, research and production). The operational mode is designed for assisting the Missile Potential Hazard Team in evaluating hazards and automatically selects many of the required input parameters, although the program user is provided an opportunity to modify the selected default values. When the research mode is selected, more information is usually input by the operator. For example, the operator can specify values of the turbulence parameters at each height where rawinsonde data is available rather than using the default turbulence profiles. The production mode of the HARM code can be used to process multiple rawinsonde soundings which are read from a tape or disc file. While the production mode can be run interactively from a CRT terminal, the primary purpose of the production

mode is to facilitate batch processing of multiple cases without operator attention.

It should be noted that the HARM computer program is intended for use in predicting the environmental impact resulting from the nearly instantaneous hypergolic reaction. In some accidents there may be residue material in the silo or on the open ground not consumed in the reaction. Material from these ground-level sources may be emitted continuously over a period of hours. The HARM computer program does not consider the environmental impact of these sources.

## 2.2 ACCIDENT SCENARIOS AND SOURCE PARAMETERS

The five major scenarios of hypergolic accidents that the HARM computer program can process are listed in Section 2.1 above. The major source parameter affecting the outcome of the calculations is the ratio of fuel to oxidizer involved in the accident. The algorithm describing the resulting products from the user input of the total weight of fuel and oxidizer involved in the accident is described in Section 3.1. In those accidents that involve stoichiometric quantities of fuel and oxidizer (no excess fuel or oxidizer), there is of course no excess fuel or oxidizer available for downwind transport in the chemical cloud produced by the accident. In those accidents where the hypergolic reaction is nearly-instantaneous (regardless of whether the accident is an above-ground major spill, in-silo accident with the silo-door closed or open, or stage ejection), there is never any excess hydrazine available for downwind transport. Finally, all the accidents are assumed to occur at ambient atmospheric pressure except those that occur in the silo with the door closed, where the pressure is assumed to be 12.0 atmospheres. Based on these assumptions, the HARM model computer program treats accidents involving an above-ground slow leak and an in-silo slow leak with the silo door open in the same manner, since both are assumed to occur at a pressure of 1 atmosphere.

Similarly, the program treats above ground major spills and the instantaneous hypergolic reaction occurring in the silo with the silo door open in the same manner.

The stage ejection accident scenario used in the computer program assumes that an instantaneous explosion occurs in the silo and an explosion of the second stage of the Titan II occurs at a user defined height. The user is also required to input the total amount of fuel and oxidizer involved in the accident. The program assumes that approximately 80 percent of the total propellant weight is involved in the silo explosion and that approximately 20 percent is involved in the explosion at the user defined height. In this scenario, the user is also asked if the silo door is open or closed. If the door is closed, the in-silo reaction is assumed to occur at a pressure of 12.6 atmospheres and the reaction aloft at a pressure of 1 atmosphere. Both reactions occur at a pressure of 1 atmosphere if the silo door is open. The cloud-rise is independently calculated for each source. In the case of the in-silo explosion, cloud-rise begins from a point at ground-level while the cloud-rise from the in-air detonation begins at the user designated detonation height. The amount of material in each atmospheric layer from both sources is calculated using an algorithm defined in Section 3 and then summed during the dispersion calculations.

### 2.3 METEOROLOGICAL INPUT PARAMETER REQUIREMENTS

As noted above, the primary meteorological input to the HARM computer program is in the form of rawinsonde observations. Each level of information (standard, mandatory and significant levels) in the rawinsonde data stream (nth observation level in the model descriptions in Section 3 and 4) is used to obtain wind and temperature profiles. The HARM code is currently designed to perform dispersion calculations in two major, meteorologically-defined, layers. The base of the lower layer ( $L=1$ ) is assumed to be at the earth's surface and the top of the layer is assumed to be located

at the base of an elevated inversion (top of the surface mixing layer). The boundaries of the upper layer (L=2) are set by the operator. If the concentration/dosage of the material assumed to be trapped in the elevated inversion is of interest, for example, the operator would set the lower boundary of the second layer equal to the top of the first layer and the top of the second layer to the height of the top of the elevated inversion. The boundaries of the two major layers must coincide with a height or level reported in the rawinsonde message. If the user designates a boundary of a major layer other than a Kth height, the program automatically selects the Kth height closest the user input value.

The selection of the boundaries of the two major layers is critical to the outcome of the concentration and dosage dispersion calculations. The gaseous products in the cloud produced by the hypergolic accident are assumed to be reflected towards the earth's surface at the tops of the major boundaries and upward at the bases of the major boundaries (including the earth's surface) in the concentration and dosage calculations. The boundaries of these two major layers are also used in the specification of the vertical profiles of the turbulence parameters used in the concentration, dosage and deposition calculations as indicated in Section 3. In the absence of user input of the layer boundaries, the program automatically sets the top of the lower layer equal to the Kth rawinsonde observation level closest to twice the cloud stabilization height. Also, the height of the base of the upper layer is defaulted to equal the top of the lower layer and the program sets the top of the upper layer to the Kth observation level closest to 3000 m. Rawinsonde measurements at heights greater than 3000 m are not used by the HARM code. This default depth of the surface mixing layer is used because the use of a Kth observation level between the cloud stabilization height and twice the stabilization height to represent the depth of the mixing layer tends to maximize the calculated ground-level vapor concentrations.

In general, program users should select the height of the base of an elevated inversion to represent the top of the lower (L=1) layer.

Because the top of the lower layer is defined in the program as an upper bound to turbulent mixing, the user should select a height above which the temperature either increases or remains constant for at least 50 to 100 m. Because the primary purpose of the HARM code is to assist in estimating ground-level environmental effects produced by hypergolic accidents, the user should generally ignore surface-based inversions or elevated inversions with tops less a few hundred meters above the surface in selecting the top of the lowest layer.

#### 2.4 BASIS OF THE HARM COMPUTER PROGRAM

The computer program described in this manual incorporates many of the dispersion model algorithms and concepts employed in the REEDM (Rocket Exhaust Effluent Diffusion Model) Computer Program developed for the National Aeronautics and Space Administration (NASA) for assessing the environmental impact of exhaust products from the normal and abnormal launches of launch vehicles (Bjorklund, et al., 1982). The REEDM model is the product of over a decade of development in preparation for real-time support of Space Shuttle launches and is currently used to support launches of the Space Shuttle at Kennedy Space Center. The task of predicting the dispersion downwind from a hypergolic accident is in many respects similar to the task of predicting dispersion of the ground cloud produced by rocket launches because both scenarios result in the buoyant rise and formation of an elevated source with relatively large horizontal and vertical dimensions. As noted in Section 1.1, models developed for predicting the downwind dispersion from ground-level continuous point sources are not generally applicable because of the large initial dimensions of the cloud, because the source is formed nearly instantaneously, and because the dispersion takes place in a relatively deep layer of the atmosphere. These factors were considered in the development of the REEDM computer program and have been incorporated in the HARM models. We also note that NASA, and particularly Langley Research Center, has conducted sampling measurement programs using ground-based and aircraft sampling equipment in conjunction

with normal launches of Titan and Space Shuttle launches over the past decade. These measurements (Gregory, et al., 1974a, 1974b; 1976: Woods, et al., 1979; Wornom, et al., 1979; Sebacher, et al., 1980 and others) have been used to verify and improve the performance of the REEDM computer program predictions of dosage and concentration. In general the predicted concentrations have been within a factor of two of the measured concentrations and the models tend to overpredict ground-level concentrations, yielding conservative estimates of the ground-level environmental impact. Thus, the decision was made to adapt many of the concepts incorporated in the NASA REEDM computer Program for use in the HARM Computer Program for the following reasons:

- REEDM has proven successful in predicting concentrations downwind from the release of large thermally buoyant clouds
- REEDM contains the requisite algorithms for calculating cloud-rise, material distributions and other source characteristics of large thermally buoyant clouds
- REEDM contains the requisite dispersion algorithms for treating the downwind transport and dispersion of clouds with initially large horizontal and vertical dimensions
- REEDM uses available meteorological input information (rawinsonde data) describing meteorological conditions in and above the surface mixing layer
- REEDM has moderate computer memory and run-time requirements suited for real-time support of hazard-safety operations.

These concepts and the algorithms employed in the HARM Computer Program to describe the source characteristics of hypergolic reactions are described in detail in Section 3 and 4 below.

## SECTION 3

### HARM SOURCE, CLOUD RISE AND METEOROLOGICAL ALGORITHMS

#### 3.1 SOURCE CHARACTERISTIC ALGORITHMS

As mentioned above, the algorithms describing the source characteristics included in the HARM model are based on the work of Prince (1982, 1983). The following discussion is principally based on these reports. The mixing of the hypergolic rocket propellant A-50 and NTO during an accidental spill or missile tank rupture converts chemical energy into thermal energy. The thermal energy is used to heat the hypergolic combustion products, vaporize excess unreacted propellant and to heat the environment in the vicinity of the accident. The thermal energy of the fireball formed by the hypergolic reaction and the size of the fireball are required in the HARM model for calculating the stabilization height of the cloud of reaction products and the chemical composition of the cloud at the stabilization height.

The thermochemical analysis performed by Martin Marietta Aerospace (Prince, 1982) proceeded as follows:

- Fireball combustion products were identified and adiabatic flame temperatures calculated using theoretical thermodynamic combustion properties of the propellant and the gaseous reaction products for stoichiometric conditions
- In cases where the oxidizer to fuel ratio was non-stoichiometric, the chemical reaction was treated as a non-equilibrium condition where the thermal energy of the fireball was reduced by that energy required to heat and vaporize the excess propellant

- The thermal energy of the fireball was further reduced by accounting for radiative heat transfer to the surrounding environment

A description of the algorithms used in the HARM program for calculating the chemical composition of the material in the fireball, the thermal energy available for rise of the fireball and the dimensions of the fireball are given below.

### 3.1.1 Chemical Composition and Fireball Temperatures

Determination of the fireball combustion products and the calculation of fireball adiabatic temperatures resulting from stoichiometric reactions of A-50 and NTO was accomplished by Martin Marietta Aerospace using a computer program for the calculation of complex chemical equilibrium composition (NASA SP-273). The program reiteratively solves equations that minimize the Gibbs free energy of the chemical reaction products and maintains a mass balance between the chemical reactants (hypergolic propellants) and chemical products (combustion products, oxidation products and unreacted propellants). The output for stoichiometric combinations of A-50 and NTO reacting at 1 and 12.6 atmospheres is reproduced in Table 3-1.

Flame temperatures of the fireball provided to the H. E. Cramer Company were calculated under an adiabatic assumption where conductive, convective and radiative heat losses to the environment were not considered. Thus the heat of reaction caused by combining A-50 with NTO at 25°C was used to heat the reaction products in the fireball from 25°C to the temperature at time t, or T(t). The reaction equation is:

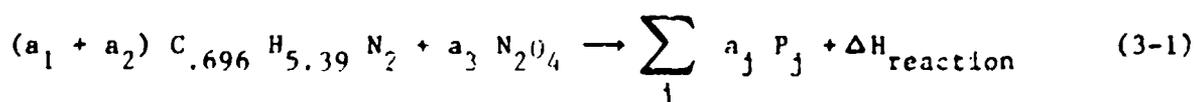


TABLE 3-1

THERMODYNAMIC PROPERTIES AND MOLE FRACTIONS FOR STOICHIOMETRIC MIXING  
OF A-50 AND NTO (AFTER PRINCE, 1982)

Property	Pressure (atmospheres)	
	1	12.6
Molecular Weight	22.448	22.993
Heat Capacity $c'_p$ (cal g <sup>-1</sup> °K <sup>-1</sup> )	2.0417	1.4782
Mole Fraction:		
CO	0.06301	0.05825
CO <sub>2</sub>	0.05210	0.05965
H	0.02952	0.01668
HNO	--	0.00001
HO <sub>2</sub>	0.00001	0.00003
H <sub>2</sub>	0.05926	0.04868
H <sub>2</sub> O	0.34523	0.37526
H <sub>2</sub> O <sub>2</sub>	--	0.00001
N	--	0.00001
NO	0.01260	0.01551
NO <sub>2</sub>	--	0.00001
N <sub>2</sub>	0.32797	0.33462
O	0.01682	0.01028
OH	0.05366	0.04920
O <sub>2</sub>	0.03980	0.03182

where

$a_1$  = moles of reacted liquid hydrazine

$a_2$  = moles of reacted liquid UDMH

$a_3$  = moles of reacted liquid  $N_2O_4$

$a_j$  = moles of the product  $P_j$

$\Delta H_{\text{reaction}}$  = heat evolving from the chemical reaction

=  $1.54 \times 10^5$  cal mole<sup>-1</sup> of reacting A-50

For an adiabatic process

$$\Delta H_f(\text{reactants}) = \Delta H_f(\text{products}) + \int_{298^\circ}^{T(t)} c'_p dT'(\text{products}) \quad (3-2)$$

where

$c'_p$  = low pressure heat capacity of the products (cal mole<sup>-1</sup> °K<sup>-1</sup>)

$$\equiv A + BT(t) + C(T(t))^2 + D(T(t))^3$$

A, B, C, D = coefficients defined below

$T(t)$  = temperature in °K at time  $t$

Integrating Equation (3-2) yields the expression

$$\begin{aligned} \Delta H_f(\text{reactants}) = & \Delta H_f(\text{products}) + AT(t) + (B/2)(T(t))^2 \\ & + (C/3)(T(t))^3 + (D/4)(T(t))^4 - E \end{aligned} \quad (3-3)$$

where

$$E = A(298) + (B/2)(298)^2 + (C/3)(298)^3 + (D/4)(298)^4 \quad (3-4)$$

Values of the coefficients A, B, C, D and E required to solve Equation (3-3) are given in Table 3-2 and are based on the values recommended by Prince (1982) in his Table IV. The 4th degree polynomial in T{t} is solved for T{t} using Newton's method. The value of T{t} of the fireball at the time of lift-off from the ground T{t=t<sub>B</sub>} is used in calculating the fireball size and heat content of the cloud at liftoff from the ground as outlined below.

### 3.1.2 Fireball Size and Heat Content

Prince (1982) based the calculations of the fireball size and heat content of the cloud at lift-off from the ground on a mathematical model, developed by Sandia Laboratories, that expresses the reaction time t<sub>B</sub> in seconds for the mass of hypergolic propellant W<sub>b</sub> to mix and react to completion as

$$t_B = 0.6845 W_b^{1/6} \quad (3-5)$$

where the units of W<sub>b</sub> are in kilograms. The radius of the fireball varies as a function of the fireball temperature T{t} according to the expression

$$r(t) = \left( \frac{3 W_b R' T(t)}{4 \pi P \bar{M}_w} \right)^{1/3} \quad (3-6)$$

Coefficient Equation (3-1)	Species*	$\Delta H_f$ (cal/mole)	Temp Range ( $^{\circ}$ K)	Coefficients in Equation (3-3)				
				A [cal/(mole-K)]	$B \cdot 10^2$ [cal/(mole-K <sup>2</sup> )]	$C \cdot 10^5$ [cal/(mole-K <sup>3</sup> )]	$D \cdot 10^9$ [cal/(mole-K <sup>4</sup> )]	$E \cdot 10^{-3}$ (cal/mole)
$a_1$	$N_2H_4(l)$	12054	--	--	--	--	--	--
$a_2$	UDMH(l)	12339	--	--	--	--	--	--
$a_3$	$N_2O_4(l)$	-4676	--	--	--	--	--	--
$a_4$	CO	-26416	273-3700	6.480	0.1566	-0.0239	0	1.998
$a_5$	CO <sub>2</sub>	-94052	273-3700	6.393	1.0100	-0.3405	0	2.324
$a_6$	H	52094	1000-5000	4.968	0	0	0	1.480
$a_7, a_{17}$	H <sub>2</sub>	0	273-3700	6.424	0.1039	-0.0078	0	1.960
$a_8$	H <sub>2</sub> O	-57798	273-3700	6.970	0.3464	-0.0484	0	2.227
$a_9$	NO	21600	273-3700	6.462	0.2358	-0.0770	0.0873	2.024
$a_{10}, a_{18}$	N <sub>2</sub>	0	273-3700	6.529	0.1488	-0.0227	0	2.010
$a_{11}$	OH	9625	1000-5000	5.785	0.1906	-0.0386	0.0273	1.805
$a_{12}$	O <sub>2</sub>	0	273-3700	6.732	0.1505	-0.0179	0	2.071
$a_{13}$	$N_2H_4$	22434	1000-5000	10.12	1.85	-0.6680	1.119	3.780
$a_{14}$	UDMH	20705	0-2000	4.06	6.54	-2.18	0	3.921
$a_{15}$	NO <sub>2</sub>	7960	273-1500	5.481	1.366	-0.842	1.88	2.170
$a_{16}$	NH <sub>3</sub>	-11040	273-1500	6.586	0.6126	0.2366	-1.598	2.253
$a_{19}$	$N_2O_4$	2114	273-1500	7.945	4.46	-2.71	0	4.109

\* Species are gaseous unless otherwise noted.

where

$P$  = ambient atmospheric pressure (Pascals)

$R'$  =  $8.31432 \text{ J}^\circ\text{K}^{-1} \text{ mole}^{-1}$

$\bar{M}_w$  = average molecular weight of the cloud (kg mole weight)

$$= \frac{\sum_j M_{wj} a_j}{\sum_j a_j} \quad (3-7)$$

$M_{wj}$  = molecular weight of species  $j$

and  $T(t)$  is the fireball temperature at time  $t$ . The final radius of the cloud at cloud lift-off  $r_R$  is obtained when  $t$  is equal to  $t_B$ . That is,

$$r_R = r(t=t_B) \quad (3-8)$$

when  $T(t) = T(t=t_B)$ . The value of  $T(t=t_B)$  is calculated from the time history of the fireball temperature and is obtained numerically by using a fourth-order Runge-Kutta method to solve the following nonlinear differential equation:

$$\frac{dT}{dt'} = \left\{ \frac{1}{t' \bar{c}_p} \Delta H_F(\text{reactants}) - \Delta H_F(\text{products}) \right. \\ \left. - \frac{4\pi \epsilon \sigma_B}{1.667 W_b^{1/6}} \left[ \frac{3 t' R'}{4\pi P \bar{M}_w} \right]^{2/3} T(t')^{14/3} \right\} \quad (3-9)$$

where

$t'$  = nondimensional time

$$= t/t_B$$

$\epsilon$  = emissivity (set equal to 1 for black body radiation)

$\sigma_B$  = Boltzmann's constant

$$= 5.67 \times 10^{-8} \text{ W}_b \text{ J s}^{-1} \text{ m}^{-3} \text{ }^\circ\text{K}^{-4}$$

$$\bar{c}'_p = \frac{\sum_j \bar{c}'_p a_j}{\sum_j a_j} \quad (3-10)$$

The total effective heat available for cloud rise, H, is calculated from the expression

$$H = \bar{c}'_p W_b T(t=t_B) \quad (3-11)$$

### 3.1.3 Propellant Decay and Decay By-Products

Non-stoichiometric ratios of oxidizer to fuel allow excess propellants to remain in the cloud of reactants. Both components of the fuel as well as the oxidizer also react with chemical species found in the atmosphere to produce species not originally present in the fireball. The HARM model assumes that the decay of material in the cloud after the time of cloud stabilization is of the exponential form

$$\exp [-k_1 t] \quad (3-12)$$

where  $k_1$  is the rate coefficient of decay for the  $i$ th species. Rate coefficients, half-lives, major products and yields of the fuel and oxidizer are given in Table 3-3 based on the values reported by Prince (1983). At concentrations below 1 ppm, both hydrazine and UDMH have second order rate coefficients which are much larger than at higher concentrations and are dependent on concentration. They both disappear rapidly as the concentration decreases below 1 ppm. Since the reaction products of hydrazine are the relatively harmless species  $N_2$  and  $H_2$ , changing to  $H_2O_2$  when the concentration is below 1 ppm, the HARM model uses the rate coefficient  $0.141 \text{ hr}^{-1}$  to describe the decay of hydrazine at all concentration levels. The principal exposure limits for hydrazine are 10 to 30 ppm and the overestimation of hydrazine at concentrations less than 1 ppm will not affect hazard calculations. The exposure limits for UDMH (30 to 100 ppm) are also much larger than the concentration level where the reaction rate becomes second order and the use of the linear rate of  $0.015 \text{ hr}^{-1}$  shown in Table 3-3 will not affect the hazard calculations for UDMH. The major products of the UDMH reaction with air and water vapor are NDMA and FDH at concentrations above 1 ppm. The production of these species is modeled using the expression

$$P_K\{i\} = E_K\{i\}[1 - \exp(-k_1 t)] \quad (3-13)$$

where  $E_K\{i\}$  is the efficiency (yield) of the conversion from UDMH to NDMA or FDH and the value of  $k_1$  equals  $0.015 \text{ hr}^{-1}$ .

The decay of the oxidizer is of third order as shown by the units ( $\ell^2 \text{ mole}^{-2} \text{ s}^{-1}$ ) given in Table 3-3. The half-life varies from less than 12 minutes for concentrations greater than 50 ppm to greater than 5 hours for concentrations less than 10 ppm. Principle exposure limits for  $NO_2$  and  $N_2O_4$  are in the range from 1 to 5 ppm. For use in the HARM model calculations, a first order decay coefficient appropriate at a concentration of 1 ppm was estimated from considering the rate of conversion of  $NO_2$  to  $HNO_2$  in the chemical reaction

TABLE 3-3

## ATMOSPHERIC REACTION RATE CONSTANTS (PRINCE, 1983) USED IN HARM

Species	Concentration (ppm)	Rate Constant k	Half-Life (Hours)	Major Reaction Products	Yield E <sub>k</sub> (%)
Hydrazine	0-1	0.2 (a)	2 (b)	H <sub>2</sub> O <sub>2</sub>	NA (e)
Hydrazine	> 1	0.141 (c)	4.9	N <sub>2</sub> , H <sub>2</sub> O	100
UDMH	0-1	0.15 (a)	0.2 (b)	NDMA	60
UDMH	> 1	0.015 (c)	46	FDH NDMA	67 0.2
NO <sub>2</sub>	10	5.5 x 10 <sup>4</sup> (d)	5	HNO <sub>3</sub>	100
NO <sub>2</sub>	50	5.5 x 10 <sup>4</sup> (d)	0.2	HNO <sub>3</sub>	100

(a) Units are ppm<sup>-1</sup> min<sup>-1</sup>

(b) For a clean unpolluted atmosphere.

(c) Units are hr<sup>-1</sup>.

(d) Units are l<sup>2</sup> mole<sup>-2</sup> s<sup>-1</sup>.

(e) Not available.



The differential equation expressing the rate of conversion is:

$$\frac{d[\text{NO}_2]}{dt} = k_3 [\text{H}_2\text{O}] [\text{NO}_2]^2 \quad (3-15)$$

where

$$\begin{aligned} k_3 &= \text{third-order decay rate} \\ &= 5.5 \times 10^4 \text{ l}^2 \text{ mole}^{-2} \text{ s}^{-1} \end{aligned}$$

and the brackets indicate the concentration of the enclosed chemical compound. Separating variables, integrating and solving for the time  $t_1$  required for the initial concentration of nitrogen dioxide  $[\text{NO}_2]_0$  to decay to 1 ppm yields the expression

$$t_1 = \frac{[\text{NO}_2]_0 - 1 \text{ ppm}}{k_3 [\text{H}_2\text{O}] [\text{NO}_2]_0 [1 \text{ ppm}]} \quad (3-16)$$

The equivalent first order coefficient  $k_1$  required to produce the same time  $t_1$  for the decay of  $\text{NO}_2$  to a concentration of 1 ppm is

$$k_1 = \frac{\ln[\text{NO}_2]_0}{t_1} \quad (3-17)$$

where  $[\text{NO}_2]_0$  is expressed in ppm. Equation (3-17) is used in the HARM model to obtain the decay coefficient for the oxidizer.

### 3.2 CLOUD RISE AND ASSOCIATED ALGORITHMS

#### 3.2.1 HARM Cloud Rise Model

The determination of the stabilized height of the buoyant cloud produced by hypergolic reactions is an important factor in the dosage/concentration calculations because the maximum dosage/concentration calculated at the earth's surface is approximately inversely proportional to the cube of the stabilized height. According to the algorithm described in Section 3.1 above, the cloud of buoyant gas or "fireball" from the hypergolic reaction forms and is ready to lift from the ground over a time period of about 5 seconds. Experience in predicting the cloud rise from the launch of solid rocket launches (Bjorklund, et al., 1982) with similar formation times indicates that the instantaneous cloud rise model based on the work of Briggs (1970) yields stabilization heights that are in good agreement with observed heights.

The time  $t_k$  for the cloud produced by the hypergolic reaction to reach a height  $z_k$  in a stable atmosphere is given by the expression

$$t_k = s^{-0.5} \arccos \left\{ 1 - \frac{\gamma^3 s}{4F_I} \left[ \left( z_k + \frac{r_R}{\gamma} \right)^4 - \left( \frac{r_R}{\gamma} \right)^4 \right] \right\} \quad (3-18)$$

where  $t_k$  is constrained to be less than the cloud stabilization time  $t^*$  and

$$c^* = \pi s^{-0.5} \quad (3-19)$$

s = stability parameter

$$= \frac{g}{T} \frac{\Delta\phi}{\Delta z} \quad (3-20)$$

g = gravitational acceleration ( $9.8 \text{ m s}^{-2}$ )

$\frac{\Delta\phi}{\Delta z}$  = vertical gradient of virtual potential temperature ( $^{\circ}\text{K m}^{-1}$ )  
between the surface and height  $z_k$

$\gamma$  = entrainment coefficient (0.64)

$F_I$  = initial buoyancy term

$$= \frac{3g H}{4\pi c_p T_p} \quad (3-21)$$

H = total effective heat release (cal) obtained from the source algorithm

$c_p$  = specific heat of air at constant pressure ( $0.24 \text{ cal g}^{-1} \text{ }^{\circ}\text{K}^{-1}$ )

T = ambient air temperature ( $^{\circ}\text{K}$ ) near the surface

$\rho$  = ambient air density ( $\text{g m}^{-3}$ ) near the surface

$r_R$  = initial radius of the fireball (m) obtained from the source algorithm

The cloud stabilization height is defined as

$$z_I = \left[ \frac{8 F_I}{\gamma^3} + \left( \frac{r_R}{\gamma} \right)^4 \right]^{1/4} - \frac{r_R}{\gamma} \quad (3-22)$$

According to the above formulas, the final stabilization height  $z_I$  is related to the vertical gradient of virtual potential temperature measured over the same height. The value of  $z_I$  in Equation (3-22) must therefore be determined through iteration. The iteration process is initiated by assuming that  $z_I$  lies in the first height interval ( $k=1$ ) above the surface bounded by the rawinsonde observations at ( $k=1$ ) and ( $k=2$ ) and solving Equation (3-22) for  $z_I$  with

$$\frac{\Delta\phi}{\Delta z} = \frac{\phi_2 - \phi_1}{z_2 - z_1} \quad (3-23)$$

If  $z_I$  exceeds  $z_2$ , the iteration continues using the virtual potential temperature from the next height  $K$ th observation level with the vertical gradient  $\Delta\phi/\Delta z$  estimated from the least-squares approximation

$$\frac{\Delta\phi}{\Delta z} = \frac{\sum_{i=1}^k \left[ \left[ z_i - \left( \sum_{i=1}^k z_i/k \right) \right] \left[ \phi_i - \left( \sum_{i=1}^k \phi_i/k \right) \right] \right]}{\sum_{i=1}^k \left[ z_i - \left( \sum_{i=1}^k z_i/k \right) \right]^2} \quad (3-24)$$

Providing that  $z_I < 3000$  m, the program finds a value of  $z_I$  within an interval ( $z_{i-1} \leq z_I \leq z_i$ ). At this point the program assumes that the gradient of virtual potential temperature in this height interval is linear and linearly interpolates to determine, within  $\pm 10$  m, the value of  $z_I$ . Momentum flux is not considered in this application of the cloud-rise model because inclusion of the momentum term does not affect the final cloud stabilization height.

The cloud-rise model described above was theoretically derived for use in thermally stable atmospheric layers ( $\Delta\phi/\Delta z > 0$ ). A model based on similar considerations is easily derived for an adiabatic atmosphere. However, the adiabatic model predicts the cloud to rise over all time, and the rate of rise approaches zero asymptotically at longer times. Experience shows that the height at which the rate of rise determined from the adiabatic model becomes negligible for practical purposes can be predicted using a

small value of  $\Delta\phi/\Delta z$  in the stable model described above. For this reason, the program sets  $\Delta\phi/\Delta z$  equal to  $3.322 \times 10^{-4}$  when the value developed from the rawinsonde measurements indicate  $\Delta\phi/\Delta z$  is less than  $3.322 \times 10^{-4}$ .

### 3.2.2 Dimensions and Material Distribution in the Stabilized Cloud

The dispersion models described in Section 4 are derived under the assumptions that a vertical finite line source can be used to represent the source of material in each of the K layers defined by the rawinsonde observation heights and that the radius of the cloud at the stabilization height  $z_I$  is consistent with that used in deriving the cloud-rise model, e.g.:

$$r_I = \gamma z_I + r_R \quad (3-25)$$

Under these assumptions, the alongwind and crosswind dimensions of the cloud in the Kth layer are

$$R_k = \left[ r_I \left( 1 - \frac{z_o^2}{r_I^2} \right) \right]^{1/2} \quad (3-26)$$

where

$$z_o = |\bar{z} - z_I| \quad (3-27)$$

$$\bar{z} = (z_{TK} + z_{BK})/2 \quad (3-28)$$

$z_{TK}$  = height of the top of the Kth layer

$z_{BK}$  = height of the base of the Kth layer

The HARM model assumes that the source material in each Kth layer is uniformly distributed in the vertical and Gaussian distributed alongwind and crosswind in the horizontal plane consistent with the Gaussian model approach used in the dispersion models. The initial standard deviations of the alongwind  $\sigma_{x_0}$  and crosswind  $\sigma_{y_0}$  source dimensions used in the cloud expansion formulas described in Section 4 are defined as follows:

$$\sigma_{x_0}\{K\} = \sigma_{y_0}\{K\} = R_K/2.15 \quad (3-29)$$

under the assumption that the concentration at one radius from the cloud centerline is one-tenth of the maximum concentration at the cloud centerline. While the vertical distribution in each Kth layer is assumed uniform with height in the layer, the fraction of the total material in the cloud residing in the Kth layer at the time of cloud stabilization is derived under the assumption that the material is Gaussian distributed over the entire vertical extent of the cloud. Thus the fraction by weight of the material of each species  $F\{K\}$  determined from the algorithm described in Section 3.1 above is given by the expression

$$F\{K\} = a_j M_{wj} [P\{z_{TK}\} - P\{z_{BK}\}] \quad (3-30)$$

where

$$P\{z\} = \frac{2.15}{\sqrt{2\pi} r_I} \int_{-a}^z \exp\left[-\frac{1}{2}\left(\frac{2.15(z-z_I)}{r_I}\right)^2\right] dz \quad (3-31)$$

### 3.2.3 Spatial Position of the Cloud at Stabilization Time

The spatial position in the plane of the horizon of the portion of the cloud produced by the reaction and residing in the Kth layer at the stabilization time  $t^*$  is determined in the HARM computer program from the wind directions and wind speeds obtained from the rawinsonde and the time from Equation (3-18) required for the cloud to rise through the tops of the various K layers. The distance  $R_{CK}$  and bearing  $\theta_{CK}$  at time  $t^*$  of that portion of the cloud in the Kth layer is defined by the following expressions:

$$R_{CK} = \left\{ [x_K + \bar{u}_K(t^* - t_p) \sin \bar{\theta}_K]^2 + [y_K + \bar{u}_K(t^* - t_p) \cos \bar{\theta}_K]^2 \right\}^{1/2} \quad (3-32)$$

$$\theta_{CK} = (\pi/2) - \tan^{-1} \left[ \frac{y_K + \bar{u}_K(t^* - t_p) \sin \bar{\theta}_K}{x_K + \bar{u}_K(t^* - t_p) \cos \bar{\theta}_K} \right] \quad (3-33)$$

where

$$x_K = x_{K-1} - \xi_K \sin(\phi_{sK}) \quad (3-34)$$

$$y_K = y_{K-1} - \xi_K \cos(\phi_{sK}) \quad (3-35)$$

$$\bar{u}_K = \text{mean wind speed in the Kth layer}$$

$$= (u_{TK} + u_{BK})/2 \quad (3-36)$$

$$u_{TK} = \text{wind speed measured at the top of the Kth layer}$$

$$u_{BK} = \text{wind speed measured at the base of the Kth layer}$$

$$t_p = \text{time the cloud passes through the top } z_{TK} \text{ of the Kth layer, obtained by setting } z_K \text{ in Equation (3-18) to } z_{TK}$$

$$\begin{aligned}\bar{\theta}_K &= \text{mean wind direction in the Kth layer} \\ &= (\theta_{TK} + \theta_{BK})/2\end{aligned}\quad (3-37)$$

$\theta_{TK}$  = wind direction measured at the top of the Kth layer

$\theta_{BK}$  = wind direction measured at the base of the Kth layer

For the layers below the Kth layer containing the stabilization height  $z_I$ ,

$$\xi_K = \tau_p \bar{u}_K \quad (3-38)$$

$$\phi_{SK} = \bar{\theta}_K \quad (3-39)$$

For the layer containing  $z_I$ ,  $\xi_K$  and  $\phi_{SK}$  are defined as

$$\xi_K = \left[ \bar{u}_K \left( \frac{z_I - z_{BK}}{z_{TK} - z_{BK}} \right) + u_{BK} \right] \left[ \tau^* - \tau_p(z_{BK}) \right] \quad (3-40)$$

$$\phi_{SK} = \frac{1}{2} \left[ \left( \frac{\theta_{TK} - \theta_K}{z_{TK} + z_{BK}} \right) (z_I - z_{BK}) + 2 \theta_{BK} \right] \quad (3-41)$$

Finally, for all K layers above  $z_I$  ( $z_{BK} > z_I$ ),

$$R_{CK} = R_{CK}(z=z_I) \quad (3-42)$$

$$\theta_{CK} = \theta_{CK}(z=z_I) \quad (3-43)$$

### 3.3 TURBULENCE PROFILE ALGORITHM

The HARM dispersion models use profiles of the standard deviations of the azimuth wind angle  $\sigma'_A$  and elevation angle  $\sigma'_E$  as prime predictors of lateral and vertical cloud growth downwind from the point of cloud stabilization. The computer program calculates default vertical profiles of turbulence which can be adjusted by the user. The algorithm used to calculate the profiles begins by determining a reference standard deviation of the wind azimuth angle  $\sigma'_{AR}(\tau_o=600s)$ , assumed representative of a measurement made over a ten-minute period at the lowest height reported on the rawinsonde observation (usually from 2 to 10 m above the surface).

#### 3.3.1 Calculation of the Default Value for: $\sigma'_{AR}(\tau_o=600s)$

The calculation method (Goldford, et al, 1977), based on the application of similarity relationships outlined by Golder (1972), assumes that

$$\sigma'_{AR}(\tau_o=600s) = \frac{\sigma_V(600s)}{\bar{u}} \approx \frac{k_A f(B)}{\ln\left(\frac{z}{z_o}\right) - \psi(Ri)} \quad ; \quad Ri \neq 0 \quad (3-44)$$

where

$\sigma_V$  = standard deviation of the crosswind component of the wind

$\bar{u}$  = mean wind speed at the measurement height of  $\sigma_V$

$\tau_o$  = reference time for the measurement of  $\sigma'_{AR}$  and  $\sigma_V$

$f(B)$  = function of the bulk Richardson number B

$k_A$  = Von Karman's constant = 0.4

$\bar{z}$  = geometric mean height of the layer of interest

$z_0$  = roughness length (default value set to 0.2 m)

$\psi\{Ri\}$  = function of the Richardson number  $Ri$

In the program, values of  $f\{B\}$  and  $\psi\{Ri\}$  are obtained from the expressions

$$f\{B\} = \left. \begin{array}{ll} \begin{array}{l} 2.7 \\ 2.7+112(.008+B) \\ 3.4-725.5(.00175+B) \\ 1.55+38.04(B+.0008) \\ 2.35+5.43(B-.029) \end{array} & \begin{array}{l} B < -0.008 \\ -0.008 \leq B < -.00175 \\ -.00175 \leq B < .008 \\ .0008 \leq B < .029 \\ .029 \leq B \end{array} \end{array} \right\} \quad (3-45)$$

and

$$\psi\{Ri\} = \left. \begin{array}{ll} \begin{array}{l} 2 \ln \left[ \frac{(1+\xi)}{2} \right] + \ln \left[ \frac{(1+\xi)^2}{2} \right] + 2 \tan^{-1} \xi + \pi/2 \\ 7Ri/(1-7Ri) \end{array} & \begin{array}{l} Ri < 0 \\ Ri > 0 \end{array} \end{array} \right\} \quad (3-46)$$

where

$$\xi = (1-16Ri)^{-1/4}; \quad Ri < 0 \quad (3-47)$$

$$B = \frac{g \bar{z}^2}{T \bar{u}^2} \frac{\Delta\phi}{\Delta\bar{z}} \quad (3-48)$$

$\frac{\Delta\phi}{\Delta\bar{z}}$  = vertical gradient of potential temperature over the height  $\bar{z}$

$T$  = average temperature ( $^{\circ}K$ ) over the height  $\bar{z}$

$$Ri = \left[ -\frac{1}{14 k_A \sqrt{B}} + \frac{1}{2} \sqrt{\frac{1}{49 k_A^2 B} + \frac{4(k_A+1)}{7 k_A}} \right]^2; \quad Ri > 0 \quad (3-49)$$

For  $Ri < 0$ , the following equation is solved by Newton's method to obtain a value of  $\xi$  for use in Equation (3-46)

$$0 = \frac{1 - \xi^4}{16\xi^2 \left[ \ln(z/z_0) + 0.50864 - 2[\ln(1+\xi)] - \ln(1+\xi^2) + 2\tan^{-1}\xi \right]^2}^{-B} \quad (3-50)$$

where  $\xi$  is defined by Equation (3-47).

Finally, for  $Ri=0$ ,  $\sigma_{AR}(\tau_0=600s)$  is calculated from the relationship

$$\sigma_{AR}(\tau_0=600s) = \frac{48.816}{\ln\left(\frac{z}{z_0}\right)} ; Ri = 0 \quad (3-51)$$

The program does not permit  $\sigma'_{AR}(\tau_0=600s)$  to be greater than 0.349 radians (20 degrees).

### 3.3.3 Vertical Profiles of $\sigma'_A$ and $\sigma'_E$

The dispersion models described in Section 4 use mean values of  $\sigma'_A$  and  $\sigma'_E$  in the two major meteorological layers ( $L=1,2$ ). In the case where the user enters values of  $\sigma'_A$  and  $\sigma'_E$  at each  $k$  rawinsonde observation level, the program computes height-weighted mean values for the  $L$ th layer from the expression

$$\bar{\sigma}'_L = \frac{\sum_{k=z_{BL}}^{BK} (z_{k+1} - z_k) [(\sigma'(k+1) + \sigma'(k))/2]}{z_{TL} - z_{BL}} \quad (3-52)$$

where

$\sigma'_L$  = mean value of the standard deviation ( $\sigma'_A$  or  $\sigma'_E$ ) in the  $L$ th layer

$z_{TL}$  = top of the  $L$ th layer

$z_{BL}$  = base of the  $L$ th layer

When values of  $\sigma'_A$  and  $\sigma'_E$  are not entered at each k level, the program calculates the mean value of  $\sigma'_A$  under the assumption that  $\sigma'_A$  decreases with height in the surface mixing layer according to a power-law relationship (Swanson and Cramer, 1965; Lumley and Panofsky, 1964; Dumbauld, 1982) given by

$$\sigma'_A(z) = \sigma'_{AR}(\tau_o = 600s) \left(\frac{z}{z_R}\right)^m \quad (3-53)$$

where  $m$  takes on negative values and  $z_R$  is the reference height (lowest measurement level reported on the rawinsonde message). The mean value of  $\bar{\sigma}'_A$  in the L=1 layer is defined as

$$\frac{\sigma'_{AR}(\tau_o = 600s)}{z_{TL} - z_R} \int_{z_R}^{z_{TL}} z^m dz = \frac{\sigma'_{AR}(\tau_o = 600s) [z_{TL}^{1+m} - z_R^{1+m}]}{(z_{TL} - z_R)(1+m)z_R^m} \quad (3-54)$$

It can be shown, for reasonable combinations of the values of  $m$  and  $z_{TL}$ , that the value of  $\sigma'_A(L=1, \tau_o = 600s)$  obtained from Equation (3-54) can be approximated by the simple expression

$$\bar{\sigma}'_A(L=1, \tau_o = 600s) = \frac{\sigma'_{AR}(\tau_o = 600s)}{2} \quad (3-55)$$

The value of  $\sigma'_A$  at the top of the L=1 layer can be approximated by the expression

$$\bar{\sigma}'_A(z_{TL}(L=1), \tau_o = 600s) = \frac{\sigma'_{AR}(\tau_o = 600s)}{2.7} \quad (3-56)$$

The assumption is also made (Cramer, et al., 1964; Osipov, 1972) that the value of  $\sigma'_A$  can be adjusted for the time  $t^*$  required to form the stabilized cloud from the relationship

$$\bar{\sigma}'_A\{L=1; \tau=t^*\} = \bar{\sigma}'_A\{L=1, \tau_o=600s\} \left(\frac{t^*}{600}\right)^{0.2} \quad (3-57)$$

and

$$\bar{\sigma}'_A\{z_{TL}(L=1), \tau_o=t^*\} = \bar{\sigma}'_A\{z_{TL}(L=1), \tau_o=600s\} \left(\frac{t^*}{600}\right)^{0.2} \quad (3-58)$$

As noted in Section 2.3, the HARM code in the default mode assumes the surface mixing layer is capped by an elevated inversion where atmospheric turbulence levels are expected to be minimal. To account for the expected reduction in turbulence levels above the surface mixing layer, the program reduces the level of turbulence at the top of the next Kth layer above the surface mixing layer to 0.01745 radians (1 degree). The average value in this Kth layer is then assumed to be given by

$$\sigma'_A\{K, \tau=t^*\} = \frac{\bar{\sigma}'_A\{z_{TL}(L=1), \tau_o=t^*\} + .01745}{2} \quad (3-59)$$

The top of the second major meteorological layer (L=2) is defaulted to the top of the data considered by the program (~3000 m). The height-weighted mean value of  $\bar{\sigma}'_A$  in the second layer is defined by the expression

$$\bar{\sigma}'_A\{L=2, \tau=t^*\} = \frac{\bar{\sigma}'_A\{K, \tau=t^*\}(z_{TK} - z_{TL}\{L=1\}) + .01745(z_{TL}\{L=2\} - z_{TK})}{z_{TL}\{L=2\} - z_{TL}\{L=1\}} \quad (3-60)$$

If the user chooses to assign the base of the major upper layer at some Kth layer above the surface mixing layer not coincident with the top of the surface mixing layer and uses the default turbulence profile, the program assumes the average value of  $\sigma'_A$  in the layer is 0.01745 radians. Finally, the program assumes that the mean turbulence over the layer depths of interest is approximately isotropic and thus that the mean effective value of  $\sigma'_E$  is equal to the mean value of  $\sigma'_A$  calculated for the layer.

## SECTION 4

### HARM DISPERSION MODELS

The dispersion models used in the HARM computer program are based on Gaussian model concepts which experience has shown to be well suited for most practical applications. Pasquill (1975) and Gifford (1975) discuss Gaussian dispersion modeling concepts and alternative approaches. As pointed out by Gifford, the Gaussian approach, when properly used, "is peerless as a practical diffusion modeling tool. It is mathematically simple and flexible, it is in accord with much though not all of working diffusion theory, and it provides a reliable framework for the correlation of field diffusion trials as well as the results of both mathematical and physical diffusion modeling studies." In the HARM diffusion model applications, the material in the cloud formed by the hypergolic reaction is assumed to be uniformly distributed in the vertical within each Kth layer bounded by rawinsonde observations and to have a bivariate Gaussian distribution in the plane of the horizon at the time of cloud stabilization. It follows from these assumptions that the models are of the general form identified with Gaussian models for line sources (in this case, a vertical line source) of finite extent.

#### 4.1 DOSAGE AND CONCENTRATION MODELS

For convenience, the dosage and concentration formulas described below are written with reference to a rectangular coordinate system with an origin at the ground beneath the spatial position of the cloud residing in the Kth layer at the time of cloud stabilization. The x axis is directed along the axis of the mean wind direction in the Lth layer and the y axis is directed crosswind or perpendicular to the mean wind direction. In the computer program, the origin of the polar coordinate system is at the point of the accident and appropriate coordinate transformation formulas are used to adjust for the displacement of the source cloud in the Kth layer from this point.

The dosage, or time-integrated concentration, at any point (x, y, z) in the Lth layer due to a source in an internal Kth layer is given by the expression

$$\begin{aligned}
 D_{L,p} = & \frac{F(K)}{2\sqrt{2\pi} \sigma_{yL} (z_{TK} - z_{BK}) \bar{u}_L} \left\{ \exp \left[ -\frac{1}{2} \left( \frac{y}{\sigma_{yL}} \right)^2 \right] \right\} \\
 & \left\{ \sum_{i=0}^{\infty} \left[ \gamma^i \left[ \operatorname{erf} \left( \frac{2i(z_{TL} - z_{BL}) - z_{BK} + z}{\sqrt{2} \sigma_{zL}} \right) \right. \right. \right. \\
 & \quad \left. \left. \left. + \operatorname{erf} \left( \frac{-2i(z_{TL} - z_{BL}) + z_{TK} - z}{\sqrt{2} \sigma_{zL}} \right) \right] \right. \right. \\
 & \quad \left. \left. + \gamma^{i+1} \left[ \operatorname{erf} \left( \frac{2i(z_{TL} - z_{BL}) - 2z_{BL} + z_{TK} + z}{\sqrt{2} \sigma_{zL}} \right) \right. \right. \right. \\
 & \quad \left. \left. \left. + \operatorname{erf} \left( \frac{-2i(z_{TL} - z_{BL}) + 2z_{BL} - z_{BK} - z}{\sqrt{2} \sigma_{zL}} \right) \right] \right] \right\} \\
 & + \sum_{i=1}^{\infty} \left[ \gamma^i \left[ \operatorname{erf} \left( \frac{2i(z_{TL} - z_{BL}) + z_{TK} - z}{\sqrt{2} \sigma_{zL}} \right) \right. \right. \\
 & \quad \left. \left. + \operatorname{erf} \left( \frac{-2i(z_{TL} - z_{BL}) - z_{BK} + z}{\sqrt{2} \sigma_{zL}} \right) \right] \right]
 \end{aligned} \tag{4-1}$$

$$+ \gamma^{i+1} \left[ \operatorname{erf} \left( \frac{2i(z_{TL} - z_{BL}) + 2z_{BL} - z_{BK} - z}{\sqrt{2} \sigma_{zL}} \right) \right.$$

(4-1)  
(Continued)

$$\left. + \operatorname{erf} \left( \frac{-2i(z_{TL} - z_{BL}) - 2z_{BL} + z_{TK} + z}{\sqrt{2} \sigma_{zL}} \right) \right] \left. \right\}$$

where, for convenience,  $0^\circ$  is set equal to unity and

$F(K)$  = fraction of the material in the Kth layer (see Section 3.3)

$\gamma$  = reflection coefficients permitting the user to assume, if justified, partial reflection of material at the base of major layer boundaries (default = 1 for complete reflection)

$\sigma_{zL}$  = standard deviation of the vertical distribution of material in the Lth layer due to the source in the Kth layer

$$= \sigma'_{EL} x_{rz} \left( \frac{x}{x_{rz}} \right)^\beta \quad (4-2)$$

$x_{rz}$  = distance downwind from a vertical point source over which the vertical cloud expansion is linear (default value equals 100 m in the HARM code).

$\beta$  = coefficient of vertical cloud expansion (default value equals 1.0 in the HARM code).

$\sigma'_{EL}$  = effective value of  $\sigma'_E$  in the Lth layer (see Section 3.3)

$\sigma_{yL}$  = standard deviation of the crosswind distribution of material in the Lth layer due to the source in the Kth layer

$$= \left\{ \left[ \sigma'_{\Delta L} x_{ry} \left( \frac{x + x_v - x_{ry}(1-a)}{a x_{ry}} \right)^a \right]^2 + \left[ \frac{\Delta \theta'_L x}{4.3} \right]^2 \right\}^{1/2} \quad (4-3)$$

$x_{ry}$  = distance downwind from a virtual point source over which the crosswind cloud expansion is linear (default equals 100 m in the HARM code)

$x_v$  = virtual distance

$$= x_{ry} \left( \frac{\sigma_{yo}(K)}{\sigma'_{AL} x_{ry}} \right)^{1/\alpha} + x_{ry} (1-\alpha) \quad (4-4)$$

$\alpha$  = coefficient of crosswind cloud expansion (default equals 1 in the HARM code)

$\sigma'_{AL}$  = effective value of  $\sigma'_A$  in the Lth layer (see Section 3.3)

$$\Delta\theta'_L = (\theta_{TL} - \theta_{BL}) (\pi/180) \quad (4-5)$$

$$\bar{u}_L = \left( \frac{1}{z_{TL} - z_{BL}} \right) \sum_{k=z_{BL}}^{z_{TL}} (z_{k+1} - z_k) \bar{u}_k \quad (4-6)$$

The total dosage at the receptor position (x, y, z) is calculated by summing the contributions from all sources, i.e.,  $D_L = \sum_k D_{L,k}$ .

The peak concentration, or highest concentration which occurs as the exhaust cloud passes the point (x,y,z), is given by the expression

$$x_{P,K} = D_L \left( \frac{\bar{u}_L}{\sqrt{2\pi} \sigma_{xL}} \right) \quad (4-7)$$

where

$\sigma_{xL}$  = standard deviation of the alongwind distribution of material in the Lth layer due to the source in the Kth layer

$$= \left[ \left( \frac{L(x)}{4.3} \right)^2 + \sigma_{x0}^2(K) \right]^{1/2} \quad (4-8)$$

$L(x)$  = alongwind cloud length at the distance  $x$

$$L(x) = \left\{ \begin{array}{ll} \frac{0.28 \Delta \bar{u}_L x}{\bar{u}_L} ; & \Delta \bar{u}_L \geq 0 \\ \frac{0.28 |\Delta \bar{u}_L| x}{\bar{u}_L} ; & \frac{\Delta \phi}{\Delta z} < 0, \Delta \bar{u}_L < 0 \\ 0 & ; \frac{\Delta \phi}{\Delta z} \geq 0, \Delta \bar{u}_L < 0 \end{array} \right\} \quad (4-9)$$

$$\Delta \bar{u}_L = \frac{\sum_{k=1}^{z_{TL}} (z_{k+1} - z_k) (\bar{u}_{k+1} - \bar{u}_k)}{z_{TL} - z_{BL}} \quad (4-10)$$

The peak time-mean concentration, or highest time-mean concentration to occur as the exhaust cloud passes the point  $(x, y, z)$ , is

$$\chi_{P,K}(T_A) = \frac{D_L}{T_A} \left\{ \operatorname{erf} \left( \frac{\bar{u}_L T_A}{2\sqrt{2} \sigma_{xL}} \right) \right\} \quad (4-11)$$

where

$T_A$  = time in seconds over which the concentration is averaged  
(default is 10 minutes in the HARM code)

#### 4.2 PRECIPITATION SCAVENGING MODEL

The weight of material from the  $K$ th layer deposited on the ground as a result of washout of material by rain is given by the expression

$$WK_K = \left\{ \frac{\Lambda F(K)}{\sqrt{2\pi} \sigma_{yL} \bar{u}_L} \exp \left[ -\frac{1}{2} \left( \frac{y}{\sigma_{yL}} \right)^2 \right] \right\} \left\{ \exp \left[ -\Lambda \left( \frac{x}{\bar{u}_L} - t_1 \right) \right] \right\} \quad (4-12)$$

where

$\Lambda$  = fraction of material removed per unit time

$t_1$  = time precipitation begins

The principal assumptions made in deriving Equation (4-12) are:

- (1) The rate of precipitation is steady over an area that is large compared to the horizontal dimension of the cloud of material
- (2) The precipitation originates at a level above the top of the cloud so that hydrometeors pass vertically through the entire cloud
- (3) The time duration of the precipitation is sufficiently long so that the entire alongwind length of the cloud passes over the point (x,y)

Most laboratory, theoretical and field studies to determine the scavenging coefficient  $\Lambda$  for gases have focused on sulfur dioxide ( $SO_2$ ) because of concerns about the environmental impacts of this industrial air pollutant. As referenced by McMahon and Dennison (1979), Chamberlain (1953) derived a theoretical expression relating  $\Lambda$  to the rainfall rate  $J$  for  $SO_2$  given by

$$\Lambda (s^{-1}) = 10^{-4} J^{0.53} \quad (4-13)$$

where J has units of mm per hour. Also as referenced by McMahon and Dennison (1979), the laboratory experiments of Beilke (1970) indicate that  $\Lambda$  for  $\text{SO}_2$  is

$$\Lambda\{\text{s}^{-1}\} = 1.7 \times 10^{-4} J^{0.6} \quad (4-14)$$

Assuming a linear relationship between  $\Lambda$  and J, Maul (1978) inferred from sequential hourly  $\text{SO}_2$  concentrations in rural areas that

$$\Lambda\{\text{s}^{-1}\} = 3 \times 10^{-5} J \quad (4-15)$$

On the basis of a literature review, McMahon, et al. (1976) selected for use in their long-range transport model the similar expression

$$\Lambda\{\text{s}^{-1}\} = 6 \times 10^{-5} J \quad (4-16)$$

Table 4-1 lists values of  $\Lambda$  calculated using Equations (4-13) through (4-16) for a range of rainfall rates. The theoretical values of  $\Lambda$  given by Equation (4-13) are approximately double the values obtained from laboratory experiments given by Equation (4-14) over the range of precipitation rates shown in the table. Although Equation (4-15) should tend to overestimate scavenging coefficients because it implicitly includes other removal mechanisms such as chemical conversions, the values of  $\Lambda$  obtained are the lowest in the table. The  $\Lambda$  value obtained using Equations (4-13) and (4-16) tend to become equivalent as the intensity of precipitation increases. For a precipitation rate of  $5 \text{ mm hr}^{-1}$ , Thompson and Cicerone (1982) give  $\Lambda$

TABLE 4-1

SCAVENGING COEFFICIENTS FOR SO<sub>2</sub> AS A FUNCTION OF PRECIPITATION RATE

Precipitation Rate J (mm · hr <sup>-1</sup> )	SO <sub>2</sub> Scavenging Coefficient $\Lambda$ (s <sup>-1</sup> )			
	Equation (4-13) Chamberlain (1953) Theoretical Relationship	Equation (4-14) Beilke (1970) Laboratory Relationship	Equation (4-15) Maul (1978) Empirical (Field) Relationship	Equation (4-16) McMahon, et al. (1976) Literature Review Relationship
1	1.7 x 10 <sup>-4</sup>	1.0 x 10 <sup>-4</sup>	3.0 x 10 <sup>-5</sup>	6.0 x 10 <sup>-5</sup>
2	2.6 x 10 <sup>-4</sup>	1.5 x 10 <sup>-4</sup>	6.0 x 10 <sup>-5</sup>	1.2 x 10 <sup>-4</sup>
5	4.5 x 10 <sup>-4</sup>	2.4 x 10 <sup>-4</sup>	1.5 x 10 <sup>-4</sup>	3.0 x 10 <sup>-4</sup>
10	6.8 x 10 <sup>-4</sup>	3.5 x 10 <sup>-4</sup>	3.0 x 10 <sup>-4</sup>	6.0 x 10 <sup>-4</sup>

for nitric acid vapor ( $\text{HNO}_3$ ) as  $2 \times 10^{-4}$ , which is consistent with the predictions calculated from all four equations. It is important to note that most field estimates of  $\Lambda$  are lower than the values given in Table 4-1. For example, excluding a case in which desorption of  $\text{SO}_2$  from rain drops is believed to have occurred, the field measurements of  $\Lambda$  for  $\text{SO}_2$  summarized by McMahon and Dennison (1979) range from  $1.3 \times 10^{-5}$  to  $6.0 \times 10^{-5}$ . The decision was made to use Equation (4-16) as the default expression for  $\Lambda$  in the HARM model because it is based on field measurements and because it predicts values of  $\Lambda$  that are intermediate between Equations (4-13) and (4-15). Because precipitation rates  $J$  are often expressed in inches per hour, the expression for  $\Lambda$  in the HARM model is

$$\Lambda\{\text{s}^{-1}\} = 1.524 \times 10^{-3} R \quad (4-17)$$

where  $R$  is the precipitation rate in units of inches per hour.

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## SECTION 5

### HARM COMPUTER PROGRAM OPERATION

This section provides the complete execution and data-preparation instructions for the HARM computer program. The HARM computer program is designed for use on most computers supporting FORTRAN 77. The HARM program consists of a main program element HARM and the following primary subroutines, all scheduled by the main program: HINOM, HDATM, GDATM, HCLDM, FIREM, HCONM, HCDRM, HPDPM, HPDRM, HCIMM, HMMRM and HISOM. The HARM operating instructions in Section 5.1 assume the user has assembled and loaded the HARM program and has prepared a meteorological upper-air (rawinsonde) data file. Section 5.2 describes the method made available in the HARM program for automated generation of forms for use in subsequent plotting of meteorological data and peak centerline concentrations, peak centerline time-average concentrations and peak centerline dosages. Formats for rawinsonde input data that the HARM program is designed to accept are given in Section 5.3.

#### 5.1 GENERAL HARM OPERATING INSTRUCTIONS

The HARM computer program can be executed in a completely interactive environment, in a completely batch environment or in a combination of the two. Schedule the HARM computer program according to the normal method on your computer. Section 5.1.1 below specifies the operating instructions for an interactive environment and Section 5.1.2 contains instructions for a batch environment.

##### 5.1.1 Interactive Processing

The HARM computer program is executed in an interactive environment only when the logical unit number specified by DATA UNIT is an

interactive device (CRT,TTY,etc.). After the user schedules HARM, the HARM program begins execution by displaying the following message:

```
*****
*****          HYPERGOLIC ACCIDENT RELEASE MODEL          *****
*****          (HARM)                                       *****
*****          UPDATE ### LOCATION KSC                     *****
*****          ENTER BA TO CHANGE PREVIOUS INPUT VALUE.    *****
*****          ENTER RS TO START AT BEGINNING OF PROGRAM.  *****
*****          ENTER EX TO ABORT PROGRAM.                  *****
*****          THE FIRST INPUT OPTION SHOWN IS THE DEFAULT. *****
*****
```

where the value of ### is the update level of the copy of HARM the user is executing. The above display also reminds the user of certain conventions that will apply to most input requests throughout the operation of the program. Specifically, the following conventions apply to interactive processing:

- The first option shown is the default option unless stated otherwise in the explanation of the option. The default option is obtained by typing the SPACE key followed by the RETURN key. In the following text, the SPACE key will be denoted by  $\nabla$  and the RETURN key by  $C_R$ .
- Most options can be entered by typing the first character of the option name followed by  $C_R$ . However, for those options that have the same first characters, you must enter sufficient characters to make the entry unique or type the entire name of the option. Underlining has been used in this section to indicate the minimum set of characters to be entered for each option.
- For most input options, the entry of an RS followed by  $C_R$  will cause the HARM program to restart.

- For most input options, the entry of a BA followed by C<sub>R</sub> will cause the program to go back to the previous input option display.
- For input options where multiple values are required, the values are positional and each must be separated by a comma. Two consecutive commas indicate an empty field with the respective variable retaining its previous (default) value. Do not type C<sub>R</sub> until the entire string of values has been entered.

The remainder of this section will show the HARM prompt as a display asking for either data or for a response that will direct the program along optional paths. Each display is printed in uppercase type with a leading display number (record number). The display number is used for order and cross-referencing against batch data record numbers and is accompanied by a code in parenthesis (ORP;CW). The letters O, R and/or P that appear prior to the semi-colon indicate that the display will appear under the Operational, Research or Production modes of operation. The letters C and/or W indicate that the display will appear for Concentration (dosage) or Washout deposition. If the particular letter does not occur in parenthesis, the display does not appear for that mode of operation and/or that calculation. The program will prompt with only those displays that are required for the mode of operation and calculation quantity you select. The HARM interactive display prompts are explained below in the order they appear to the user.

1. - (ORP;CW)

ENTER DATA UNIT, MET. DATA UNIT, OUTPUT UNIT, PLOT UNITS (UP TO THREE)  
 DEFAULTS ARE: 1, 8, 6, 12, 12, 12:

where

DATA UNIT - Logical input number from which the HARM program is to read the input data and control information. The number specified

DATA UNIT - determines whether the program will execute in an interactive or batch environment. If the number entered (or default) is the logical unit number of an interactive device (CRT,TTY,etc.), the program assumes an interactive environment and solicits all input data and commands via displays to the device specified by DATA UNIT. The default is obtained by typing a comma indicating an empty field. The default logical unit will then be the unit from which the HARM program was scheduled. If the number entered for DATA UNIT is the logical unit number of a non-interactive device (magnetic tape, card reader, paper tape, etc.) or a number equated with a disc file, the program assumes a batch environment. The program will be completely batch or will require some interactive user input, depending on the input data. All program interactive messages and displays are written to the unit from which the batch run was initiated. See Section 5.2 for special input values for DATA UNIT used for generating meteorological and maximum centerline plot forms.

MET. DATA UNIT - Logical unit number previously equated to the file containing the meteorological upper-air (rawinsonde) data.

OUTPUT UNIT - Logical unit number for print output. The default printer unit (6) is obtained by typing a comma indicating an empty field.

PLOT UNIT 1 - Logical unit number for meteorological profile plot output. The default unit (12), is obtained by typing a comma indicating an empty field.

PLOT UNIT 2 - Logical unit number for maximum centerline (concentration, dosage, deposition) profile plot output. The default unit

PLOT (12) is obtained by typing a comma indicating an empty  
UNIT 2 field.  
(Cont.)

PLOT - Logical unit number for isopleth (concentration, dosage,  
UNIT 3 deposition) plot output. The default unit (12) is obtained  
by typing a comma indicating an empty field.

2. - (ORP;CW)

ENTER RUN TITLE

\*

A title of up to 48 characters in length may be entered, the asterisk indicates the 48th character position. This title will appear in all headers printed to the output unit. The default is a blank line.

3. - (ORP;CW)

ENTER RUN TYPE (OPERATIONAL, RESearch, PRODUCTION):

As explained in Section 2.1, the Operational (O) mode is designed for use during real-time accident support operations and automatically calculates many of the user inputs. The Research (R) mode allows the user to specify a more complete array of inputs and provides more detailed output which is useful for case studies. The Production (P) mode is used to process multiple cases and is primarily executed in a batch environment as described in Section 5.1.2.

4. - (ORP;CW)

METEOROLOGICAL DATA FILE FORMAT IS (WMO, FREE-FIELD):

The default is the world-wide standard WMO format described in Section 5.3. For Production mode runs, multiple cases (data sets) may be

stacked in the file provided each data set is separated by a logical end of file (zero length record). Because Production mode runs require a response to prompt 4 for each case, both WMO and free-field formatted cases may be contained in the same file.

5. - (P;CW)

ENTER NUMBER OF RUNS TO BE MADE (1):

This display only occurs for production mode runs and asks for the number of cases you wish to process. The default value is given in parenthesis. There must be this number of data cases stacked in the file referenced in Display 4.

6. - (ORP;CW)

ENTER MODEL TYPE (CONCENTRATION/DOS., WASHOUT DEP.):

The HARM program contains two different dispersion model options. The user has the option of either calculating concentration, dosage and time average concentration (C) or deposition due to washout by precipitation (W).

7. - (OKP;CW)

ENTER ACCIDENT TIME AND DATE (1000 EST 22 MAR 1982):

The program uses the current time and date for the default displayed in parenthesis. If you desire to enter another time and date or change any part of the default, the values are entered immediately below the corresponding time, day, month, etc. of the default display. Abbre-

viations for the month are - JAN, FEB, MAR, APR, MAY, JUN, JUL, AUG, SEP, OCT, NOV, DEC.

8. - (ORP;CW)

ACCIDENT OCCURRED IN A SILO/OPEN FIELD:

The following entries through Display 13 define the conditions existing at the moment of the hypergolic reaction and therefore are the determining factors in the calculation of cloud composition, size and heat content. Enter the answer most closely describing the accident description. If the accident occurred above ground the program skips to Display 12.

9. - (ORP;CW)

SECOND STAGE EJECTION (NO/HEIGHT):

The HARM model allows the user to enter the height in meters above ground level (AGL) at which the ejected second stage detonated. An entry of (N) for no ejection or a detonation height  $\leq 0.0$  will cause the program to include the propellant in the second stage with that of the first stage in the computation of the fireball parameters (see Section 2.2).

10. - (ORP;CW)

REACTION WAS SLOW LEAK/INSTANTANEOUS:

In reactions where the oxidizer to fuel ratio is less than the stoichiometric ratio, the initial rate of reaction determines the fate of the hydrazine component of the fuel. If the accident was not initiated by the rapid mixing of large quantities of fuel and oxidizer, the slow leak option should be chosen.

11. - (ORP;CW)

SILO DOOR WAS CLOSED/OPEN:

A reaction in a silo with the door closed takes place at a higher pressure than one with the door open, resulting in different reaction products and different final proportions of chemical species.

12. - (ORP;CW)

POUNDS FUEL IN REACTION; (DEFAULT=106500):

The default is the total amount of A-50 fuel contained in the first and second stage of a Titan II missile ready for launch, enter only the amount of fuel consumed in the reaction. If the second stage was ejected and detonated above the ground, then the fuel on board both stages should be entered here. The program automatically allots fuel to the first and second stages in approximately an 80-20 ratio.

13. - (ORP;CW)

POUNDS OXIDIZER IN REACTION: (DEFAULT=201015):

The default is the total amount of NTO contained in the first and second stages of a Titan II missile ready for launch. Enter only the amount of oxidizer consumed in the reaction. The second stage ejection is treated in a similar way as explained under Display 12 above.

14. - (R;CW)

ENTER CLOUD SHAPE (SPHERICAL, ELLIPTICAL):

This parameter defines the shape of the cloud and the distribution of source material. The option allows an Elliptical (E) shape

and a uniform vertical distribution of source material in each Kth meteorological layer (see Section 3.2). The default is a spherical (S) shape with a Gaussian vertical distribution of material within the cloud. We suggest the (S) option be used for most accidents and the (E) option be used only when there is evidence that no residual material remained near the ground.

15. - (R;CW)

ENTER GAMMAX, GAMMAY, GAMMAZ (0.64, 0.64, 0.64):

These entrainment parameters control the growth of the cloud between formation and stabilization in the alongwind, crosswind and vertical directions respectively. The default values are (0.64, 0.64, 0.64).

16. - (ORP;CW)

ENTER ACCIDENT SITE LOCATION (UTM COORDINATES IN KILOMETERS):

Enter the Universal Transverse Mercator (UTM) coordinates of the accident site as a pair of numbers separated by a comma with the UTM east coordinate first followed by the UTM north coordinate. The UTM coordinates in meters may readily be determined from the standard USGS series of topographical maps. Divide the values found on the maps by 1000 (conversion from meters to kilometers) and enter the resulting numbers. If the users facility has a plotting capability and a standard hazard map exists, the accident site coordinates will be checked to see if they are within the map boundaries. If not, then the following message is displayed:

ACCIDENT SITE LOCATION IS OUTSIDE OF LOCAL MAP  
CONTINUE? (Y/N):

The default response proceeds with data entry. The negative (N) response causes a return to Display 16 to correct the accident site location.

17. - (ORP;C)

DO CALCULATIONS AT? (SURFACE, STABILIZATION, DEFAULT=0.0 METERS):

This display only appears for concentration/dosage calculations. Washout deposition is calculated only at the surface. An entry of (S) results in calculations of concentration/dosage at the surface. An entry of (ST) results in calculations performed at the cloud stabilization height. If a numerical quantity is entered, the calculations are performed at the entered height.

18. - (R;CW)

ENTER REFLECTION COEFFICIENT (DEF.=TOTAL=1.0):

Enter the fraction of material reflected at the surface. The value entered here refers to the fraction of vapor material reflected at the ground surface and/or the base of an upper layer. The default value is total reflection or unity.

19. - (R;CW)

ENTER DIFFUSION COEFFICIENTS (ALPHA=1.0, BETA=1.0):

This option permits the user to change the coefficients of the crosswind  $\alpha$  and vertical  $\beta$  cloud expansion coefficients from the default values to values other than unity.

20. - (R;CW)

ENTER DOWNWIND EXPANSION DISTANCES (XRY=100.0 XRZ=100.0):

This option permits the user to change the alongwind distance in meters over which rectilinear cloud expansion in the crosswind and/or

vertical directions occurs (see Equations 4-2 and 4-4). If a change is desired, enter a pair of numbers for XRY, XRZ respectively.

21. - (R;C)

ENTER CONCENTRATION AVERAGING TIME (TIMAV=600.0 SEC.):

This option allows the user to change the time over which peak time-mean concentration is calculated (see Equation 4-11). The default value is shown in parenthesis. If a change is desired, enter the new time.

22. - (ORP;W)

CALCULATE (MAXIMUM POSSIBLE, TIME-DEPENDENT) WASHOUT DEPOSITION?:

This display appears only for calculations of washout deposition. Maximum possible (M) produces the maximum possible deposition on the ground due to precipitation scavenging independent of the time when precipitation begins ( $t_1 = x/u_L$  in Equation 4-12). Time dependent (T) washout deposition produces the deposition on the ground due to precipitation scavenging that begins at the time  $t_1$  specified in Display 25.

23. - (ORP;W)

ENTER RAINFALL RATE (HEAVY, MODERATE, LIGHT, ANOTHER INCHES PER HOUR):

This display appears only for washout deposition and asks for the rainfall rate in inches per hour. The standard rates of heavy, moderate and light correspond to 0.3, 0.2 and 0.1 inches per hour respectively. If the user wishes to specify a different rainfall rate, enter the rate in inches per hour.

24. - (R;W)

ENTER RAINFALL SCAVENGING COEFFICIENT (LAMBDA=4.572E-04):

The rainfall scavenging coefficient  $\Lambda$  appearing in Equation 4-12 has units of  $s^{-1}$  and is determined from Equation 4-17 depending on the value of R in Display 23. The value of  $\Lambda$  in parenthesis above (LAMBDA=4.572E-04) is for heavy rain (R=0.3 in/hr in Display 23). If the user desires to use a value of  $\Lambda$  other than the value calculated using Equation 4-17, the desired value must be entered here.

25. - (ORP;W)

ENTER TIME RAIN STARTS AFTER ACCIDENT (TIME1=0.00 MINUTES):

This display appears only for time-dependent washout deposition. The default time of start of precipitation is displayed in parenthesis. If the user wishes to specify the start time, enter the time desired.

26. - (R;CW)

PRINT DETAIL MODEL PARAMETERS? (NO,YES):

This option allows the user to select a summary or detailed print-output and is available only in the research mode.

27. - (ORP;CW)

At this point the input parameters have been selected and HARM displays all of the parameters and program options selected for review.

DO YOU WISH TO CONTINUE WITH THE MODEL CALCULATIONS? (YES/NO):

If a review of the displayed program options and parameters discloses an error, the user has two options: 1) either use "BA" repeatedly to back up

to the prompt for the parameter or option needing correction or 2) enter (N) to restart HARM.

28. - (ORP;CW)

DO YOU WISH TO PLOT THE METEOROLOGICAL PROFILE (YES,NO):

The meteorological data profile is used to assess the quality of the rawinsonde data and to determine the height of the layer boundaries to be used in the dispersion calculations. The program plots vertical profiles of wind direction, wind speed, temperature and virtual potential temperature as well as the dimensions of the stabilized cloud layer projected on a vertical plane extending from the accident site in the direction of the mean wind direction in the lowest layer. (Examples are given in Appendix A).

29. - (ORP;CW)

MOUNT A METEOROLOGICAL PROFILE FORM ON PLOTTER LU##  
SPACE - RETURN WHEN READY  
ENTER F TO PLOT THE FORM:

This display appears only when (Y) is given in response to Display 28 above. The logical unit to which the program sends the plot is given by ## in Display 29. A meteorological profile form or blank paper must be mounted on the plotter and the plotter left in a ready state before a response is entered to this display. Forms generation for meteorological profiles is discussed further in Section 5.2.

30. - (ORP;CW)

HEIGHT AT THE TOP OF THE UPPER LAYER (METERS):	3048.00
HEIGHT AT THE BASE OF THE UPPER LAYER (METERS):	2438.40
HEIGHT AT THE TOP OF THE LOWER LAYER (METERS):	2438.40
+ + + + + STABILIZATION HEIGHT + + + + +	1246.39
+ + + + + CALCULATION HEIGHT + + + + +	0.00
HEIGHT AT THE BASE OF THE LOWER LAYER (METERS):	0.00
DO YOU WISH TO CHANGE (NEITHER,UPPER,LOWER) TRANSITION LAYER:	

The HARM program uses two major meteorologically defined layers as discussed in Section 2.3. The boundaries of these layers must coincide with heights reported in the rawinsonde data file. If the user selects any height other than those shown in Display 30 above, the program will automatically select the height from the rawinsonde data file closest to the value entered by the user in the following displays. The program sets the base of the lower layer to 0 (surface) and defaults to twice the cloud stabilization height for the top of the lower layer. The program also uses the top of the lower layer as a default value for the base of the upper layer and sets the top of the upper layer to the highest rawinsonde measurement level read by the program (nominally 3000 m). These layer heights are used as defaults because a value for the height of the top of the lower layer between the stabilization height and twice the stabilization height maximizes ground-level vapor concentrations. However, the user is expected to alter the default values of the base and top of the major layers based on the print output of the rawinsonde data, the plot of the meteorological profile, or forecasts of meteorological conditions at the time of the accident. The user should generally select the height of the base of an elevated inversion to represent the top of the lower layer and base of the upper layer. It should be noted that the primary function of selecting the top of the lower layer is to represent a boundary to turbulent mixing. For this reason, the temperature should begin to increase or remain constant above the selected height for at least 50 to 100 m. The primary purpose of the HARM program is to assist users in estimating environmental effects. The user must, therefore, reflect on the expected effects of the selected layer heights on the calculated concentration/dosage levels. For this reason, the user should likely ignore surface-based inversions or elevated inversions with tops less than a few hundred meters above the surface in the selection of the top of the lower layer unless there is very strong evidence that the cloud above this layer will not penetrate to the surface. Also, if the model is being used to estimate concentrations at the flight level of sampling aircraft and this flight level is in an elevated inversion, the base and top of the upper layer should correspond to the base and top of the elevated inversion. If there

is no elevated inversion, the user can specify a single layer by entering 0 for the top or bottom of the upper layer or by changing the top of the lower layer to a height greater than the calculation height. Also the user is cautioned to limit the top of the upper layer to the height precipitation originates when calculating washout deposition.

31. - (ORP;CW)

ENTER THE HEIGHT AT THE TOP OF THE LOWER LAYER (DEFAULT=2438.40 METERS):

The program will use the height from the rawinsonde data file closest to the value entered here. If the value entered here equals the top of the sounding, the program assumes that only a single layer is being considered and will set both the top and base of the upper layer to zero. If the value entered is greater than the base of the upper layer, producing a region of overlap between the layers, the program changes the height of the base of the upper layer to the value entered, removes the overlap and goes to Display 30. If the value entered produces a gap between layers the program goes to Display 33 if concentration/dosage is being calculated. If washout deposition is being calculated, the program automatically removes the gap by changing the base of the upper layer to the value entered and then goes to Display 30.

32. - (ORP;CW)

DO YOU WISH TO CHANGE (T,B) HEIGHT OF THE UPPER LAYER:

Options to modify either the height of the top (T) or base (B) of the upper layer.

33. - (ORP;CW)

ENTER THE HEIGHT AT THE BASE OF THE UPPER LAYER (DEFAULT=2438.40 METERS):

The program will use the height from the rawinsonde data field closest to the value entered here. If the value entered equals zero,

the program assumes that only a single layer is being considered and will set the top of the upper layer to zero and, if the top of the lower layer is less than the top of the sounding, will go to Display 31. Otherwise the program will go to Display 30. If the value entered is less than the top of the lower layer, producing a region of overlap between the layers, the program changes the height of the top of the lower layer to the value entered, removes the overlap and goes to Display 30. If the value entered produces a gap between layers, the program goes to Display 31 if concentration/dosage is being calculated. If washout deposition is being calculated, the program automatically removes the gap by changing the top of the lower layer to the value entered and then goes to Display 30.

34. - (ORG;CW)

ENTER THE HEIGHT AT THE TOP OF THE UPPER LAYER (DEFAULT=3048.00 METERS):

The program will use the height from the rawinsonde data file closest to the value entered here. If 0 is entered the program assumes that only a single layer is being considered. If the height entered is less than the top of the sounding or 3048 m, whichever is less, the program asks for confirmation by repeating Display 34. Other conditions which are checked are: Calculation height must be below the top of the highest layer defined; the top of the upper layer if used, must be higher than the top of the lower layer.

35. - (ORP;CW)

ENTER SIGMA AZ, SIGMA EL (13.82 DEG):

The default turbulent intensity SIGMA AZ and SIGMA EL value shown in parenthesis are the program's approximation to the standard deviation of the azimuth and elevation wind directions at a height of approximately 5 m. The SIGMA AZ value corresponds to  $\sigma'_{AR}(\tau_o=600)$  in Equation 3-44. The program follows the rules outlined in Section 3.3 for calculating and

assigning SIGMA AZ values to the meteorological sounding levels. If the user is in the Research mode and does not intend to input SIGMA AZ at each sounding level (see Display 36 below), the program calculates the SIGMA AZ at each sounding level using the same rules specified in Section 3.3.3 (Equations 3-55 and 3-56) as if the program had selected  $\sigma'_{AR}(\tau_0=600 \text{ s})$ . However, if the user is in the Research mode and intends to input SIGMA AZ at each sounding level in Display 36, the value entered here is used unmodified as the value at the base of the first meteorological sounding layer and the remaining values are entered in Display 36 below.

The default value of SIGMA EL shown in parenthesis is identical to the defaulted value of SIGMA AZ. This value of SIGMA EL is automatically treated similarly to SIGMA AZ in the program. That is, the layer values used in the program are derived from this input using the same rules given by Equations 3-52 through 3-56 under the assumption that, after the rules have been followed, the turbulence over the layer depths of interest is isotropic. However, if the user is running in the Research mode and chooses to input SIGMA EL at each sounding level in Display 36 below, the value entered here is used unmodified as the value at the base of the first meteorological layer and the remaining values are entered in Display 36.

36. - (R;CW)

DO YOU WISH TO INPUT SIGMA A & SIGMA E FOR EACH LEVEL? (NO,YES):

When SIGMA A AND SIGMA E values are entered for each meteorological sounding level, the program uses a height-weighted mean (similar to Equation 3-54) to calculate the value used within each meteorological layer. If the user desires to enter the SIGMA A AND SIGMA E values, enter a (Y) here and enter the values for sounding level 2 through the top sounding level in Display 37. The program assumes the values for level 1 (surface) were entered in Display 35 above.

37. - (R;CW)

ENTER SIGMA A, SIGMA E (IN DEG) FOR LEVEL ## (20.000,20.000):

Enter the values for SIGMA A and SIGMA E respectively, in degrees and separated by a comma. The display gives the level number as ## and the default values shown in parenthesis. The program will repeat this display for each meteorological sounding level.

At this point, values for all of the program variables and options have been entered and the calculations are being performed. After a short period of time during which the line

NAME MODEL PROCESSING RANGE AT N000 METERS

is displayed once for each range at which calculations are made, the program prints the centerline values of concentration, dosage, time-mean concentration or washout deposition. Here "NAME" will be either "CONCENTRATION/DOSAGE" or "WASHOUT DEPOSITION" and "N000" will be the range from the accident site where "N" is the distance in kilometers.

38. - (OR;CW)

DO YOU WISH TO PLOT MAXIMUM CENTERLINES? (YES,NO):

This option enables the user to plot maximum centerline profiles of concentration, dosage, time-mean concentrations or washout deposition.

39. - (OR;CW)

MOUNT A CENTERLINE PROFILE FORM ON PLOTTER LU ##  
SPACE - RETURN WHEN READY  
ENTER F TO PLOT THE FORM:

Mount a maximum centerline profile form or blank paper (see Section 5.2) on the plotter with the logical unit number specified by ## in

the display. Make sure the plotter is ready to receive commands prior to entering  $\nabla C_R$  if a form is mounted or prior to entering (F) if a blank sheet of paper is mounted.

40. - (OR;CW)

PLOT MAXIMUM CENTERLINE VALUES FOR: (NO2,N2H4,UDMH,NDMA,FDH):

This display will appear only if there is more than one species present. Only species present will be displayed.

41. - (OR;CW)

DO YOU WISH TO PLOT CENTERLINE PROFILES FOR ANOTHER SPECIES? (YES, NO):

This option enables the user to replot the just completed profile or to plot a maximum centerline concentration, dosage, time-mean concentration or washout deposition profile for another species.

42. - (OR;CW)

DO YOU WISH TO PLOT ISOPLETHS? (YES,NO):

This option allows the user to plot isopleth patterns of concentration, dosage, time-mean concentration or washout deposition.

43. - (OR;C)

PLOT ISOPLETHS OF: (CONCENTRATION,DOSAGE,TIME MEAN CONCENTRATION)

This option is displayed only if concentration has been calculated.

44. - (OR;CW)

PLOT ISOPLETHS FOR: (NO2,N2H4,UDMH,NDMA,FDH)

This option is displayed only if there is more than one species present. Only species present will be displayed.

45. - (OR;W)

PLOT ISOPLETHS FOR SUM OF LAYERS OR LOWER LAYER OR UPPER LAYER?:

Washout deposition on the ground is calculated as the contribution from the lower layer, the upper layer or the total given as the sum of layers. This option allows the user to plot the contribution of each layer separately or the total deposition and the default is the total deposition (sum of layers).

46. - (OR;CW)

MAXIMUM CONCENTRATION OF N2H4 = .9723	PPM
DEFAULT ISOPLETHS ARE: .9723E-01	PPM
.2917	PPM
.4862	PPM
.6806	PPM
.8751	PPM

ENTER FIRST ISOPLETH VALUE (SPACE - RETURN FOR DEFAULTS)

This display shows the maximum value of the quantity (concentration) calculated by the program for the species (N2H4) to be plotted. Also, default isopleth levels chosen by the program are shown. If the user chooses to use the defaults,  $VC_R$  is entered. However, if the user wishes to specify the isopleth levels, the first specified value (in the same units as shown in the display) is entered at this point. The second through tenth values are then entered in Display 47 below.

47. (OR;CW)

ENTER SECOND ISOPLETH VALUE (SPACE - RETURN TO TERMINATE ISOPLETH INPUTS)

Upon entering the second isopleth value, the program will return to this display replacing the word SECOND by THIRD, THIRD by FOURTH, etc. until  $VC_R$  is entered or until ten values have been entered.

48. - (OR;CW)

DO YOU WISH TO PLOT ISOPLETHS FOR ANOTHER VARIABLE  
OR SPECIES? (VARIABLE, SPECIES, NEITHER):

This option allows the user to plot isopleths of any combination of variables or species. The word variable applies only to concentration, dosage and time-mean concentration. When calculating washout deposition entering either a (V) or an (S) will allow plotting of an alternate species.

49. - (ORP;CW)

DO YOU WISH DISCRETE RECEPTOR CALCULATIONS? (YES,NO,LU# OF DATA FILE):

This option allows the user to calculate values of concentration, dosage, time-mean concentration or washout deposition at a specified location relative to the accident site. If the user wishes to enter the discrete receptors interactively, a (Y) is entered and the location is entered in Display 50. If the user desires to enter the receptors from a data file, the logical unit number previously equated with the receptor data file is entered at this point. The discrete receptor data file contains a maximum of 50 discrete receptors. Each discrete receptor is entered on a new line (record) in the following format -

RANGE(METERS),AZIMUTH(DEGREES),HEIGHT(METERS),COMMENTS

Type the range to the receptor in meters relative to the accident site followed by a comma. Type the azimuth bearing in degrees measured in the clockwise direction from 0 degrees north relative to the accident site. Also, if concentration/dosage is being calculated by the program, the user can specify the calculation height by entering a comma after the azimuth

entry followed by the calculation height. Comment information may be entered in columns 31 through 50 and is printed along with the results of each receptor point. If you do not enter 50 points in the discrete receptor data file, the last image in the file must be a -1 beginning in column 1.

50. (ORP;CW)

ENTER DISCRETE RECEPTOR LOCATION RELATIVE TO ACCIDENT  
SITE. A 20 CHAR. COMMENT MAY BE ENTERED STARTING  
UNDER THE ASTERISK. \*  
RANGE(M), BEARING(DEG), HEIGHT(M):

The word HEIGHT does not appear for washout deposition calculations because this quantity can only be calculated at the surface. The range is entered in meters relative to the accident site and is followed by a comma. The bearing is entered in degrees and is measured relative to the accident site in a clockwise direction from 0 degrees north and is followed by a comma if the height is to be entered. Enter the calculation height in meters only for concentration calculations. If comment information (town name, etc.) is desired, begin the comment immediately under the asterisk that appears on your CRT screen or TTY page by entering spaces following the height or bearing. A maximum of 20 comment characters per discrete point are saved for print output. As each discrete receptor location is entered, there will be a short pause to calculate the quantity. The program will then display the calculation results on the CRT or TTY and print the results or save for later printing depending on previous options.

51. - (ORP;CW)

DO YOU WISH TO ENTER ANOTHER DISCRETE RECEPTOR LOCATION?  
(YES,NO):

This display appears only if the answer to display 50 was yes (Y) and allows you to return to enter up to 50 discrete receptors interactively.

52. - (OR;C)

DO YOU WISH RESULTS FOR ANOTHER CALCULATION HEIGHT (Y,N):

This display asks whether or not the user wishes to calculate concentration at another height. If (Y) is entered, the program returns to Display 17, then skips to Display 26 to continue processing.

53. - (OR;W)

DO YOU WISH TO CHANGE WASHOUT DEPOSITION  
CALCULATION TYPE? (Y,N):

This display asks whether the user wishes to change the washout deposition calculation from maximum to time-dependent or from time-dependent to maximum. If you enter a (Y), the program will return to Display 22.

54. - (ORP;CW)

DO YOU WISH TO PROCESS ANOTHER METEOROLOGICAL CASE (Y,N):

This is the last HARM display and asks whether the user wishes to continue with another meteorological data case. If (N) is entered, the program terminates. If (Y) is entered, the program restarts at Display 1.

### 5.1.2 Batch Processing

The HARM computer executes in batch environment when the input logical unit number specified by DATA UNIT is a non-interactive device (card reader, magnetic tape, paper tape, disc file, etc.). The program can be executed completely as a batch run or may require some interactive input depending on the user selected options. All messages and interactive displays are written to the logical unit from which the batch run was initiated.

After being scheduled, the HARM program prints the following message with system log device or scheduling logical unit:

```
*****
*****          HYPERGOLIC ACCIDENTAL RELEASE MODEL          *****
*****                      HARM                      *****
*****          UPDATE###          LOCATION HEC          *****
*****          ENTER BA TO CHANGE PREVIOUS INPUT VALUE.    *****
*****          ENTER RS TO START AT BEGINNING OF PROGRAM.  *****
*****          ENTER EX TO ABORT PROGRAM.                  *****
*****          THE FIRST INPUT OPTION SHOWN IS THE DEFAULT  *****
*****
```

Where the value of ### is the update level of the copy of HARM you are executing. The reminders in the above display (a "BA" returns to a previous display option and "RS" restarts the program) are applicable in the batch environment only when the program solicits an interactive response and only "BA" should be used. In the following text, each input option is shown with the respective record or reference number. These record numbers are the same as those given in Section 5.1.1 under Interactive Processing. In addition, each record number is accompanied by a code in parenthesis (OP;CW). The letters O and P that appear prior to the semicolon indicate if the input option is required for the Operational and/or Production modes of operation. The letters C and/or W indicate if the option is required for concentration or washout deposition. An optional parameter must be present in the input data file if the record code for that parameter contains the letter (O, P, C, or W) of an option chosen by the user. In setting up the input batch data file, the following conventions must be observed:

- The first option shown in the record description below is the default option, unless stated otherwise in the explanation of the option. The default option is obtained by entering  $\nabla C_R$  (space return).
- For input options where multiple values are required, the values are positional and each must be separated by a comma.

Two consecutive commas indicate an empty field with the respective variable being defaulted.

- Input options that require an interactive response are treated in the same manner as outlined in Section 5.1.1 under Interactive Processing.
- All input options and values typed into the input data file must begin in column 1 of each new record.

Enter the HARM input control data in the following order:

1. - (ORP;CW)

ENTER DATA UNIT, MET. DATA UNIT, OUTPUT UNIT, PLOT UNITS (UP TO THREE)  
DEFAULTS ARE: 1, 8, 6, 12, 12, 12.

where

DATA UNIT - Logical input number from which the HARM program is to read the input data and control information. The number specified determines whether the program will execute in an interactive or batch environment. If the number entered (or default) is the logical unit number of an interactive device (CRT, TTY, etc.), the program assumes an interactive environment and solicits all input data and commands via displays to the device specified by DATA UNIT. The default is obtained by typing a comma indicating an empty field. The default logical unit will then be the unit from which the HARM program was scheduled. If the number entered for DATA UNIT is the logical unit number of a non-interactive device (magnetic tape, card reader, paper tape, etc.) or a number equated with a disc file, the program assumes a batch

DATA UNIT (Cont.) environment. The program will be completely batch or will require some interactive user input, depending on the input data. All program interactive messages and displays are written to the unit from which the batch run was initiated. See Section 5.2 for special input values for DATA UNIT used for generating meteorological and maximum centerline plot forms.

MET. DATA UNIT Logical unit number previously equated to the file containing the meteorological upper-air (rawinsonde) data.

OUTPUT UNIT - Logical unit number for print output. The default printer unit (6) is obtained by typing a comma indicating an empty field.

PLOT UNIT 1 - Logical unit number for meteorological profile plot output. The default unit (12) is obtained by typing a comma indicating an empty field.

PLCT UNIT 2 - Logical unit number for maximum centerline (concentration, dosage, deposition) profile plot output. The default unit (12) is obtained by typing a comma indicating an empty field.

PLOT UNIT 3 - Logical unit number for isopleth (concentration, dosage, deposition) plot output. The default unit (12) is obtained by typing a comma indicating an empty field.

2. - (OP;CW)

RUN TITLE - A title of up to 48 characters in length may be entered. This title will appear in all headers printed to the output unit. The default is a blank line.

3. - (OP;CW)

Run Type - Enter (O) (default) for operational or (P) for production mode. Note that batch processing does not allow a research mode.

4. - (OP;CW)

Meteorological - Enter (W) for WMO or (F) for free-field to designate  
Date File Format the format of the next data set to be read. For Production mode runs, multiple cases (data sets) may be stacked in the file equated with the MET. DATA UNIT provided each data set is separated by a logical end of file (zero length record). The Operational mode processes only one case per program execution.

5. - (P;CW)

Number of - Under the Production mode only, enter the number of  
Runs data cases to be processed from the file specified in Record 4. The default value is 1.

6. - (OP;CW)

Model - Enter a (C) (default) for concentration, dosage and time-mean concentration. Enter a (W) for washout deposition.

7. - (OP;CW)

Accident Date - Enter the accident time and date or leave a blank record for the default. The HARM program assumes the current time is the default time and date. The format

7. - (OP;CW)  
(Cont.)

of the default time and date is the same as that used  
to enter the date here and is

HHHVESTVDDVMMVYYYY

where:

HHHH - the hour (1000)

EST - Eastern standard Time, but may be entered  
as LST, PST, etc.

DD - the day (22)

MMM - the month, selected from - JAN, FEB, MAR,  
APR, MAY, JUN, JUL, AUG, SEP, OCT, NOV, DEC

YYYY - the year (1982)

V - space

Entries made in Records 8 through 13 define the conditions  
existing at the moment of the hypergolic reaction and therefore are the  
determining factors in the calculation of cloud composition, size and heat  
content. Enter the answer most closely describing the accident description.  
If the accident occurred above ground, the program skips to Record 12.

8. - (OP;CW)

Accident Location- Enter (S) if the accident occurred in a silo and (0) if  
the accident occurred above ground.

9. - (OP;CW)

Stage Ejection - Enter the height in meters AGI at which the ejected  
second stage detonated. An entry of (N) for no ejection

9. - (OP;CW)  
(Cont.)

or a detonation height  $\leq 0.0$  will cause the program to include the propellant in the second stage with that of the first stage in the computation of the fireball parameters.

10. - (OP;CW)

Reaction Rate - Enter (S) if the reaction was initiated by a slow leak; enter (I) if the reaction was initiated by the rapid mixing of fuel and oxidizer. If the accident was not initiated by the rapid mixing of large quantities of fuel and oxidizer, the slow leak option should be chosen.

11. - (OP;CW)

Silo Door - Enter (C) if the silo door was closed; enter (O) if the  
Position door was open. A reaction in a silo with the door closed takes place at higher pressure than one with the door open, resulting in different reaction products and different final proportions of chemical species.

12. - (OP;CW)

Fuel Weight - The default is the total amount of A-50 fuel in pounds contained in the first and second stage of a Titan II missile ready for launch, enter only the amount of fuel consumed in the reaction. If the second stage was ejected and detonated above the ground, then the fuel on board both stages should be entered here. The program automatically allots fuel to the first and second stages in approximately an 80-20 ratio.

13. - (OP;CW)

**Oxidizer Weight** - The default is the total amount of NTO in pounds contained in the first and second stages of a Titan II missile ready for launch, enter only the amount of oxidizer consumed in the reaction. The second stage ejection is treated in a similar way as explained under Record 12.

(Records 14 and 15 are not used in batch operations)

16. - (OP;CW)

**Accident Site -  
Coordinates** Enter the Universal Transverse Mercator (UTM) coordinates of the accident site as a pair of numbers separated by a comma with the UTM east coordinate first followed by the UTM north coordinate. The UTM coordinates in meters may readily be determined from the standard USGS series of topographical maps. Divide the values found on the maps by 1000 (conversion from meters to kilometers) and enter the resulting numbers. If the users facility has a plotting capability and a standard hazard map exists, the accident site coordinates will be checked to see whether they are within the map boundaries. If not, then the following message is printed:

ACCIDENT SITE LOCATION IS OUTSIDE OF LOCAL MAP

17. - (OP;C)

**Calculation -  
Height** This record is required only for concentration/dosage calculations. Washout deposition is calculated only at the surface. An entry of (S) results in calculations

17. - (OP;C) at the surface, (ST) in calculations at the cloud  
(Cont.) stabilization height and any numerical entry will  
result in calculations at the entered height.

(Records 18 through 21 are not used in batch operations.)

22. - (OP;W)

Washout - This record is required only for calculations of  
Deposition Type washout deposition. Maximum possible (M) produces the  
maximum possible deposition on the ground due to  
precipitation scavenging independent of the time when  
precipitation begins ( $t_1 = x/u_L$  in Equation 4-12). Time  
dependent (T) washout deposition produces the deposi-  
tion on the ground due to precipitation scavenging that  
begins at the time  $t_1$  specified in Record 25.

23. - (OP;W)

Rainfall Rate - This record is used only for washout deposition. Enter  
the rainfall rate in inches per hour. The standard  
rates of heavy (H), moderate (M) and light (L) corre-  
spond to 0.3, 0.2 and 0.1 inches per hour respectively.  
These rates may be selected by entering the appropriate  
letter.

(Record 24 is not used in batch operations)

25. - (OP;W)

Time Rain Starts - This record is used only for time-dependent washout  
deposition. To specify the start time, enter the time  
desired.

(Records 26 and 27 are not used in batch operations)

28. - (OP;CW)

Plot Meteorological Profile - Enter (Y) (default) for yes, (N) for no or (F), which specifies the profile form also be plotted. Meteorological profiles are plotted on the logical unit specified by PLOT UNIT 1 in the run command.

(Record 29 is not used in batch operations)

30. - (OP;CW)

Boundary Layering - Because the default boundary layer values are not known a priori, enter (Y) to display the default boundary layer values. Any other entry causes the program to use the default boundary layer values and go to Record 35. When a (Y) is entered, the program temporarily enters interactive processing. The program will then interactively prompt the user for the layer values in the same manner indicated under Display 30 through 34 under Interactive Processing, Section 5.1.1. At the end of interactive processing, the program continues with Record 35.

35. - (OP;CW)

Wind Direction Standard Deviation - Because the default SIGMA(A) and SIGMA(E) values are not known a priori, enter (A) to display the default values and interactively modify them if desired.

Any other entry will cause the program to use the default values and go to Record 38.

(For a Production run, Records 38 and 42 are not entered)

(Records 36 and 37 are not used in batch operations.)

38. - (O;CW)

Plot Maximum Centerline - Enter (Y) (default) for yes, (N) for no or (F), which specifies the maximum centerline form also be plotted. If (Y) or (F) is entered, the program enters interactive processing and will remain there during the plotting of all maximum centerline displays. The interactive prompt displays for maximum centerline plotting are shown in Display 39 through 41 under Interactive Processing, Section 5.1.1. All maximum centerline plots are plotted on the logical unit specified by PLOT UNIT 2 in the run command.

42. - (O;CW)

Plot Isopleths - Enter (Y) (default) for yes or (N) for no. If (Y) is entered, the program enters interactive processing and will remain there during all isopleth plotting. The interactive prompt displays for isopleths are shown in Display 43 through 48 under Interactive Processing, Section 5.1.1. All isopleth plots are plotted on the logical unit specified by PLOT UNIT 3 in the run command.

49. - (OP;CW)

Discrete Receptors - Enter (Y) (default) for yes, (N) for no or the logical unit number of the data file containing the discrete receptors. If (Y) is entered, the program enters interactive processing and prompts the user for the discrete receptors as shown in Displays 50 and 51 under Interactive Processing, Section 5.1.1. If a logical

49. - (OP;CW)  
(Cont.)

unit number is entered, the program will read all discrete receptor points from successive records from that unit in the following format

RANGE(M),AZIMUTH(DEG),HEIGHT(M),COMMENTS

Enter the range in meters to the receptor relative to the accident site. Enter the azimuth bearing in degrees to the receptor, measured clockwise from 0 degrees north relative to the accident site. Enter the height in meters only if this is a concentration calculation. These three values are separated by commas and begin in column 1 of the record. A maximum of 20 characters of comment information may be entered beginning in column 31. There are a maximum of 50 discrete points possible and if you have less than 50 points, the last discrete point must be followed by a record containing -1.

(Records 50 and 51 are not used in batch operations.)

52. - (O;C)

Another Calculation Height - Enter (Y) if calculations for another height are desired or (N) if not. If (Y) is entered, the new height is entered in a record immediately following this record and a continued data file must be built starting with Record 18 above.

53. - (O;W)

Another Washout Deposition Type - Enter (Y) if an alternate washout deposition calculation type is desired (maximum possible or time-dependent) or (N) if not. If (Y) is entered, this record must be followed with a continued data file starting with Record 22.

54. - (OP;CW)

Another Case - Enter (Y) (default) if the program is to continue with another data case or file containing multiple cases. An (N) terminates the program. If (Y) is entered, the input data file must be continued from Record 1.

## 5.2 PLOT FORMS GENERATION

The HARM computer program has the option of generating plot forms for the meteorological profiles and for the maximum centerline (concentration, dosage and deposition) profiles independent from the normal program operations. Prior to executing the program, prepare the plotter to receive the plot because the HARM program starts to plot immediately upon execution.

To generate meteorological profile forms, enter 99 as the output unit number in response to Display 1

At the completion of each plot form, the program will display the following message on your interactive unit:

DO YOU WANT TO PLOT ANOTHER METEOROLOGICAL PROFILE FORM?  
CHANGE PLOT PAPER BEFORE A YES (YES OR NO)

The default reply is (Y) and will continue to plot forms as long as you desire. An (N) response terminates the HARM program.

To generate maximum centerline profile forms enter 98 as the output unit number in response to Display 1.

At the completion of each plot form, the program will display the following message on your interactive unit.

DO YOU WANT TO PLOT ANOTHER CENTERLINE PROFILE FORM?  
CHANGE PLOT PAPER BEFORE A YES (YES OR NO)

The default reply is (Y) and will continue to plot forms as long as you desire. An (N) response terminates the HARM program.

### 5.3 DESCRIPTION OF METEOROLOGICAL DATA FORMATS

The HARM program accepts rawinsonde data in two formats: 1) The world-wide standard as defined by the World Meteorological Organization (WMO) and used by the National Weather Service for dissemination within the United States and 2) a plain language unencoded format useful for entering data from the archived data available from the National Climatic Center.

The WMO data format is designed for transmitting meteorological information rapidly and accurately and therefore the information is encoded. The procedures for encoding the data may be found in the Manual on Codes, Volumes 1 and 2 available from the World Meteorological Organization and are used by the National Weather Service and the Air Weather Service. Algorithms to decode FM35-V TEMP (upper-level pressure, temperature, humidity and wind report from a land station) and FM32-V PILOT (upper-wind report from a land station) are included in HARM. These two code forms each are divided into four parts, two parts contain data for levels at or below 100 hPa (about 50,000 ft) and two parts for levels above 100 hPa (1 hPa = 1 mb). The algorithms are designed to ignore those parts for levels above 100 hPa and decode only the standard and significant data levels at or below 100 hPa. The algorithms then discard all data above the first reported level greater than 3000 m (about 10,000 ft) above ground level. An example of a typical transmission is shown in Figure 5-1. The ability to decode these standard forms permits HARM to access the required rawinsonde data with a minimum of operator involvement.

The other format represents all data in plain language and uses positional information in assigning values to variables. This format is designed to permit rapid transcription of data from the hard copies of archived rawinsonde data as supplied by the National Climatic Center. The

TTAA	62157	74794	99017	22456	33515	00150	20456	33517
85526	11665	00513	70129	05273	35017	51515	10159-	
TTBB	6215/	74794	00017	22456	11982	18445	22948	15222
33940	14419	44914	13216	55900	11600	66891	12260	77882
12265	88870	12270	99850	11665	11820	09463	22801	07861
33790	07464	44778	06867	55762	06064	66754	05663	77734
06472	88730	06475	99707	05673	11700	05273-		
PFBB	62150	74794	90012	33515	35020	00519	90345	02018
01516	00514	90678	35010	36010	00512	909//	36015	910//
35515-								

FIGURE 5-1. Typical coded WMO upper-air transmission. The coded meteorological data in this figure corresponds to the meteorological data used in the example problems described in Appendix A.

archived data sheets are copies of the output printed by the computer system at the upper air reporting station and therefore may also be available for case studies and post-accident review from individual station records. The data is organized into two types (pressure/temperature data and height/wind data). The format for both types is free field where the individual elements are separated by commas. The first type (the pressure/temperature data) requires that four data items be entered on each line: pressure [hPa], height above mean sea level (MSL) [m], temperature [°C] and dew point depression [°C]. If the height is unknown, the program will compute the height  $z_k$  using the hypsometric equation between the adjacent data levels  $k$  and  $(k-1)$

$$z_k = z_{k-1} - 29.271 \bar{T}^* \ln(P_k/P_{k-1}) \quad (5-1)$$

where

$\bar{T}^*$  = the mean virtual temperature for the layer between levels  $k$  and  $(k-1)$

$z_0$  = the altitude of the upper air reporting station

If the height is missing from the input of the pressure/temperature data type, its position must still be accounted for by entering a pair of commas. The second data type (height/wind data) has three data items on each input line: height (MSL) [m], wind direction (deg) and wind speed (knots). Data of both types should be entered in sufficient density to define the temperature, wind speed and wind direction profiles from the surface to 3000 m AGL to within 1°C, ±1 m/s and ±5° respectively. A negative value in the first data position is taken to indicate the end of data. If the height/wind data are entered for the same heights as the pressure/temperature data, the two data types are automatically combined for use by HARM. Otherwise the number of meteorological data levels will be the number of distinctly different heights reported or calculated for

the two data types as entered. Interpolation of temperature, wind speed and wind direction is done linearly with height. It is required that the highest entered pressure/temperature data value be at a height  $z_{MAX}$  equal to or greater than 3000 m AGL and the highest entered height/wind data value be at or above  $z_{MAX}$ .

To maintain compatibility with the WMO standard, a header record is required which contains a five digit station identification number (IIIII), the day of the month (dd), the time of the observation GGmm to the nearest minute in GMT. The three data items are entered in a free field format with each data item separated by commas. Figure 5-2 is an example of the plain language format.

74794,12,1515  
1017,5,22.4,6.4  
5,337,15  
1000,150,20.4,5.7  
150,337,17  
982,305,18.5,4.5  
305,351,20  
950,590,15.4,2.3  
590,003,19  
948,610,15.2,2.2  
610,004,19  
940,681,14.4,1.9  
681,008,19  
914,914,13.2,1.6  
914,019,18  
900,1047,11.7,0  
1047,028,17  
891,1133,12.2,10  
1133,018,16  
882,1219,12.2,14.5  
1219,015,16  
870,1334,12.2,20.4  
1334,013,16  
850,1526,11.6,14.9  
1526,004,13  
820,1829,9.5,12.6  
1829,351,10  
800,2029,7.8,11.1  
2029,352,10  
790,2134,7.4,13.5  
2134,358,10  
778,2263,6.8,16.5  
2263,005,11  
762,2438,6.0,14.2  
2438,006,12  
754,2520,5.6,13.2  
2520,007,13  
750,2559,5.7,15.1  
2559,006,14  
734,2743,6.4,22.4  
2743,000,15  
730,2786,6.5,24.5  
2786,359,16  
707,3048,5.6,22.6  
3048,354,17

Figure 5-2. The free field format rawinsonde data used to enter the data for the example problems described in Appendix A.

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APPENDIX A  
EXAMPLE HARM PROGRAM CALCULATIONS

Example HARM program calculations have been made to obtain concentration and dosage downwind from a number of hypothetical accidents. The accident scenarios are described in Section A.1 below. Section A.2 describes the meteorological data used in the program calculations and the results of the calculations, including the computer printout, are described in Section A.3.

A.1 ACCIDENT SCENARIOS

Three example calculations have been made to illustrate the operational applications of the HARM computer program. The scenarios are:

- A large above-ground major spill occurs in which the total fuel (A-50) in the first and second stage of the fuel holding trailer (107,650 pounds) and the total oxidizer (NTO) in the first and second stages of the oxidizer holding trailer (216,000 pounds) are involved in an instantaneous hypergolic reaction.
  
- A smaller above-ground spill occurs. In this scenario it is assumed that the A-50 and NTO for the first stage of the Titan II have been loaded into the missile. The A-50 in the second stage of the fuel holding trailer (21,400 pounds) and the NTO in the second stage of the oxidizer holding trailer (54,000 pounds) are assumed to be involved in the accident, which begins as a slow leak and ends in a hypergolic reaction.

- An accident occurs in a silo with the silo door closed. The missile is fully loaded with A-50 (106,500 pounds) and NTO (201,015 pounds) and the accident is assumed to be an instantaneous hypergolic reaction.

The accidents are all assumed to occur at the same location (Titan Complex 41) at Kennedy Space Center (KSC). We point out that the accidents are purely hypothetical and that KSC was selected as a site because rawinsonde data and site maps were available for our use in making the calculations.

## A.2 METEOROLOGICAL DATA

The meteorological sounding data file for a rawinsonde released at 1015 EST on 12 November 1981 at KSC has been used as the meteorological input file for all the accident scenarios described below. The free field input format described in Section 5.3 was used to input the data. The data input file read by HARM is shown in Figure 5-2. The left-hand portion of Figure A-1 shows a plot of the vertical profiles of wind speed (WS), wind direction (WD), dry bulb temperature (DT) and virtual potential temperature (PT) created by the HARM computer program based on the data file in Figure 5-2. As shown in Figure A-1, the user has selected the depth of the mixing layer to be 1048.8 m, which corresponds to the base of an elevated inversion signified by an increase in temperature above this altitude. Thus the top of the lower major meteorological (L=1) layer is 1048.8 m, which also forms the base of the second (L=2) major meteorological layer. The top of the second meteorological layer has been set to 3048 m.

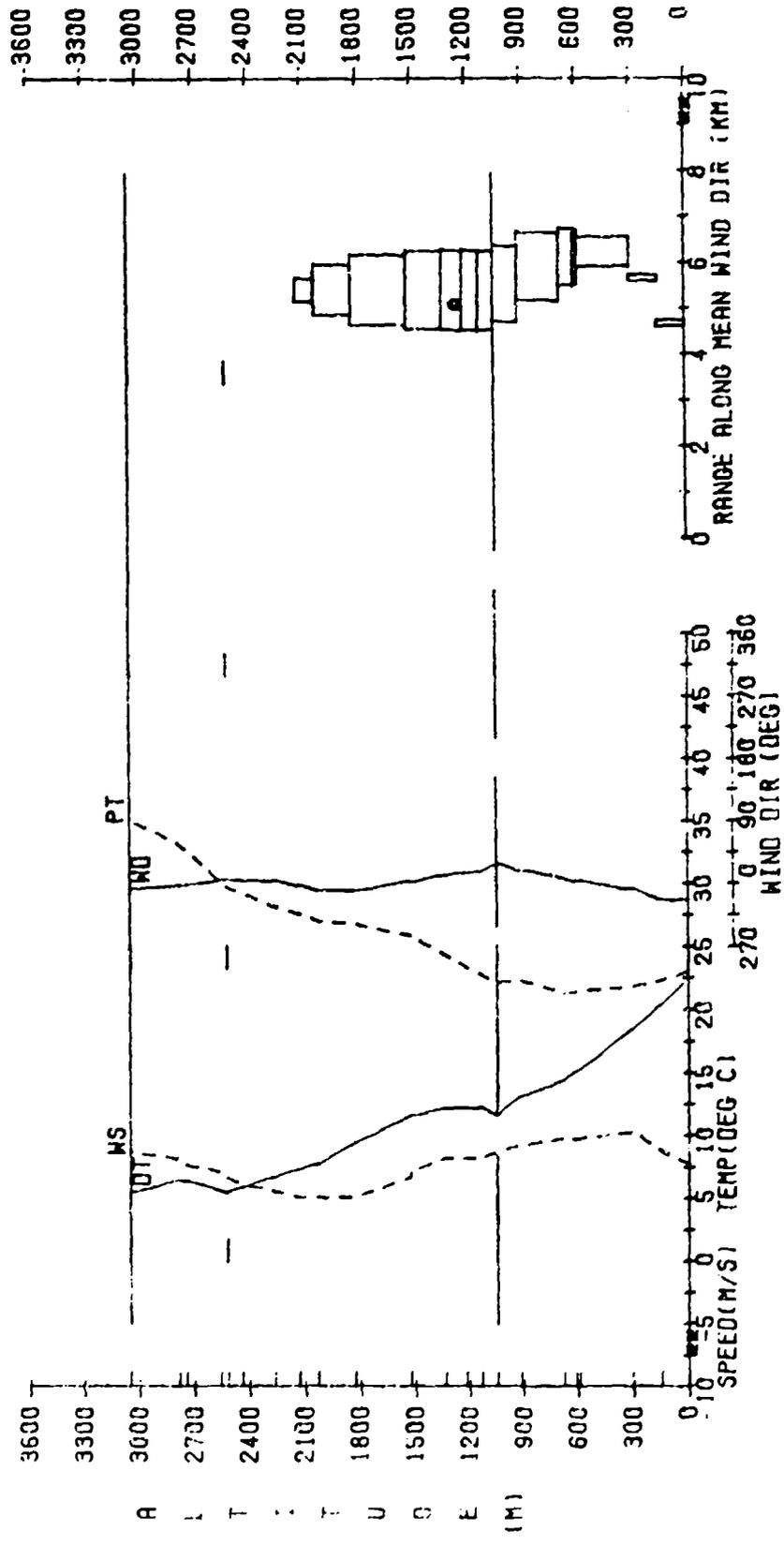
## A.3 RESULTS OF THE HARM PROGRAM CALCULATIONS

### A.3.1 Large Above-Ground Major Spill

Figure A-2 shows the HARM program output of  $N_2H_4$ , UDMH, NDMA and FDH concentrations, dosage and 10-min time mean concentrations for the

DATE: 12 NOV 1981 TIME: 1015 EST PLOTTED AT: HEC FROM FILE: VK1215  
 SURFACE PRESSURE: 1016.9MB DENSITY: 1190.6G/M<sup>3</sup> STAB HT: 1253.5M - - CALC HT: 0.0M

	LAYER1		LAYER2	
	SURFACE	TOP	BOT	TOP
ALTIITUDE (M)	0.0	1048.8	1048.8	3048.0
DRY TEMP (DEG C)	22.4	11.7	11.7	5.6
POT TEMP (DEG C)	23.0	22.2	22.2	35.1
WIND SPEED (M/S)	7.7	8.8	8.8	8.8
WIND DIR (DEG)	337.0	28.0	28.0	354.0



PLOTTED AT: 1127/ 9 FEB 1984 0000

FIGURE A-1. Meteorological profile (left portion of the figure) plot of wind speed (MS), wind direction (WD), temperature (DT) and virtual potential temperature (PT) for the rawinsonde released at 1515Z, 12 November 1981 at KSC. The right hand portion shows the position of the cloud at stabilization time

```

.....
***** HYPERBOLIC ACCIDENTAL RELEASE MODEL *****
***** (HARM) *****
***** UPDATE 8350 LOCATION HEC *****
*****
***** ABOVE GROUND, LARGE SPILL *****
*****
***** TIME OF EXECUTION: 2200 EST DATE: 9 FEB 1984 *****
***** TIME OF ACCIDENT: 1015 EST DATE: 12 NOV 1981 *****
.....

```

\*\*\*\*\*MODEL INPUT OPTIONS SELECTED ARE AS FOLLOWS:\*\*\*\*\*

```

RUN TYPE: OPERATIONAL
METEOROLOGICAL DATA FILE NAME: YK1213
MODEL TYPE: CONCENTRATION/DOSE
THE ACCIDENT OCCURRED IN THE: OPEN
POUNDS OF FUEL INVOLVED IN THE ACCIDENT: 107630.
POUNDS OF OXIDIZER INVOLVED IN THE ACCIDENT: 216900.
ENTRAINMENT PARAMETERS:
GAMMAX= .64
GAMMAY= .64
GAMMAZ= .64
ACCIDENT SITE LOCATION:
UTMX= 17.30
UTMY= 20.00
CALCULATIONS TO BE DONE AT (METERS):
DIFFUSION COEFFICIENTS:
ALPHA=1.00
BETA=1.00
DOWNWIND EXPANSION DISTANCES:
XRY= 100.00
XRZ= 100.00
CONCENTRATION AVERAGING TIME (SEC): 600.00
PRINT OUT WILL BE: SUMMARY

```

FIGURE A-2. HARM program output listing for an an interactive run for the above ground large spill accident scenario.

\*\*\*\*\* METEOROLOGICAL DATA \*\*\*\*\*

RUN NUMBER: 1 USING METEOROLOGICAL DATA FILE: VK1219

TEST NBR 09101 T NINUS 0 VK1219  
 RAUINSONDE RUN AN/CND-1  
 CAPE CANAVERAL AFS, FLORIDA  
 ASCENT NBR 0434

\*\*\*\*\* SOUNDING \*\*\*\*\*

TIME: 1015 EST DATE: 12 NOV 1981

SURFACE DENSITY (G/M\*\*3): 1190.43

NET LEVEL NO.	ALTITUDE (FT)	ALTITUDE (M)	DIR. (DEG)	SPEED (M/S) (KTS)	TEMP (DEG. C)	PTEMP (DEG. C)	OPTEMP	PRESS (MM.)	RH (%)
1	16	4.9	337.0	7.72 15.02	22.4	22.99	0.0	1016.9	67.0
2	493	150.3	337.0	8.79 17.02	20.4	22.29	0.0	1000.9	70.0
3	1000	304.8	351.0	10.30 20.02	18.9	21.82	0.0	982.3	75.0
4	1936	590.1	3.0	9.70 19.02	19.4	21.40	0.0	950.0	86.0
5	2000	609.6	4.0	9.70 19.02	19.2	21.46	0.0	947.9	87.0
6	2235	681.2	8.0	9.70 19.02	14.4	21.30	0.0	940.0	89.0
7	3000	914.4	19.0	9.27 18.02	13.2	22.36	0.0	914.4	90.0
8	3441	1048.8	20.0	8.79 17.02	11.7	22.26	0.0	900.0	100.0
9	3718	1133.2	18.0	8.24 16.02	12.2	22.79	0.0	891.0	90.0
10	4000	1219.2	16.0	8.24 16.02	12.2	23.43	0.0	881.9	89.0
11	4375	1332.9	13.0	8.24 16.02	12.2	24.33	0.0	870.0	84.0
12	5000	1524.0	4.0	7.21 14.02	11.7	23.96	0.0	850.4	89.0
13	5005	1525.9	4.0	6.89 13.01	11.6	23.89	0.0	850.0	89.0
14	6000	1828.8	351.0	9.13 18.01	9.5	26.82	0.0	817.9	41.0
15	6658	2029.4	352.0	9.13 18.01	7.8	27.14	0.0	800.0	45.0
16	6670	2033.0	352.0	9.13 18.01	7.8	27.19	0.0	800.0	46.0
17	7400	2133.6	359.0	9.13 18.01	7.4	27.65	0.0	790.3	38.0
18	7425	2262.1	5.0	9.66 19.01	6.8	28.24	0.0	780.0	30.0
19	8000	2438.4	6.0	6.18 12.01	6.0	29.29	0.0	761.3	35.0
20	8269	2520.4	7.0	6.89 13.01	5.6	29.77	0.0	754.0	39.0
21	8396	2559.1	6.0	7.21 14.02	5.7	30.28	0.0	750.0	34.0
22	9000	2743.2	0.0	7.72 15.02	6.4	32.75	0.0	733.0	18.0
23	9140	2785.9	359.0	8.24 16.02	6.5	33.27	0.0	730.0	15.0
24	10000	3048.0	354.0	8.79 17.02	5.6	35.14	0.0	707.0	17.0

\*\* - INDICATES THAT DATA IS LINEARLY INTERPOLATED FROM INPUT METEOROLOGY

FIGURE A-2. (Continued)

***** STABILIZED CLOUD PARAMETERS *****				
NET. LAYER NO.	TOP OF LAYER (METERS)	CLOUD RISE TIME (SECONDS)	RANGE** (METERS)	AZIMUTH BEARING FROM SITE (METERS)
1	150.3	13.4	5180.6	157.0
2	304.8	39.3	5972.0	163.9
3	590.1	103.9	6266.8	176.2
4	609.6	109.9	6118.2	181.7
5	681.2	133.6	6110.2	183.7
6	914.4	228.8	5949.3	189.6
7	1048.8	298.3	5679.0	195.7
8	1133.2	349.3	5513.9	195.2
9	1219.2	415.9	5468.4	192.6
10	1333.5	628.7 *	5471.4	192.2
11	1524.0	628.7 *	5471.4	192.2
12	1525.5	628.7 *	5471.4	192.2
13	1828.8	628.7 *	5471.4	192.2
14	2029.4	628.7 *	5471.4	192.2
15	2033.0	628.7 *	5471.4	192.2
16	2133.6	628.7 *	5471.4	192.2
17	2263.1	0.0	0.0	0.0
18	2438.4	0.0	0.0	0.0
19	2529.4	0.0	0.0	0.0
20	2559.1	0.0	0.0	0.0
21	2743.2	0.0	0.0	0.0
22	2785.9	0.0	0.0	0.0
23	3048.0	0.0	0.0	0.0

\* - INDICATES CLOUD STABILIZATION TIME WAS USED  
 \*\* - RANGE FROM SITE IS AT CLOUD STABILIZATION TIME

***** CLOUD STABILIZATION *****			
CALCULATION HEIGHT	(METERS)		0.00
STABILIZATION HEIGHT	(METERS)		1253.50
STABILIZATION TIME	(SECS)		628.72
FIRST MIXING LAYER HEIGHT:	(METERS)		TOP = 1048.82
			BASE = 0.00
SECOND SELECTED LAYER HEIGHT:	(METERS)		TOP = 3048.00
			BASE = 1048.82
SIGMA(Z) AT THE SURFACE	(DEGREES)		13.3793
SIGMA(EL) AT THE SURFACE	(DEGREES)		13.3793

FIGURE A-2. (Continued)

```

.....
*****
***** (HARR) *****
***** UPDATE 0350 LOCATION NEC *****
***** CONCENTRATION/DOSE MODEL *****
***** MAXIMUM CENTERLINE CALCULATIONS *****
*****
***** ABOVE GROUND, LARGE SPILL *****
*****
***** FOR SPECIES H204 *****
*****
.....

```

CALCULATIONS WERE DONE AT 0.00 M AGL  
 AND APPLY TO THE LAYER BETWEEN 0.00 AND 1048.02 M AGL  
 DOWNWIND FROM THE ACCIDENT SITE AT ( 17.50, 20.06)

THE METEOROLOGICAL DATA IS FROM 1015 EST 12 NOV 1981  
 ACCIDENT TIME IS 1015 EST 12 NOV 1981  
 TIME OF EXECUTION IS 2200 EST 9 FEB 1984

RANGE FROM SITE (METERS)	BEARING FROM SITE (DEGREES)	PEAK CONCENTRATION (PPM)	CLOUD ARRIVAL TIME (MIN)	CLOUD DEPARTURE TIME (MIN)
5394.013	157.963	1.447	10.800	11.061
6330.070	161.413	.219	9.423	13.039
7200.394	166.470	.340	10.964	15.029
8163.261	160.472	.109	12.663	17.020
9002.406	170.673	.197	14.365	19.032
10005.003	181.904	.259	16.063	21.030
11013.600	182.067	.200	17.759	23.046
12020.077	183.396	.277	19.442	25.036
13019.361	183.144	.259	21.089	27.069
14020.090	183.007	.236	22.723	29.076
15022.932	183.189	.213	24.364	31.007
16017.640	182.709	.192	26.001	33.090
17023.266	183.019	.174	27.636	35.109
18019.176	182.663	.159	29.270	37.121
19019.699	182.347	.149	30.902	39.132
20012.730	182.063	.133	32.534	41.144
21021.453	182.600	.122	34.164	43.136
22010.020	182.309	.113	35.794	45.160
23016.500	182.109	.109	37.423	47.186
24014.426	182.005	.097	39.051	49.192
25012.502	181.836	.090	40.678	51.204
26010.934	181.600	.084	42.305	53.216
27009.469	181.536	.079	43.931	55.220
28000.156	181.402	.074	45.557	57.241
29020.379	182.166	.069	47.183	59.253

```

RANGE    BEARING
-----
5394.0    158.0

```

1.447 IS THE MAXIMUM PEAK CONCENTRATION

FIGURE A-2. (Continued)

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.....
*****
*****          (MARR)          *****
*****          UPDATE 0350   LOCATION MEC          *****
*****          CONCENTRATION/DOSEAGE MODEL          *****
*****          MAXIMUM CENTERLINE CALCULATIONS          *****
*****          ABOVE GROUND, LARGE SPILL          *****
*****          FOR SPECIES M2H4          *****
*****
.....

```

CALCULATIONS WERE DONE AT 0.00 M AGL  
 AND APPLY TO THE LAYER BETWEEN 0.00 AND 1048.02 M AGL  
 DOWNWIND FROM THE ACCIDENT SITE AT ( 17.58, 20.06)

THE METEOROLOGICAL DATA IS FROM 1015 EST 12 NOV 1981  
 ACCIDENT TIME IS 1015 EST 12 NOV 1981  
 TIME OF EXECUTION IS 2200 EST 9 FEB 1984

RANGE FROM SITE (METERS)	BEARING FROM SITE (DEGREES)	TOTAL DOSEAGE (PPM SEC)	CLOUD ARRIVAL TIME (MIN)	CLOUD DEPARTURE TIME (MIN)
5394.813	197.963	11.500	10.000	11.061
6330.070	161.413	1.909	9.423	13.039
7200.394	166.470	3.069	10.964	15.029
8007.977	177.462	3.864	12.663	17.020
9000.521	182.511	11.969	14.363	19.032
10027.439	184.259	19.630	16.063	21.030
11032.359	184.409	23.116	17.759	23.046
12037.166	184.523	23.535	19.442	25.056
13037.322	184.356	22.390	21.005	27.065
14029.400	183.729	20.679	22.723	29.076
15033.740	183.859	18.929	24.364	31.087
16028.072	183.411	17.310	26.001	33.090
17023.266	183.015	15.902	27.636	35.109
18031.570	183.410	14.600	29.270	37.121
19027.770	183.115	13.621	30.902	39.132
20024.414	182.849	12.693	32.534	41.144
21021.453	182.608	11.874	34.164	43.156
22018.828	182.309	11.146	35.794	45.160
23016.500	182.109	10.496	37.423	47.180
24014.426	182.003	9.911	39.051	49.192
25027.192	182.600	9.303	40.678	51.204
26025.242	182.543	8.910	42.305	53.216
27023.480	182.408	8.477	43.931	55.228
28021.871	182.283	8.000	45.557	57.241
29020.379	182.166	7.716	47.183	59.253

23.535 IS THE MAXIMUM TOTAL DOSEAGE

RANGE	BEARING
12037.2	184.5

FIGURE A-2. (Continued)





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.....
*****
***** (HARM) *****
***** UPDATE 8350 LOCATION NEC *****
***** CONCENTRATION/DOSAGE MODEL *****
***** MAXIMUM CENTERLINE CALCULATIONS *****
*****
***** ABOVE GROUND, LARGE SPILL *****
*****
***** FOR SPECIES UOHH *****
*****
.....

```

CALCULATIONS WERE DONE AT 0.00 M AGL  
 AND APPLY TO THE LAYER BETWEEN 0.00 AND 1048.82 M AGL  
 DOMINANT FROM THE ACCIDENT SITE AT ( 17.58, 20.06 )

THE METEOROLOGICAL DATA IS FROM 1015 EST 12 NOV 1981  
 ACCIDENT TIME IS 1015 EST 12 NOV 1981  
 TIME OF EXECUTION IS 2200 EST 9 FEB 1984

RANGE FROM SITE (METERS)	BEARING FROM SITE (DEGREES)	TOTAL DOSAGE (PPM SEC)	CLOUD ARRIVAL TIME (MIN)	CLOUD DEPARTURE TIME (MIN)
3394.813	137.963	6.138	10.888	11.061
6330.878	163.413	1.023	9.423	13.039
7200.394	166.470	1.644	10.964	13.029
8007.977	177.462	2.076	12.665	17.020
9000.521	182.511	6.463	14.365	19.032
10027.439	184.259	10.654	16.063	21.030
11032.359	184.409	12.596	17.759	23.046
12037.166	184.523	12.878	19.442	25.056
13037.322	184.356	12.303	21.089	27.065
14029.400	183.729	11.410	22.729	29.076
15033.740	183.859	10.486	24.364	31.087
16028.072	183.411	9.635	26.001	33.090
17023.266	183.013	8.804	27.636	35.109
18031.570	183.410	8.236	29.270	37.121
19027.770	183.115	7.674	30.902	39.132
20024.414	182.849	7.180	32.534	41.144
21021.453	182.608	6.745	34.164	43.156
22018.828	182.389	6.358	35.794	45.168
23016.900	182.189	6.012	37.423	47.180
24014.426	182.005	5.701	39.051	49.192
25027.152	182.688	5.420	40.678	51.204
26029.242	182.543	5.167	42.305	53.216
27023.488	182.408	4.936	43.931	55.228
28021.871	182.283	4.725	45.557	57.241
29020.379	182.166	4.531	47.183	59.253

12.878 IS THE MAXIMUM TOTAL DOSAGE

RANGE	BEARING
12037.2	184.3

FIGURE A-2. (Continued)

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.....
*****
*****          (HARM)          *****
*****          UPDATE 8359   LOCATION HEC          *****
*****          CONCENTRATION/DOSAGE MODEL          *****
*****          MAXIMUM CENTERLINE CALCULATIONS          *****
*****
*****          ABOVE GROUND, LARGE SPILL          *****
*****
*****          FOR SPECIES UDAH          *****
*****
.....

```

CALCULATIONS WERE DONE AT 0.00 M AGL  
 AND APPLY TO THE LAYER BETWEEN 0.00 AND 1048.82 M AGL  
 DOWNWIND FROM THE ACCIDENT SITE AT ( 17.58, 20.06)

THE METEOROLOGICAL DATA IS FROM 1015 EST 12 NOV 1981  
 ACCIDENT TIME IS 1015 EST 12 NOV 1981  
 TIME OF EXECUTION IS 2200 EST 9 FEB 1984

RANGE FROM SITE (METERS)	BEARING FROM SITE (DEGREES)	10.0 MIN. MEAN CONCENTRATION (PPM)	CLOUD ARRIVAL TIME (MIN)	CLOUD DEPARTURE TIME (MIN)
5394.813	157.963	.010	10.800	11.061
6330.878	161.413	.002	9.423	13.039
7200.394	166.470	.003	10.964	15.029
8007.977	177.462	.003	12.663	17.028
9008.521	182.511	.011	14.363	19.032
10027.439	184.239	.018	16.063	21.038
11032.339	184.409	.021	17.759	23.046
12037.166	184.323	.021	19.442	25.056
13037.322	184.356	.021	21.005	27.063
14029.400	183.729	.019	22.725	29.076
15033.748	183.839	.017	24.364	31.087
16028.072	183.411	.016	26.001	33.098
17023.266	183.013	.015	27.636	35.109
18031.570	183.410	.014	29.270	37.121
19027.770	183.113	.013	30.902	39.132
20024.414	182.849	.012	32.534	41.144
21021.453	182.608	.011	34.164	43.156
22018.828	182.389	.011	35.794	45.168
23016.500	182.189	.010	37.423	47.180
24014.426	182.005	.010	39.051	49.192
25027.132	182.688	.009	40.678	51.204
26025.242	182.543	.009	42.305	53.216
27023.488	182.408	.008	43.931	55.228
28021.871	182.283	.008	45.557	57.241
29020.379	182.166	.008	47.183	59.253

RANGE BEARING

-----  
 12037.2 184.9

.021 IS THE MAXIMUM 10.0 MIN. MEAN CONCENTRATION

FIGURE A-2. (Continued)

```

.....
*****
*****          (HARM)          *****
*****          UPDATE 8350   LOCATION NEC          *****
*****          CONCENTRATION/DOSAGE MODEL          *****
*****          MAXIMUM CENTERLINE CALCULATIONS          *****
*****          ABOVE GROUND, LARGE SPILL          *****
*****          FOR SPECIES HDRA          *****
*****
.....

```

CALCULATIONS WERE DONE AT 0.00 M AGL  
 AND APPLY TO THE LAYER BETWEEN 0.00 AND 1048.02 M AGL  
 DOWNWIND FROM THE ACCIDENT SITE ( 17.50, 20.06)

THE METEOROLOGICAL DATA IS FROM 1015 EST 12 NOV 1981  
 ACCIDENT TIME IS 1015 EST 12 NOV 1981  
 TIME OF EXECUTION IS 2200 EST 9 FEB 1984

RANGE FROM SITE (METERS)	BEARING FROM SITE (DEGREES)	PEAK CONCENTRATION (PPM)	CLOUD ARRIVAL TIME (MIN)	CLOUD DEPARTURE TIME (MIN)
11018.967	103.381	.002	17.759	23.046
12020.877	103.396	.001	19.442	25.056
13019.361	103.144	.001	21.085	27.065
14020.090	103.087	.001	22.725	29.076
15022.932	103.185	.002	24.364	31.087
16017.648	102.709	.002	26.001	33.098
17023.266	103.015	.002	27.636	35.109
18019.176	102.663	.002	29.270	37.121
19013.699	102.347	.001	30.902	39.132
20012.730	102.063	.001	32.534	41.144
21021.453	102.608	.001	34.164	43.156
22018.820	102.389	.001	35.794	45.168
23016.500	102.189	.001	37.423	47.180
24014.426	102.005	.002	39.051	49.192
25012.592	101.836	.002	40.678	51.204
26010.934	101.680	.002	42.305	53.216
27009.469	101.536	.002	43.931	55.228
28021.871	102.283	.001	45.557	57.241
29029.379	102.166	.001	47.183	59.253

.002 IS THE MAXIMUM PEAK CONCENTRATION

RANGE	BEARING
16017.6	102.7

FIGURE A-2. (Continued)

```

.....
*****
*****          (HARR)          *****
*****          UPDATE 0350      LOCATION MEC          *****
*****          CONCENTRATION/DOSE MODEL              *****
*****          MAXIMUM CENTERLINE CALCULATIONS      *****
*****
*****          ABOVE GROUND, LARGE SPILL            *****
*****
*****          FOR SPECIES MORR                      *****
*****
.....

```

CALCULATIONS WERE DONE AT 0.00 M AGL  
 AND APPLY TO THE LAYER BETWEEN 0.00 AND 1048.82 M AGL  
 DOWNWIND FROM THE ACCIDENT SITE AT ( 17.58, 20.46)

THE METEOROLOGICAL DATA IS FROM 1015 EST 12 NOV 1981  
 ACCIDENT TIME IS 1015 EST 12 NOV 1981  
 TIME OF EXECUTION IS 2200 EST 9 FEB 1984

RANGE FROM SITE (METERS)	BEARING FROM SITE (DEGREES)	TOTAL DOSAGE (PPH SEC)	CLOUD ARRIVAL TIME (MIN)	CLOUD DEPARTURE TIME (MIN)
5394.813	157.963	.001	10.808	11.061
6330.878	161.413	.001	9.423	13.039
7206.916	166.269	.002	10.964	13.079
8007.977	177.462	.003	12.665	17.029
9014.372	183.277	.017	14.369	19.032
10033.643	184.712	.039	16.063	21.038
11040.383	184.921	.058	17.759	23.046
12037.166	184.923	.071	19.442	25.056
13037.322	184.356	.079	21.085	27.065
14040.473	184.371	.083	22.725	29.076
15033.748	183.859	.086	24.364	31.087
16028.072	183.411	.087	26.001	33.098
17023.266	183.015	.088	27.636	35.109
18031.578	183.410	.089	29.270	37.121
19027.770	183.115	.090	30.902	39.132
20024.414	182.849	.090	32.534	41.144
21021.453	182.608	.091	34.164	43.156
22018.828	182.389	.091	35.794	45.168
23016.500	182.189	.091	37.423	47.180
24014.426	182.003	.092	39.051	49.192
25027.152	182.688	.092	40.678	51.204
26025.242	182.543	.092	42.305	53.216
27023.488	182.408	.092	43.931	55.228
28021.871	182.283	.092	45.557	57.241
29020.379	182.166	.093	47.183	59.253

093 IS THE MAXIMUM TOTAL DOSAGE

RANGE	BEARING
29920.4	182.2

FIGURE A-2. (Continued)

```

.....
..... (NARR) .....
..... UPDATE 0350 LOCATION MEC .....
..... CONCENTRATION/DOSE MODEL .....
..... MAXIMUM CENTERLINE CALCULATIONS .....
..... ABOVE GROUND, LARGE SPILL .....
..... FOR SPECIES NDHA .....
.....

```

CALCULATIONS WERE DONE AT 0.05 M AGL  
AND APPLY TO THE LAYER BETWEEN 0.00 AND 1740.02 M AGL  
DOWNWIND FROM THE ACCIDENT SITE AT ( 17.50, 20.06)

THE METEOROLOGICAL DATA IS FROM 1015 EST 12 NOV 1981  
ACCIDENT TIME IS 1015 EST 12 NOV 1981  
TIME OF EXECUTION IS 2200 EST 9 FEB 1984

RANGE FROM SITE (METERS)	BEARING FROM SITE (DEGREES)	10.0 MIN.	CLOUD	CLOUD
		MEAN CONCENTRATION (PPM)	ARRIVAL TIME (MIN)	DEPARTURE TIME (MIN)

	RANGE	BEARING
.000 IS THE MAXIMUM 10.0 MIN. MEAN CONCENTRATION	29020.4	102.2

FIGURE A-2. (Continued)

```

.....
*****
              (HARM)
*****
              UPDATE 0350   LOCATION HEC
*****
              CONCENTRATION/DOSEAGE MODEL
*****
              MAXIMUM CENTERLINE CALCULATIONS
*****
              ABOVE GROUND, LARGE SPILL
*****
              FOR SPECIES PDM
*****
.....

```

CALCULATIONS WERE DONE AT 0.00 M AGL  
 AND APPLY TO THE LAYER BETWEEN 0.00 AND 1048.82 M AGL  
 DOWNWIND FROM THE ACCIDENT SITE AT ( 17.50, 20.06)

THE METEOROLOGICAL DATA IS FROM 1015 EST 12 NOV 1981  
 ACCIDENT TIME IS 1015 EST 12 NOV 1981  
 TIME OF EXECUTION IS 2200 EST 9 FEB 1984

RANGE FROM SITE (METERS)	BEARING FROM SITE (DEGREES)	PEAK CONCENTRATION (PPM)	CLOUD ARRIVAL TIME (MIN)	CLOUD DEPARTURE TIME (MIN)
5354.813	137.963	.053	10.808	11.061
6330.878	161.413	.043	9.423	13.035
7200.354	166.470	.077	10.964	15.025
8173.607	160.189	.071	12.665	17.038
9002.486	178.673	.092	14.365	19.032
10005.883	181.984	.166	16.063	21.038
11018.967	183.381	.232	17.759	23.046
12020.877	183.396	.276	19.442	25.056
13019.361	183.144	.302	21.085	27.065
14020.090	183.087	.315	22.725	29.076
15022.932	183.184	.321	24.364	31.087
16017.648	182.704	.322	26.001	33.098
17023.266	183.015	.322	27.636	35.107
18019.176	192.663	.321	29.279	37.121
19015.699	182.747	.318	30.902	39.132
20012.738	182.063	.315	32.534	41.144
21021.453	182.608	.312	34.164	43.156
22018.828	182.389	.308	35.794	45.168
23016.560	182.189	.304	37.423	47.180
24014.426	182.009	.300	39.051	49.192
25012.582	181.836	.296	40.679	51.204
26010.934	181.680	.292	42.305	53.216
27009.469	181.536	.287	43.931	55.228
28021.871	182.283	.283	45.557	57.241
29020.379	182.166	.278	47.183	59.253

RANGE	BEARING
16017.6	182.7

.322 IS THE MAXIMUM PEAK CONCENTRATION

FIGURE A-2. (Continued)



```

.....
( HARM )
.....
UPDATE 0350 LOCATION MEC
.....
CONCENTRATION/DOSE MODEL
.....
MAXIMUM CENTERLINE CALCULATIONS
.....
ABOVE GROUND, LARGE SPILL
.....
FOR SPECIES FDM
.....

```

CALCULATIONS WERE DONE AT 0.00 M AGL  
AND APPLY TO THE LAYER BETWEEN 0.00 AND 1948.02 M AGL  
DOWNWIND FROM THE ACCIDENT SITE AT ( 17.50, 20.06)

THE METEOROLOGICAL DATA IS FROM 1015 EST 12 NOV 1981  
ACCIDENT TIME IS 1015 EST 12 NOV 1981  
TIME OF EXECUTION IS 2208 EST 9 FEB 1984

RANGE FROM SITE (METERS)	BEARING FROM SITE (DEGREES)	10.0 MIN. NEAR CONCENTRATION (PPB)	CLOUD ARRIVAL TIME (MIN)	CLOUD DEPARTURE TIME (MIN)
5354.813	157.963	.001	10.008	11.061
6330.878	161.413	.001	9.423	13.039
7206.516	166.269	.001	10.964	15.029
8007.977	177.462	.002	12.663	17.028
9014.572	183.277	.011	14.365	19.032
10033.643	184.712	.022	16.063	21.038
11040.383	184.921	.032	17.759	23.046
12077.166	184.923	.040	19.442	25.036
13037.322	184.356	.044	21.085	27.065
14040.473	184.371	.046	22.725	29.076
15033.748	183.859	.048	24.364	31.087
16078.072	183.411	.049	26.001	33.098
17023.266	183.015	.049	27.636	35.109
18031.570	183.410	.050	29.270	37.121
19027.770	183.115	.050	30.902	39.132
20024.414	182.845	.050	32.534	41.144
21021.453	182.608	.051	34.164	43.156
22018.828	182.389	.051	35.794	45.168
23016.500	182.189	.051	37.423	47.180
24014.426	182.005	.051	39.051	49.192
25027.152	182.688	.051	40.678	51.204
26029.242	182.543	.051	42.305	53.216
27023.488	182.408	.052	43.931	55.228
28021.871	182.283	.052	45.557	57.241
29020.379	182.166	.052	47.183	59.253

RANGE	BEARING
29020.4	182.2

052 IS THE MAXIMUM 10.0 MIN. NEAR CONCENTRATION  
FIGURE A-2. (Continued)

large above-ground major spill of A-50 and NTO. This output was produced from an interactive run where all parameters except the layer-height and accident description parameters were defaulted. The first page of Figure A-2 (page A-4) shows the time and date of the hypothetical accident, the time and date of the program execution, and the options selected for execution of the HARM program. The second page (page A-5) of Figure A-2 shows the meteorological data, based on the input data in Figure 5-2, used by the program in performing the calculations. Page 3 of Figure A-2 (Page A-6) shows the results of the cloud-rise calculation. The time for the cloud to rise through the kth meteorological layer and the range and azimuth bearing of that position of the cloud in the kth layer at the time of cloud stabilization is given at the top of the page. For example, the cloud took 13.4 s to rise through 150.3 m. At the cloud stabilization time of 628.7 s, the portion of the cloud remaining in the lowest layer was located 5471.4 m from the accident site on an azimuth bearing of 192 deg. The cloud stabilization height, as shown at the bottom of the page, was calculated as 1253.5 m and the reference values  $\sigma_{AR}(\tau_o=600s)$  and  $\sigma_{ER}$  were both calculated to be 13.6 deg. Page 4 (A-7) shows the peak centerline ground-level concentrations of  $N_2H_4$  in parts per million (ppm) parts of air as a function of distance downwind from the accident site along the cloud trajectory. In this case the highest calculated concentration of  $N_2H_4$  (1.4 ppm) occurred at 5395 m downwind from the accident on an azimuth bearing of about 158 deg. It must be stressed that the HARM computer program does not calculate concentrations that may have occurred at distances less than the point of cloud stabilization. For this reason, there may be higher ground-level concentrations at distances less than 5395 m from the accident site. The last two columns on the page provide estimates of the time the leading edge of the cloud arrived at this distance and azimuth bearing from the site and the time the trailing edge of the cloud left the point. The peak centerline ground-level total dosage (time-integrated concentration or ppm sec) produced along the cloud trajectory is shown on Page 5 (page A-8) of Figure A-2. Page 6 of Figure A-2 (page A-9) shows the values of peak centerline 10-minute mean concentration along the cloud trajectory. For example, the calculations show that the highest 10-minute mean ground-level

concentration that could be experienced is 0.039 ppm at a distance of about 12037 m from the accident at a bearing of 185 deg. Pages 7 through 9 (pages A-10 through A-12) show the results of the calculations respectively for UDMH concentrations, total dosage and time-mean concentrations. Because there was an excess of fuel in the postulated accident, no NO<sub>2</sub> was present in the stabilized cloud. Pages 10 through 12 of Figure A-2 (pages A-13 through A-15) show the results of the calculations for NDMA. Note that the units of concentration, dosage and time-mean concentration are respectively parts per billion (ppb), ppb sec and ppb. Also note that no values of time-mean concentration are listed on page 12 of Figure A-2 (page A-15). The HARM program does not print values less than  $5 \times 10^{-4}$  (ppm, ppb, ppm sec, ppb sec). Thus, the time-mean concentrations of NDMA in this scenario are less than  $5 \times 10^{-4}$  ppb. Finally, pages 13 through 15 of Figure A-2 (pages A-16 through A-18) show the results calculated for FDH.

The HARM program was also asked to produce graphic displays for this accident. Note that the right-hand portion of Figure A-1 shows the dimensions of the stabilized cloud as viewed from a point at a right-angle to the mean wind direction. Figure A-3 shows a plot of peak-centerline ground-level UDMH concentration (solid line), total dosage (++++) and 10-minute time-mean concentration (oooo) downwind from the site and is based on the results of the calculations printed on pages 4 through 6 of Figure A-2 (pages A-10 through A-12). Finally Figure A-4 shows UDMH concentration isopleths plotted by the HARM program on the map of KSC for the above-ground large spill. The isopleth labeled B is for a concentration of 0.2 ppm. The area enclosed within this isopleth is expected to experience peak concentrations equal to or greater than 0.2 ppm as a result of the hypothetical accident.

#### A.3.2 Small Above-Ground Spill

Figure A-5 shows the HARM program output of NO<sub>2</sub> concentrations, dosage and 10-minute time mean concentrations for the small above-ground spill scenario. There was no N<sub>2</sub>H<sub>4</sub>, UDMH, NDMA and FDH present in the cloud

# CONCENTRATION AND DOSAGE FOR UDMH

7

CLOUD HEIGHT	= 1264.	M	SOUNDING/PAGECOUNT	1016 EST 12 NOV 1961	CONCENTRATION
TIME OF RISE	= 0.	SEL	TIME OF EXECUTION	2317 EST 9 FEB 1964	♦ ♦ ♦ DOSAGE
TOP OF LAYER	= 1049.	M	ACCIDENT TIME	1016 EST 12 NOV 1961	0 0 0 0 10.0 MIN. AVE CONC
BOTTOM OF LAYER	= 0.	M	RUN LOCATION	NEC	
HEIGHT OF CMLC	= 0.	M	DATA FILENAME	VK1215	

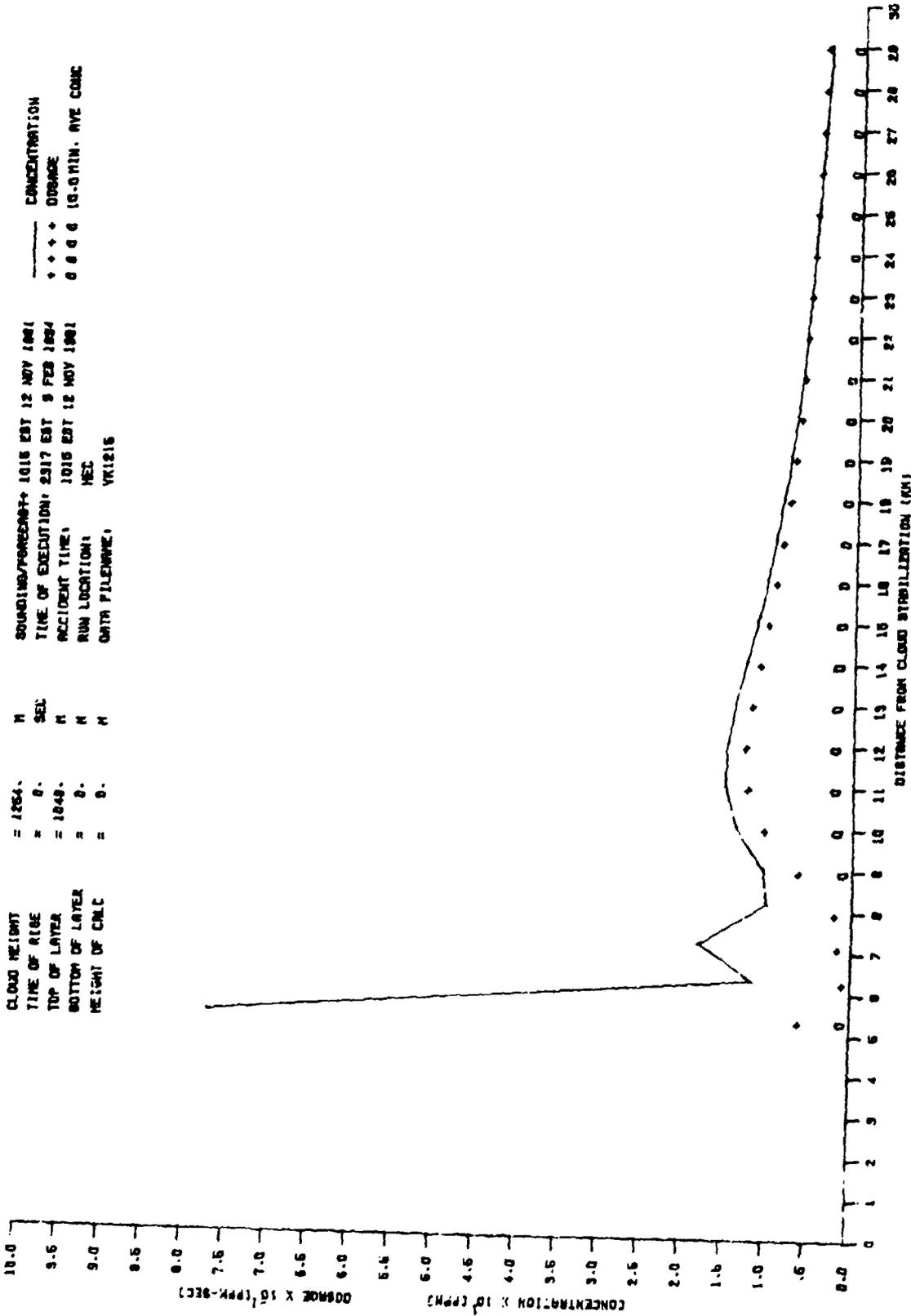


FIGURE A-3. Maximum centerline profile plot of ground-level UDMH concentrations, dosages and 10-minute time mean concentrations produced by the above-ground large spill hypothetical accident.



```

.....
***** HYPERGOLIC ACCIDENTAL RELEASE MODEL *****
***** (HARM) *****
***** UPDATE 8350 LOCATION NEC *****
*****
***** ABOVE GROUND, SMALL SPILL *****
*****
***** TIME OF EXECUTION: 2226 EST DATE: 9 FEB 1984 *****
***** TIME OF ACCIDENT: 1013 EST DATE: 12 NOV 1981 *****
.....

*****MODEL INPUT OPTIONS? SELECTED ARE AS FOLLOWS:*****

RUN TYPE: OPERATIONAL
METEOROLOGICAL DATA FILE NAME: VK1215
MODEL TYPE: CONCENTRATION/DOSE
THE ACCIDENT OCCURRED IN THE: OPEN
POUNDS OF FUEL INVOLVED IN THE ACCIDENT: 21400.
POUNDS OF OXIDIZER INVOLVED IN THE ACCIDENT: 34900.
ENTRAINMENT PARAMETERS:
GARRAX= .64
GARRAY= .64
GARRAZ= .64

ACCIDENT SITE LOCATION: UFMX= 17.50
UTMY= 20.06

CALCULATIONS TO BE DONE AT (METERS): 0.00
DIFFUSION COEFFICIENTS: ALPHA=1.00
BETA=1.00

DOWNWIND EXPANSION DISTANCES: XEY= 100.00
XEZ= 100.00

CONCENTRATION AVERAGING TIME (SEC): 600.00
PRINT OUT WILL BE: SUMMARY

```

FIGURE A-5. HARM program output listing for an interactive run for the small above-ground spill accident scenario.

\*\*\*\*\* METEOROLOGICAL DATA \*\*\*\*\*

RUN NUMBER: 1 USING METEOROLOGICAL DATA FILE: VK1215

TEST NBR 09101 T MINUS 0 VK1215  
 RAINSONDE RON AN/GND-1  
 CAPE CANAVERAL AFS, FLORIDA  
 ASCENT NBR 0434

\*\*\*\*\* SOUNDING \*\*\*\*\*  
 TIME: 1015 EST DATE: 12 NOV 1981

SURFACE DENSITY (G/M\*\*3): 1190.43

NET LEVEL NO.	ALTITUDE (FT)	DIR. (M)	DIR. (DEG)	SPEED (M/S)	SPEED (KTS)	TEMP (DEG. C)	PTEMP (DEG. C)	DPTEMP	PRESS (MM.)	RH (%)
1	16	4.9	337.0	7.72	15.02	22.4	22.99	0.0	1016.9	67.0
2	493	150.3	337.0	8.73	17.02	20.4	22.29	0.0	1000.0	70.0
3	1090	304.8	351.0	10.30	20.02	18.3	21.83	0.0	982.3	75.0
4	1936	590.1	3.0	9.78	19.02	15.4	21.40	0.0	950.0	86.0
5	2000	609.6	4.0	9.78	19.02	15.2	21.46	0.0	947.9	87.0
6	2235	681.2	8.0	9.78	19.02	14.4	21.30	0.0	940.0	88.0
7	3000	914.4	19.0	9.27	18.02	13.2	22.36	0.0	914.4	90.0
8	3441	1048.8	28.0	8.73	17.02	11.7	22.20	0.0	900.0	100.0
9	3718	1133.2	18.0	8.24	16.02	12.2	22.75	0.0	891.0	90.0
10	4000	1219.2	16.0	8.24	16.02	12.2	23.43	0.0	881.9	39.0
11	4375	1333.5	13.0	8.24	16.02	12.2	24.33	0.0	870.0	24.0
12	5000	1524.0	4.0	7.21	14.02	11.7	25.96	0.0	850.4	35.0
13	5005	1525.5	4.0	6.69	13.01	11.6	25.89	0.0	850.0	35.0
14	6000	1828.0	351.0	5.15	10.01	9.5	26.82	0.0	815.9	41.0
15	6658	2029.4	352.0	5.15	10.01	7.8	27.14	0.0	800.0	45.0
16	6670	2033.0	352.0	5.15	10.01	7.8	27.15	0.0	800.0	46.0
17	7000	2133.6	358.0	5.15	10.01	7.4	27.65	0.0	790.3	38.0
18	7425	2263.1	5.0	5.66	11.01	6.8	28.24	0.0	778.0	30.0
19	8000	2438.4	6.0	6.18	12.01	6.0	29.29	0.0	761.5	35.0
20	8269	2520.4	7.0	6.69	13.01	5.6	29.77	0.0	754.0	39.0
21	8396	2559.1	6.0	7.21	14.02	5.7	30.28	0.0	750.0	34.0
22	9000	2743.3	0.0	7.72	15.02	6.4	32.75	0.0	733.8	19.0
23	9140	2785.9	359.0	8.24	16.02	6.5	33.27	0.0	730.0	15.0
24	10000	3048.0	354.0	8.73	17.02	5.6	35.14	0.0	707.0	17.0

\*\* - INDICATES THAT DATA IS LINEARLY INTERPOLATED FROM INPUT METEOROLOGY

FIGURE A-5. (Continued)

..... STABILIZED CLOUD PARAMETERS .....

NET. LAYER NO.	TOP OF LAYER (METERS)	CLOUD RISE TIME (SECONDS)	RANGE** FROM SITE (METERS)	AZIMUTH BEARING FROM SITE (METERS)
1	150.3	21.0	7797.2	157.0
2	304.0	63.3	8907.3	163.9
3	590.1	204.4	9423.7	176.1
4	609.6	217.4	9209.4	181.2
5	681.2	269.3	9193.3	183.1
6	914.4	500.6	8962.3	188.4
7	1048.0	793.1	8642.5	192.9
8	1133.2	946.3 *	8578.6	193.2
9	1219.2	946.3 *	8578.6	193.2
10	1333.5	946.3 *	8578.6	193.2
11	1524.0	946.3 *	8578.6	193.2
12	1525.5	946.3 *	8578.6	193.2
13	1828.0	946.3 *	8578.6	193.2
14	2029.4	0.0	0.0	0.0
15	2033.0	0.0	0.0	0.0
16	2133.6	0.0	0.0	0.0
17	2263.1	0.0	0.0	0.0
18	2438.4	0.0	0.0	0.0
19	2520.4	0.0	0.0	0.0
20	2559.1	0.0	0.0	0.0
21	2743.2	0.0	0.0	0.0
22	2785.3	0.0	0.0	0.0
23	3048.0	0.0	0.0	0.0

\* - INDICATES CLOUD STABILIZATION TIME WAS USED  
 \*\* - RANGE FROM SITE IS AT CLOUD STABILIZATION TIME

..... CLOUD STABILIZATION .....

CALCULATION HEIGHT	(METERS)	0.00
STABILIZATION HEIGHT	(METERS)	1067.09
STABILIZATION TIME	(SECS)	946.26
FIRST MIXING LAYER HEIGHT:	(METERS)	TOP = 1048.82
SECOND SELECTED LAYER HEIGHT:	(METERS)	BASE = 0.00
		TOP = 3048.00
		BASE = 1048.82
SIGMA(Z) AT THE SURFACE	(DEGREES)	13.5793
SIGMA(EL) AT THE SURFACE	(DEGREES)	13.5793

FIGURE A-5. (Continued)

```

.....
( HARR )
UPDATE 0350 LOCATION HEC
CONCENTRATION/DOSE MODEL
MAXIMUM CENTERLINE CALCULATIONS
.....
ABOVE GROUND, SMALL SPILL
.....
FOR SPECIES NO2
.....

```

CALCULATIONS WERE DONE AT 0.00 M AGL  
 AND APPLY TO THE LAYER BETWEEN 0.00 AND 1048.02 M AGL  
 DOWNWIND FROM THE ACCIDENT SITE AT ( 17.58, 29.06 )

THE METEOROLOGICAL DATA IS FROM 1015 EST 12 NOV 1981  
 ACCIDENT TIME IS 1015 EST 12 NOV 1981  
 TIME OF EXECUTION IS 2226 EST 9 FEB 1984

RANGE FROM SITE (METERS)	BEARING FROM SITE (DEGREES)	PEAK CONCENTRATION (PPH)	CLOUD ARRIVAL TIME (MIN)	CLOUD DEPARTURE TIME (MIN)
0561.344	159.156	.399	17.305	17.475
9309.339	161.338	.121	14.834	19.470
10307.042	165.981	.461	16.150	21.474
11280.586	167.213	.214	17.807	23.482
12000.075	179.327	.178	19.461	25.491
13025.758	183.623	.284	21.113	27.502
14031.316	183.848	.338	22.762	29.513
15031.730	183.743	.346	24.410	31.524
16037.281	183.927	.330	26.055	33.536
17037.625	183.828	.305	27.698	35.548
18029.688	183.307	.278	29.339	37.560
19033.652	183.427	.254	30.978	39.572
20027.715	183.034	.231	32.616	41.584
21022.633	182.678	.212	34.252	43.596
22030.055	183.012	.195	35.887	45.608
23025.898	182.737	.179	37.521	47.620
24022.227	182.484	.166	39.154	49.633
25018.988	182.252	.154	40.786	51.645
26029.962	182.766	.143	42.417	53.657
27027.023	182.581	.133	44.047	55.670
28024.402	182.410	.125	45.676	57.682
29022.016	182.251	.117	47.305	59.695

.399 IS THE MAXIMUM PEAK CONCENTRATION

```

RANGE      BEARING
-----
0561.3     159.2

```

FIGURE A-5. (Continued)





because there was an excess of oxidizer involved in the hypergolic reaction. As indicated on page 3 of Figure A-5 (page A-25), the cloud stabilization height in this hypothetical accident (1072 m) is less than for the large above-ground spill described above because less heat was generated by the smaller amounts of fuel and oxidizer involved in the spill. The maximum peak ground-level concentration, as shown on page 4 of Figure A-5 (page A-26), is 0.60 ppm and occurs at 8561 m downwind from the accident at an azimuth bearing of 159 deg. As shown on pages 5 and 6 of Figure A-5 (pages A-27 and A-28), the maximum NO<sub>2</sub> total dosage is 28.1 ppm sec and the maximum 10-min time mean concentration is 0.05 ppm.

Figure A-6 is a plot of peak-centerline NO<sub>2</sub> concentration, dosage and 10-min mean concentration and Figure A-7 shows NO<sub>2</sub> concentration isopleths on the KSC map for the small above-ground spill scenario.

#### A.3.3 Silo Accident with the Door Closed

Figure A-8 shows the HARM program output of UDMH, NDMA and FDH concentrations for an in-silo accident with the silo door closed. There was no N<sub>2</sub>H<sub>4</sub> and NO<sub>2</sub> remaining in the cloud at the stabilization height because an excess of fuel was involved in the hypergolic reaction. The maximum peak centerline ground level concentrations of UDMH, NDMA and FDH are 0.914 ppm, 0.001 ppb and 0.464 ppb respectively. The corresponding maximum peak centerline ground-level dosages of UDMH, NDMA and FDH are 18.5 ppm sec, 0.13 ppb sec and 44.6 ppb sec respectively. The maximum peak centerline 10-min mean concentrations of UDMH, NDMA and FDH are respectively 0.03 ppm, less than  $5 \times 10^{-4}$  ppb and 0.074 ppb.

Figure A-9 shows a plot of UDMH peak centerline concentrations, dosage and 10-min mean concentrations for the in-silo accident. Isopleths of UDMH concentrations for the accident are shown in Figure A-10.

# CONCENTRATION AND DOSAGE FOR NO2

CLOUD HEIGHT	= 1007.	M	BOUNDING/PRECIPIT	1016 EST 12 NOV 1981	CONCENTRATION
TIME OF RISE	= 0.	SEC	TIME OF EXECUTION	2340 EST 9 FEB 1984	◆◆◆◆ DOSAGE
TOP OF LAYER	= 1045.	M	ACCIDENT TIME	10:55 EST 12 NOV 1981	0 0 0 0 10.0 MIN. AVE CONC
BOTTOM OF LAYER	= 0.	M	WIND LOCATION	MEC	
HEIGHT OF CLOUD	= 0.	M	DATA FILENAME	VRT215	

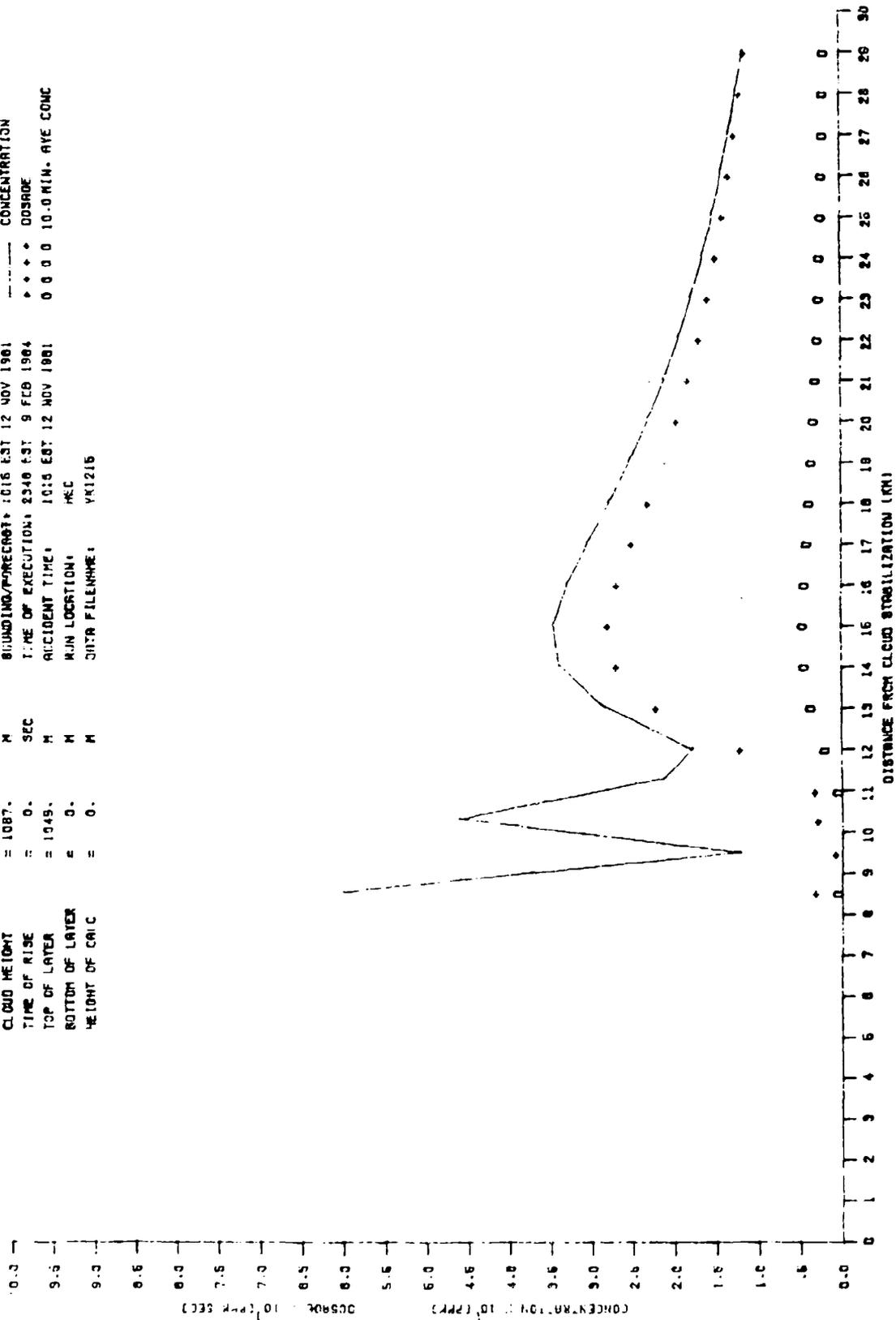


FIGURE A-6. Maximum centerline plot of ground-level NO<sub>2</sub> concentrations, dosages and 10-minute time mean concentrations for the small above-ground spill accident scenario.

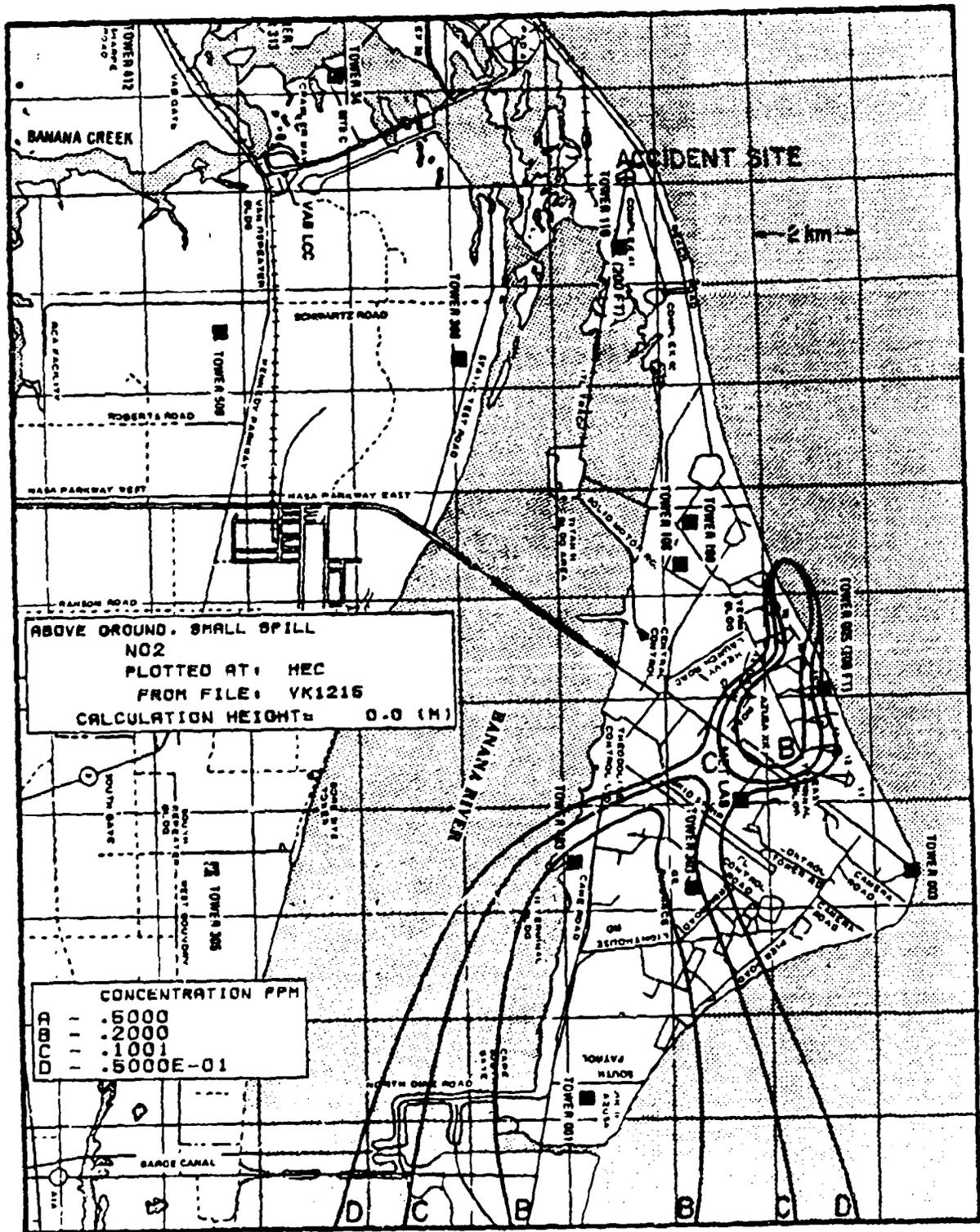


FIGURE A-7. Ground-level NO<sub>2</sub> concentration isopleth plot for the above ground small spill accident scenario.

```

.....
*****
***** HYPERGOLIC ACCIDENTAL RELEASE MODEL *****
***** (HARM) *****
***** UPDATE 8350 LOCATION NEC *****
*****
*****
***** DOOR CLOSED, INSTANTANEOUS *****
*****
***** TIME OF EXECUTION: 2148 EST DATE: 9 FEB 1984 *****
***** TIME OF ACCIDENT: 1015 EST DATE: 12 NOV 1981 *****
*****
.....

```

.....MODEL INPUT OPTIONS SELECTED ARE AS FOLLOWS:.....

```

RUN TYPE: OPERATIONAL
METEOROLOGICAL DATA FILE NAME: VK1215
MODEL TYPE: CONCENTRATION/DOSE
THE ACCIDENT OCCURRED IN THE: SILO
THE REACTION WAS: INSTANTANEOUS
THE SILO DOOR WAS: CLOSED
POUNDS OF FUEL INVOLVED IN THE ACCIDENT: 106500.
POUNDS OF OXIDIZER INVOLVED IN THE ACCIDENT: 201013.
ENTRAINMENT PARAMETERS:
GAMMAX= .64
GAMMAY= .64
GAMMAZ= .64
ACCIDENT SITE LOCATION:
UTMX= 17.38
UTRY= 20.06
CALCULATIONS TO BE DONE AT (METERS):
DIFFUSION COEFFICIENTS:
ALPHA=1.00
BETA=1.00
DOWNWIND EXPANSION DISTANCES:
XRY= 100.00
XRZ= 100.00
CONCENTRATION AVERAGING TIME (SEC):
PRINT OUT WILL BE: 600.00
SUMMARY

```

FIGURE A-8. HARM program output listing for an interactive run for the in-silo accident with the silo door closed.

\*\*\*\*\* METEOROLOGICAL DATA \*\*\*\*\*

RUN NUMBER: 1 USING METEOROLOGICAL DATA FILE: VK1215

TEST NBR 09101 T MINUS 0 VK1215  
 RAWINSONDE RUN AN/GND-1  
 CAPE CANAVERAL AFS, FLORIDA  
 ASCENT NBR 0434

\*\*\*\*\* SOUNDING \*\*\*\*\*

TIME: 1015 EST DATE: 12 NOV 1981

SURFACE DENSITY (G/M\*\*3): 1190.43

MET LEVEL NO.	ALTITUDE (FT)	ALTITUDE (M)	DIR. (DEG)	SPEED (M/S) (KTS)	TEMP (DEG. C)	PTEMP (DEG. C)	DPTEMP	PRESS (MB.)	RH (%)
1	16	4.9	337.0	7.72 15.02	22.4	22.99	0.0	1016.9	67.0
2	493	150.3	337.0	8.73 17.02	20.4	22.29	0.0	1000.0	70.0
3	1000	304.8	351.0	10.30 20.02	18.5	21.83	0.0	982.3	73.0
4	1536	390.1	3.0	9.78 19.02	15.4	21.48	0.0	950.0	86.0
5	2000	609.6	4.0	9.78 19.02	15.2	21.46	0.0	947.9	87.0
6	2235	681.2	0.0	9.78 19.02	14.4	21.30	0.0	946.0	88.0
7	3000	914.4	19.0	9.27 18.02	13.2	22.36	0.0	914.4	90.0
8	3441	1048.8	28.0	8.73 17.02	11.7	22.20	0.0	900.0	100.0
9	3710	1133.2	18.0	8.24 16.02	12.2	22.75	0.0	891.0	99.0
10	4000	1219.2	16.0	8.24 16.02	12.2	23.43	0.0	881.9	99.0
11	4375	1333.5	13.0	8.24 16.02	12.2	24.33	0.0	870.0	24.0
12	5000	1524.0	4.0	7.21 14.02	11.7	25.96	0.0	850.4	35.0
13	5005	1525.5	4.0	6.63 13.01	11.6	25.89	0.0	850.0	35.0
14	6000	1828.8	351.0	5.13 10.01	9.5	26.82	0.0	819.9	41.0
15	6650	2029.4	352.0	5.13 10.01	7.8	27.14	0.0	800.0	45.0
16	6670	2033.0	352.0	5.13 10.01	7.8	27.19	0.0	800.0	46.0
17	7000	2133.6	350.0	5.13 10.01	7.4	27.65	0.0	790.3	38.0
18	7425	2262.1	5.0	5.66 11.01	6.8	28.24	0.0	778.0	30.0
19	8000	2438.4	6.0	6.18 12.01	6.0	29.29	0.0	761.5	35.0
20	8269	2520.4	7.0	6.69 13.01	5.6	29.77	0.0	754.0	39.0
21	8396	2559.1	6.0	7.21 14.02	5.7	30.28	0.0	750.0	34.0
22	9000	2743.2	0.0	7.72 15.02	6.4	32.75	0.0	733.8	18.0
23	9140	2785.9	355.0	8.24 16.02	6.3	33.27	0.0	730.0	15.0
24	10000	3048.0	354.0	8.73 17.02	5.6	35.14	0.0	707.0	17.0

\*\* - INDICATES THAT DATA IS LINEARLY INTERPOLATED FROM INPUT METEOROLOGY

FIGURE A-8. (Continued)

\*\*\*\*\* STABILIZED CLOUD PARAMETERS \*\*\*\*\*

NET LAYER NO.	TOP OF LAYER (METERS)	CLOUD RISE TIME (SECONDS)	RANGE** FROM SITE (METERS)	AZIMUTH BEARING FROM SITE (METERS)
1	150.3	12.9	5099.7	157.0
2	304.8	34.3	5074.5	163.9
3	599.1	100.3	6169.0	176.2
4	609.6	196.1	6018.6	181.7
5	681.2	120.9	6010.9	183.8
6	914.4	220.7	5652.4	189.7
7	1048.8	287.6	5584.9	195.9
8	1133.2	336.2	5419.4	199.4
9	1219.2	398.9	5372.9	192.7
10	1333.5	618.4 *	5376.2	192.2
11	1524.0	618.4 *	5376.2	192.2
12	1525.5	618.4 *	5376.2	192.2
13	1828.8	618.4 *	5376.2	192.2
14	2029.4	618.4 *	5376.2	192.2
15	2033.0	618.4 *	5376.2	192.2
16	2133.6	618.4 *	5376.2	192.2
17	2263.1	618.4 *	5376.2	192.2
18	2438.4	0.0	0.0	0.0
19	2529.0	0.0	0.0	0.0
20	2559.1	0.0	0.0	0.0
21	2743.2	0.0	0.0	0.0
22	2765.9	0.0	0.0	0.0
23	3048.0	0.0	0.0	0.0

\* - INDICATES CLOUD STABILIZATION TIME WAS USED  
 \*\* - RANGE FROM SITE IS AT CLOUD STABILIZATION TIME

\*\*\*\*\* CLOUD STABILIZATION \*\*\*\*\*

CALCULATION HEIGHT	(METERS)	0.00
STABILIZATION HEIGHT	(METERS)	1263.50
STABILIZATION TIME	(SECS)	618.41
FIRST MIXING LAYER HEIGHT:	(METERS)	TOP = 1048.82
		BASE = 0.00
SECOND SELECTED LAYER HEIGHT:	(METERS)	TOP = 3048.00
		BASE = 1048.82
SIGMA(Z) AT THE SURFACE	(DEGREES)	13.5793
SIGMA(EL) AT THE SURFACE	(DEGREES)	13.5793

FIGURE A-8. (Continued)









```

.....
( HARM )
.....
UPDATE 8350 LOCATION NEC
CONCENTRATION/DOSE MODEL
MAXIMUM CENTERLINE CALCULATIONS
.....
DOOR CLOSED, INSTANTANEOUS
.....
FOR SPECIES NDHA
.....

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CALCULATIONS WERE DONE AT 0.00 M AGL  
AND APPLY TO THE LAYER BETWEEN 0.00 AND 1048.02 M AGL  
DOWNWIND FROM THE ACCIDENT SITE AT ( 17.58, 20.06 )

THE METEOROLOGICAL DATA IS FROM 1015 EST 12 NOV 1981  
ACCIDENT TIME IS 1015 EST 12 NOV 1981  
TIME OF EXECUTION IS 2148 EST 9 FEB 1984

RANGE FROM SITE (METERS)	BEARING FROM SITE (DEGREES)	TOTAL DOSE (PPB SEC)	CLOUD ARRIVAL TIME (MIN)	CLOUD DEPARTURE TIME (MIN)
5382.438	158.290	.002	10.790	11.042
6320.137	161.704	.002	9.262	13.021
7200.907	166.453	.003	10.964	15.013
8004.730	178.049	.006	12.663	17.012
9015.773	183.409	.028	14.365	19.016
10031.418	184.553	.060	16.062	21.023
11038.488	184.803	.086	17.759	23.031
12035.561	184.423	.103	19.451	25.041
13035.904	184.273	.114	21.093	27.051
14039.180	184.301	.120	22.733	29.061
15032.607	183.794	.123	24.371	31.072
16027.066	183.349	.125	26.007	33.083
17034.930	183.689	.127	27.642	35.093
18030.672	183.362	.128	29.275	37.106
19026.941	183.069	.129	30.907	39.118
20023.660	182.803	.130	32.538	41.130
21020.762	182.566	.130	34.168	43.141
22018.199	182.349	.131	35.797	45.153
23015.922	182.150	.131	37.426	47.165
24013.890	181.968	.132	39.053	49.177
25026.523	182.657	.132	40.680	51.190
26024.648	182.513	.132	42.307	53.202
27022.926	182.379	.133	43.933	55.214
28021.336	182.253	.133	45.558	57.226
29019.071	182.140	.133	47.184	59.238

.133 IS THE MAXIMUM TOTAL DOSE

RANGE	BEARING
29019.9	182.1

FIGURE A-8. (Continued)

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.....
( WARM )
.....
UPDATE 0350 LOCATION NEC
CONCENTRATION/DOSE/AGE MODEL
MAXIMUM CENTERLINE CALCULATIONS
.....
DOOR CLOSED, INSTANTANEOUS
.....
FOR SPECIES HDRA
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CALCULATIONS WERE DONE AT 0.00 M AGL  
 AND APPLY TO THE LAYER BETWEEN 0.00 AND 1040.92 M AGL  
 DOWNWIND FROM THE ACCIDENT SITE AT ( 17.50, 20.06 )

THE METEOROLOGICAL DATA IS FROM 1015 EST 12 NOV 1981  
 ACCIDENT TIME IS 1015 EST 12 NOV 1981  
 TIME OF EXECUTION IS 2140 EST 9 FEB 1984

RANGE FROM SITE (METERS)	BEARING FROM SITE (DEGREES)	10.0 MIN. NEAR CONCENTR- TRATION (PPM)	CLOUD ARRIVAL TIME (MIN)	CLOUD DEPARTURE TIME (MIN)
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	RANGE	BEARING
000 IS THE MAXIMUM 10.0 MIN NEAR CONCENTRATION	29019.9	182.1

FIGURE A-8. (Continued)

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*****
*****          (MARR)          *****
*****          UPDATE 0350   LOCATION NEC          *****
*****          CONCENTRATION/DOSAGE MODEL          *****
*****          MAXIMUM CENTERLINE CALCULATIONS          *****
*****
*****          DOOR CLOSED, INSTANTANEOUS          *****
*****
*****          FOR SPECIES FOM          *****
*****
.....

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CALCULATIONS WERE DONE AT 0.00 M AGL  
 AND APPLY TO THE LAYER BETWEEN 0.00 AND 1048.82 M AGL  
 DOWNWIND FROM THE ACCIDENT SITE AT ( 17.58, 20.06)

THE METEOROLOGICAL DATA IS FROM 1015 EST 12 NOV 1981  
 ACCIDENT TIME IS 1015 EST 12 NOV 1981  
 TIME OF EXECUTION IS 2148 EST 9 FEB 1984

RANGE FROM SITE (METERS)	BEARING FROM SITE (DEGREES)	PEAK CONCENTRATION (PPB)	CLOUD ARRIVAL TIME (MIN)	CLOUD DEPARTURE TIME (MIN)
5382.438	158.290	.084	10.790	11.042
6320.137	161.704	.060	9.262	13.021
7194.447	166.668	.116	10.964	13.013
8159.328	168.678	.102	12.663	17.012
9002.488	178.672	.145	14.363	19.016
10007.457	182.231	.252	16.062	21.023
11017.373	183.237	.362	17.759	23.031
12019.471	183.281	.403	19.451	25.041
13018.154	183.043	.437	21.093	27.051
14018.996	183.002	.434	22.733	29.061
15021.896	183.113	.462	24.371	31.072
16016.768	182.641	.464	26.007	33.083
17022.375	182.957	.463	27.642	35.093
18018.391	182.608	.461	29.275	37.106
19015.608	182.296	.457	30.907	39.118
20012.133	182.014	.452	32.538	41.130
21020.762	182.566	.448	34.168	43.141
22018.199	182.349	.442	35.797	45.153
23015.922	182.150	.437	37.426	47.167
24013.898	181.968	.431	39.053	49.177
25012.098	181.801	.424	40.680	51.190
26010.492	181.647	.418	42.307	53.202
27009.066	181.503	.412	43.933	55.214
28021.336	182.259	.405	45.558	57.226
29019.871	182.140	.399	47.184	59.238

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RANGE      BEARING
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16016.8    182.8

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.464 IS THE MAXIMUM PEAK CONCENTRATION  
 FIGURE A-8. (Continued)



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*****
*****      (HARR)      *****
*****      UPDATE 0350  LOCATION  MEC      *****
*****      CONCENTRATION/DOSAGE MODEL      *****
*****      MAXIMUM CENTERLINE CALCULATIONS *****
*****
*****      DADR CLOSED, INSTANTANEOUS      *****
*****
*****      FOR SPECIES FBN      *****
*****
.....

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CALCULATIONS WERE DONE AT 0.00 M AGL  
 AND APPLY TO THE LAYER BETWEEN 0.00 AND 1048.82 M AGL  
 DOWNWIND FROM THE ACCIDENT SITE AT ( 17.58, 20.06)

THE METEOROLOGICAL DATA IS FROM 1015 EST 12 NOV 1981  
 ACCIDENT TIME IS 1015 EST 12 NOV 1981  
 TIME OF EXECUTION IS 2148 EST 9 FEB 1984

RANGE FROM SITE (METERS)	BEARING FROM SITE (DEGREES)	10.0 MIN. MEAN CONCENTRATION (PPB)	CLOUD ARRIVAL TIME (MIN)	CLOUD DEPARTURE TIME (MIN)
5382.438	190.290	.001	10.790	11.042
6320.137	161.704	.002	9.262	13.021
7200.907	166.453	.002	10.964	15.013
8004.730	178.049	.003	12.665	17.012
9015.773	183.409	.016	14.365	19.016
10031.418	184.355	.033	16.062	21.023
11038.488	184.805	.048	17.759	23.031
12035.561	184.425	.058	19.451	25.041
13035.904	184.273	.064	21.093	27.031
14039.180	184.301	.067	22.733	29.061
15032.607	183.794	.069	24.371	31.072
16027.066	183.349	.070	26.007	33.083
17034.930	183.689	.071	27.642	35.095
18030.672	183.362	.071	29.275	37.106
19026.941	183.069	.072	30.907	39.118
20023.660	182.805	.072	32.538	41.130
21020.762	182.566	.073	34.168	43.141
22018.199	182.349	.073	35.797	45.153
23015.922	182.150	.073	37.426	47.165
24013.898	181.968	.073	39.053	49.177
25026.523	182.657	.074	40.680	51.190
26024.648	182.513	.074	42.307	53.202
27022.926	182.373	.074	43.933	55.214
28021.336	182.255	.074	45.558	57.226
29019.871	182.140	.074	47.184	59.238

.074 IS THE MAXIMUM 10.0 MIN MEAN CONCENTRATION 29019.9 182.1  
 /HAR01 «RUNTIME ERROR» 0493 @ 60311

FIGURE A-8. (Continued)

# CONCENTRATION AND DOSAGE FOR UDMH

CLOUD HEIGHT	= 1284.	M	SOUNDING/RECAST	= 1016 EST 12 NOV 1961	CONCENTRATION
TIME OF RISE	= 0.	SEC	TIME OF EXECUTION	= 2397 EST 8 FEB 1964	DOSAGE
TOP OF LAYER	= 1048.	M	ACCIDENT TIME	= 1016 EST 12 NOV 1961	0 0 0 0 10.0 MIN. AVE CONC
BOTTOM OF LAYER	= 0.	M	RUN LOCATION	= MEC	
HEIGHT OF CALC	= 0.	M	DATA FILENAME	= VK1216	

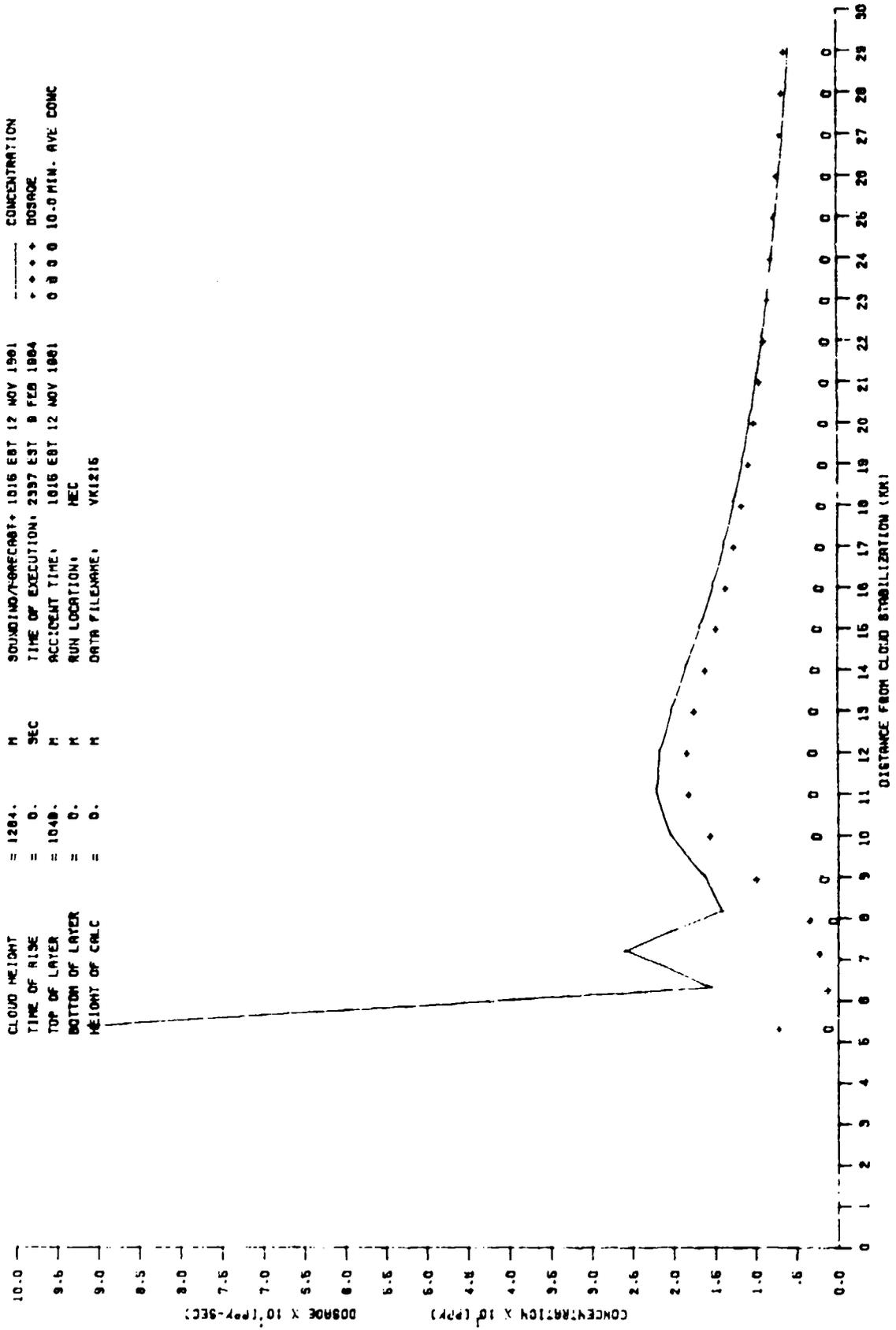


FIGURE A-9. Maximum centerline profile plot of ground-level UDMH concentrations, dosages and 10-minute time mean concentrations for the in-silo accident with the silo door closed.

