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Proceedings of the Conference on Environmental Chemistry of Hydrazine Fuels, Tyndall AFB, 13 September 1977

DET 1 (CEEDO) ADTC
ENVIRONICS DIRECTORATE
TYNDALL AIR FORCE BASE, FL 32403

MARCH 1978

FINAL REPORT FOR PERIOD 13 SEPTEMBER 1977

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Hydrazine	Environmental Quality	
Monomethylhydrazine	Missile Fuels	
1,1-Dimethylhydrazine	Nitrosamines	
Monopropellants	UDMH	

20. ABSTRACT *(Continue on reverse side if necessary and identify by block number)*

On 13 September 1977, the Civil and Environmental Engineering Development Office, ADTC, Tyndall AFB, Florida, hosted a conference on the environmental chemistry of hydrazines used for missile fuels and monopropellants. A total of 14 papers were presented on the following general topics related to hydrazine fuels:

1. Sources and Control of Fuels Emissions and Spills
2. Environmental Monitoring Techniques and Instrumentation

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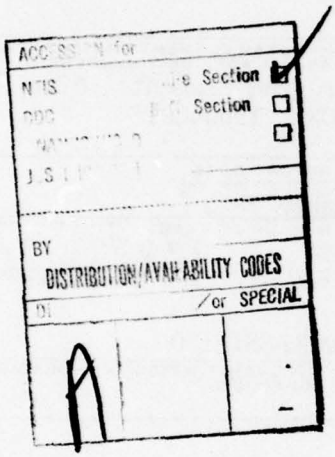
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Item 20. ABSTRACT (CONCLUDED)

3. Analysis of Fuels and Degradation Products
4. Fate of Hydrazines in the Environment



PREFACE

The use of hydrazine and its derivatives is expanding rapidly. In addition to serving as fuels for missile guidance systems, the hydrazines will be used by NASA in the space shuttle, and as monopropellant fuel on aircraft auxiliary power units. Because of the documented toxicity of the hydrazines to humans as well as other organisms, it is imperative to have reliable information on the potential environmental impact resulting from their widespread use. Accurate and current information will be needed on the sources of potential environmental contamination by the hydrazine fuels. Data will also be required on the environmental chemistry of these substances in order to develop effective control processes and make realistic predictions of the environmental impact of accidental fuel releases.

The first Conference on the Environmental Chemistry of Hydrazine Fuels was arranged by the Environmental Sciences Division of the Civil and Environmental Engineering Development Office (CEEDO) at Tyndall AFB, Florida on 13 September 1978. CEEDO directs both in-house and contracted research efforts under Program Element 62601F on environmental problems concerning the hydrazine fuels and serves as the focal point for related DOD-sponsored research. The purpose of the meeting was to stimulate discussion and interchange of information regarding environmental problems with the use, transport and handling of hydrazine fuels.

There were 65 participants at the conference including representatives from the Air Force, Army, NASA, Universities, civilian research organizations and chemical manufacturers. Attendees heard formal presentations on current technology and environmental problems arising from the use of the hydrazines and these papers are compiled in this technical report.

This report has been reviewed by the Information Office (OI) and is releasable to the National Technical Information Service (NTIS). At NTIS it will be available to the general public, including foreign nations.

This technical report has been reviewed and is approved for publication.

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Paper No 1

SYNTHESES OF HYDRAZINE AND ITS DERIVATIVES

Harry H. Sisler

and

Milap A. Mathur

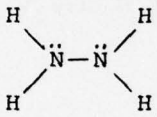
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INTRODUCTION

Because of their large heat of combustion and their high specific impulse and high density impulse, hydrazine, monomethylhydrazine (MMH), and 1,1-unsymmetricaldimethyl hydrazine (UDMH) have achieved special importance as high energy rocket fuels. UDMH is a component of several presently used liquid rocket fuel mixtures. These include Aerozine 50 (50% UDMH), MAF1 (39% UDMH), MAF3 (20% UDMH), and MAF4 (60% UDMH). Monomethyl hydrazine is a major component of the space shuttle fuels. The demand for these high energy rocket fuels is necessarily on the increase as man's desire to explore outer space and the universe is increasing.

Hydrazine and its derivatives also find many other uses besides being high energy fuels. Hydrazine is a powerful reducing agent and is used as an oxygen scavenger in the treatment of boiler water; UDMH and MMH are used for the treatment of hard water. Derivatives of hydrazine are used as plant growth regulators and herbicides and as growth inhibitors of several DNA and RNA type viruses. They are used as extenders for urethan polymers, blowing agents for plastics, anti-oxidants in soaps, and in the processing of the pressure-sensitive tapes.

For the development of early hydrazine chemistry, the credit goes to the three outstanding chemists. Fischer (1) in 1875, described the preparation of hydrazine by the hydrolysis of the potassium salt of phenylhydrazine sulfonic acid. He also identified this compound as the hypothetical base $H_2N\text{-}NH_2$, which he named hydrazine after the already known parent hydrazo compound. Curtius (2) in 1887 independently prepared hydrazine sulfate from dizaoacetic ester and de Bruyn (2) in 1894 for the first time obtained anhydrous hydrazine and investigated its properties.



Hydrazine remained a laboratory curiosity until World War II. It was during World War II the Germans produced hydrazine on a large scale and used it as the rocket fuel. Since World War II the chemistry and technical knowledge regarding hydrazine, its derivatives, and their use has been greatly expanded. The increasing demand for these chemicals has stimulated development of different techniques for their synthesis.

METHODS USED FOR THE PREPARATION OF HYDRAZINE AND SUBSTITUTED HYDRAZINES

There are various methods reported in literature for the preparation of hydrazine and substituted hydrazines. Those that are of commercial interest are the Raschig synthesis, N-nitrosodimethylamine process, nitramine process, urea process, and the Sisler process. These are described below, and their advantages and disadvantages are discussed with emphasis on the Sisler process developed in our laboratory.

Raschig Synthesis

The Raschig method was reported by Thiele (2) in 1893 and was improved and developed in 1907 by F. Raschig (3). Raschig reacted solutions of ammonia and sodium hydrochlorite to obtain hydrazine. He discovered that the yield of hydrazine can be improved by allowing a large excess of ammonia to react rapidly with sodium hypochlorite at high temperature, high pressure, and in presence of an additive such as glue or gelatin. The principal reactions involved in the Raschig process are summarized below.

$$2OH^- + Cl_2 \xrightarrow{NaOH} OCl^- + Cl^- + H_2O$$

$$OCl^- + NH_4^+ \xrightarrow[\Delta]{NaOH} NH_2Cl + H_2O$$

$$NH_2Cl + HNR_2 \xrightarrow[\Delta]{NaOH} R_2NNH_2 + H^+ + Cl^- \quad (R = H \text{ or alkyl group})$$

Since the formation of chloramine is rapid and the reaction of chloramine with ammonia is slow, the hydrazine so formed competes with ammonia for reaction with chloramine. This gives rise to several by-products.

The yield of UDMH by the Raschig process is between 30 and 60% based on chlorine, and the concentration of UDMH in water solution has to be kept between 1 and 2% to avoid the side reactions of UDMH with NH_2Cl. A low concentration of UDMH increases the overall cost of Raschig's process since additional heat is required to remove large amounts of water. This also makes the recovery of UDMH difficult and complex. Another difficulty involved with this process is the lack of information on technical details and critical processing conditions for the manufacture of both UDMH and MMH.

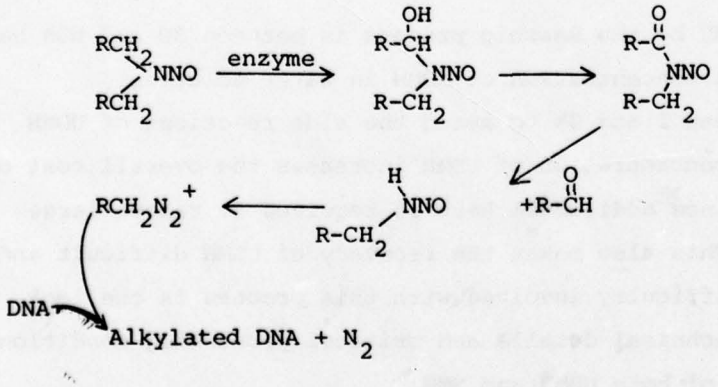
N-Nitroso-Dimethylamine Process

The chemical principles involved in this process are nitrosation of a secondary amine to an N-nitrosoamine and then the catalytic reduction of the N-nitrosoamine by hydrogen to give unsymmetrical-dimethylhydrazine (UDMH).

$$(CH_2)_2NH + HNO_2 \xrightarrow{NaNO_2 + HCl} (CH_3)_2NNO + H_2O$$

$$(CH_3)_2NNO + 2H_2 \xrightarrow[\text{catalyst}]{} (CH_3)_2NNH_2 + H_2O$$

The reaction cannot be applied to primary amines because deamination takes place. Thus, monomethylhydrazine cannot be made by this process. Also, it has been recently reported that $(CH_3)_2NNO$ causes environmental difficulties because of its proven carcinogenic character toward test animals. The details of the biological interactions through which the nitrosamines initiate tumors are unknown, but the most widely quoted hypotheses are generally based on the modification of intracellular DNA through alkylation of DNA by an electrophilic metabolite of nitrosamine (4).



Nitramine Process

In some respects the nitramine route parallels the nitrosamine route. The most notable difference is that in this process the chemical intermediate formed is dimethylnitramine instead of dimethylnitrosamine. Dimethylnitramine is then hydrongenated to give UDMH. The chemistry of this process is summarized in the following equations.

$$(CH_3)_2NH + \underset{98\%}{HNO_3} \longrightarrow (CH_3)_2NH_2NO_3$$

$$(CH_3)_2NHNO_3 + (CH_3CO)_2O \xrightarrow{HCl} (CH_3)_2NNO_2 + 2CH_3COOH$$

$$(CH_3)_2NNO_2 + 6H_2 \xrightarrow{Pd/C} (CH_3)_2NNH_2 + 2H_2O$$

Like the nitrosamine route, this method has not been developed for commercial production of MMH or hydrazine. Also, the material cost is high and dimethylnitramine is some what corrsive. Otherwise, this method works well and through distillation and purification specification grade UDMH can be obtained.

Urea Process

Another potential method for the manufacture of hydrazine is the urea process. The degradation of urea by sodium hypochlorite forms the basis of this process for the production of hydrazine.

$$NH_2-\overset{O}{\overset{\|}{C}}-NH_2 + OCl^- + 2OH^- \longrightarrow NH_2NH_2 + Cl^- + CO_3^{--} + H_2O$$

In the urea process the reactants are initially mixed cold but the heat of reaction increases the temperature to 100°C where the reaction takes place rapidly. Although N,N-Dimethyl urea ($(CH_3)_2N-CO-NH_2$) and methyl urea are now available commercially and may be used as the starting material for UDMH and MMH respectively, no such examples are reported in the literature. This process looks promising and requires serious future consideration.

Sisler Process

A process which is currently being developed for the manufactur of hydrazine fuels is the Sisler process. There are basically two steps involved in Sisler chemistry:

a. production of anhydrous chloramine from Cl_2 and NH_3.

b. allowing the chloramine to react with the desired amine or ammonia to obtain either a substituted hydrazine (MMH or UDMH) or hydrazine. Since the chloramine generated is anhydrous, and the amines and ammonia can be obtained anhydrous, one can prepare either anhydrous hydrazines or hydrazines in water solution (Modified Sisler process). The remaining sections of this paper described in more detail the nature of the Sisler Process.

In the first step of the Sisler process chloramine is prepared in a chloramine generator. Predried gaseous Cl_2 is diluted with N_2 gas (1:1 mole ratio) and passed through the central tube in the generator. Anhydrous ammonia gas is simultaneously fed into the generator through fine jets. The reaction temperature in the generator is kept between

$300^{o}C$ and $350^{o}C$ and the molar ratio of NH_3 to Cl_2 is maintained at 2:1. The reaction results in the immediate formation of chloramine and ammonium chloride.

$$2NH_3 + Cl_2 \xrightarrow[N_2]{300\text{-}350^{o}C} NH_2Cl + NH_4Cl$$

In an ideal situation, only chloramine and ammonium chloride are formed in the generator, but under non-optimum conditions the following side reactions may also result.

$$8\ NH_3 + 3Cl_2 \longrightarrow 6NH_4Cl + N_2$$

$$3\ NH_2Cl + 2NH_3 \longrightarrow N_2 + 3NH_4Cl$$

$$3\ NH_3 + 2Cl_2 \longrightarrow NHCl_2 + 2NH_4Cl$$

$$4\ NH_3 + 3Cl_2 \longrightarrow NCl_3 + 3NH_4Cl$$

These side reactions could very well reduce the overall yield of chloramine. Both at Martin Marietta and Naval Ordinance Station (NOS), Indian Head, Maryland, work is continuing to modify the chloramine generator, both to improve chloramine yield and to prevent frequent choking of the generator by NH_4Cl. The chloramine produced is filtered through glass wool pads and passed on to the reaction vessel for the reaction with amines or ammonia as desired. A high yield of chloramine based on chlorine has been obtained.

The chloramine so obtained is then passed through either anhydrous amine or ammonia to obtain anhydrous hydrazines or into water solutions to obtain aqueous solutions of hydrazines. The principal reactions involved in the formation of various hydrazines are represented by the following equations.

$$NH_2Cl + NH_3 \longrightarrow NH_2NH_2 + HCl$$

$$NH_2Cl + H_2NCH_3 \longrightarrow CH_3HNNH_2 + HCl$$

$$NH_2Cl + HN(CH_3)_2 \longrightarrow (CH_3)_2NNH_2 + HCl$$

The hydrazines are bases and are produced with HCl. They therefore react with HCl to form salts. This can be prevented by the presence of a stronger base than the hydrazine, or the free hydrazine can be recovered by neutralization of the hydrazinium salts with caustic alkali.

In the Sisler process for the manufacture of hydrazine, if a hydrazine is not effectively separated from chloramine, further reaction between chloramine and hydrazine will occur. Studies with the formation of UDMH have shown that at least three such products are formed.

$(CH_3)_2N(NH_2)_2^+Cl^-$

Dimethyltriazimium Chloride (DTC)

$(CH_3)_2NN = NN(CH_3)_2$

Tetramethyl tetrazene (TMT)

$(CH_3)_2NN = CH_2$

Formaldehyde dimethylhydrazone (FDH)

These products not only reduce the overall yield of UDMH, but are undesirable impurities. Efforts are being made to avoid or minimize the formation of these side products or to convert them back to UDMH.

In spite of the side reactions, the study at Martin Marietta on the technical feasibility of Sisler chloramine chemistry (1975 report) has shown that UDMH can be obtained in acceptable yield under the following conditions.

(1) The absorbtion and reaction of chloramine in neat dimethylamine at -70°C (anhydrous approach).

$$NH_2Cl + (CH_3)_2NH \xrightarrow[-80^{\circ}C \text{ to } -70^{\circ}C]{\text{Anhydrous}} (CH_3)_2NNH_2 + HCl$$

yield UDMH = 60-65%

UDMH/FDH ratio = 15-20

(2) The absorbtion and reaction of chloramine in aqueous solution containing approximate 10% NaOH and 20% DMA (aq. caustic approach).

$$\underset{\text{DMA}}{NH_2Cl + (CH_3)_2NH} \xrightarrow[H_2O + 10\% \text{ NaOH} + 15\% \text{ DMA}]{0^{\circ}C \text{ to } 10^{\circ}C} (CH_3)_2NNH_2 + HCl$$

yield UDMH more than 70%

UDMH/FDH ratio more than 70

Current Research on the Sisler Process

In order to increase the yield by Sisler's process, to reduce the side products, and to define conditions under which consistent results can be obtained, it is desirable to have some knowledge of kinetics of the MMH and UDMH producing reactions, as well as to understand the kinetics and mechanism of the reactions by which the side products are formed and decomposed. To fulfill this purpose a joint effort is being made involving the chemistry laboratory of the University of Florida and the White Oak Laboratory at Naval Surface Weapons Center.

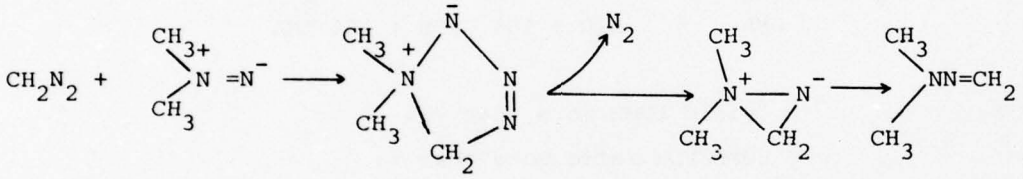
Studies have been carried out at the University of Florida relating to the synthesis of UDMH and MMH by chloramination to determine the

mechanism of formation of UDMH as well as side products TMT, DCT, and FDH. Also, investigations are in progress to regenerate UDMH from formaldehyde dimethylhydrazone (FDH) and dimethyltriazanium chloride (DCT). The results of the studies conducted at the University of Flordia so far are summarized below:

(a) Formation of FDH. Utvary and coworkers (5)(6) have suggested the mechanism of formation of formaldehyde dimethyl hydrazone through diazene and diazomethane.

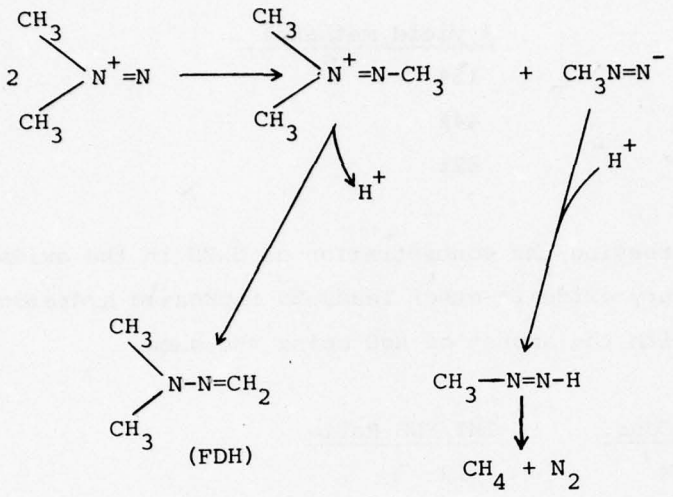
$$(CH_3)_2N\text{-}NH_2 + NH_2Cl \longrightarrow (CH_3)_2\overset{+}{N}{=}\overset{-}{N} + NH_4Cl$$

$$(CH_3)_2\overset{+}{N} = \overset{-}{N} \longrightarrow CH_4 + CH_2N_2$$



This mechanism assumes the intermediate of diazomethane in the arrangements of diazene.

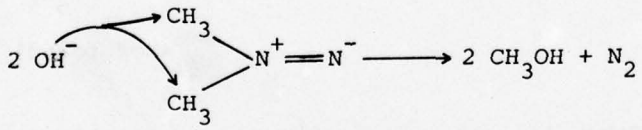
The oxidative reactions studied by Utvary et al (5)(6) leading to the postulation of this mechanism were performed in diethyl ether solution. We have demonstrated that the hydrazone is also formed in aqueous media in which the half-life of diazomethane is greatly reduced. It is therefore unlikely that the Utvary mechanism is operative in aqueous solutions. The following alternate mechanism for the rearrangement of diazene to hydrazone is proposed. As in the Utvary mechanism we assume the formation of a diazene by the oxidation of UDMH. We then propose that two diazene molecules react with each other as follows:



The data supporting this mechanism are summarized below.

(1) Both N_2 and CH_4 have been identified by gas liquid phase chromatography and mass spectroscopy as gaseous products from oxidation of UDMH.

(2) The susceptibility of the methyl group of the diazene to nucleophilic attack has been demonstrated as follows. Oxidation of UDMH by Ag_2O in aqueous NaOH solution leads to the production of methyl alcohol.



This product arises as a result of nucleophilic attack of OH^- ion on the methyl group of the diazene. Increased hydroxide ion concentration leads to increased alcohol production.

$[OH^-]$	% yield methanol
2 M	15%
5 M	44%
10 M	82%

(3) Decreasing the concentration of UDMH in the oxidation reaction with mercury oxide in ether leads to increased hydrazone production (25^{o}) with the amount of HgO being the same.

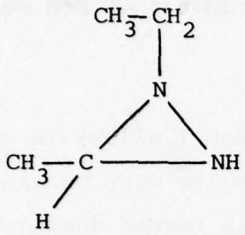
UDMH Conc.	TMT/FDH Ratio
0.52 M	19
0.26 M	10.5
0.13 M	1.6
0.065 M	0.55

(4) The diazene was generated from UDMH and Ag_2O in presence of excess of diphenyldiazomethane. If the Utvary mechanism were operative, the product arising from trapping of the diazene with diphenyldiazomethane would be benzophenone dimethyl hydrazone. This compound was not detected.

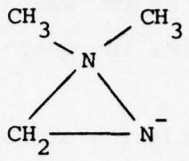
$$(C_6H_5)_2CN_2 + (CH_3)_3N^+{=}N^- \longrightarrow (CH_3)_2NN{=}C(C_6H_5)_2 + N_2$$

(not found)

(5) Other investigations reported in the literature do not support Utvary's mechanism. Lemal et al (7) synthesized diaziridine (I) and subjected it to



(I)



(II)

mild conditions of oxidation and isolated it unchanged. Utvary proposed that intermediate (II) will change to FDH on oxidation. This does not seem likely. These two compounds are very similar in structure and if (I) does not undergo oxidation, the possibility of (II) being oxidized is also remote.

(6) It is known that the presence of hydroxide ion during the dehydrogenation of UDMH leads to increased production of gaseous products (CH_4 and N_2) and it is indicated (although not proven at present) that it decreases the yields of formaldehyde dimethylhydrazone and tetramethyl tetrazene. These reactions are invariably accompained by the formation of CH_3OH and gaseous products CH_4 and N_2. A typical gas product mixture analyzes as $CH_4/N_2 = 0.5$. These results further tend to rule out the Utvary diazomethane mechanism. In the Utvary mechanism, the CH_4/N_2 ratio should equal or exceed 1.0, since methane and nitrogen are formed in two successive steps. Our proposed mechanism would predict CH_4/N_2 ratio = 1.0, since the two gaseous products are generated in the same step. The fact that the ratio is less than 1.0 results from N_2 produced by othr reactions.

(b) Factors influencing products of UDMH oxidation. The products of the oxidation of UDMH depends on a variety of factors. The oxidation of UDMH with yellow HgO in ether and in nitrogen atmosphere

was carried out at 0°C and 25°C. The major product at 0°C was FDH and a small amount of TMT was also formed. At 25°C the amount of FDH decreased and that of TMT increased.

When oxidation of UDMH was carried out with HgO (yellow) in cyclohexane at 30°C under a nitrogen atmosphere, different results were obtained. The major product in this case was TMT. No FDH was formed during the reaction. The table below lists three different experiments varying the concentration of UDMH.

UDMH in cyclohexane	HgO
(I) 100 ml 0.20M (20mmol)	4.50 g (20 mmol)
(II) 100 ml 0.10M (10 mmol)	4.5 g (20 mmol)
(III) 100 ml. .05 M (5 mmol)	4.5 g (20 mmol)

The reaction is very rapid and almost all the UDMH was consumed in 83 mins. in Ex. (I) and within 2 mins. in Exps. (II) and (III). The reaction is too fast to be followed using gas chromatogrophy. Oxidation of UDMH was also carried out with elemental oxygen in a system closed to atmosphere. The conditions of two separate experiments are shown below:

Experiment (I)

Temperature	30°C
Solvent	Ether
Oxygen	90 mmol of O_2
UDMH	50 mmol in 250 ml ether solution
Toluene Reference	1.0 g

Experiment (II)

Temperature	$30^{o}C$
Solvent	Cyclohexane
Oxygen	90 mmol of O_2
UDMH	50 mmol in 250 ml cyclohexane solution
Toluene Reference	1.0 g

The reaction is first order with respect to UDMH. The rate constants are of the order 10^{-5} sec^{-1}. A plot of log (UDMH) vs. time gives a straight line. A plot of log (FDH) vs. time does not yield a straight line whereas a plot of (FDH) vs. time gives an approximately straight line, although the points are scattered. This implies that FDH is not a direct oxidation product of UDMH, but goes through an intermediate. The main product of oxidation by oxygen is FDH with only a trace amount of TMT. Within the limits of our gas chromatograph detection there is no evidence that N,N-dimethylnitrosamine is formed by the oxidation of UDMH either by HgO or by elemental oxygen. Change of solvent does not the change rate constant appreciably.

S U M M A R Y

The ideal process for the production of hydrazine fuel would be an economical process capable of producing anhydrous hydrazine, monomethyl hydrazine and unsymmetrical-dimethylhydrazine. In addition, the process should be designed to avoid hazardous wastes, or byproducts or starting materials. The following comments summarize the capabilities and limitations of the processes described in this paper for the manufacture of hydrazines.

The Raschig process has potential for the manufacture of NH_2NH_2 as well as MMH and UDMH, but the details of the critical processing conditions are not well known. Also, this process is entirely wet, and the cost of obtaining anyhdrous MMH or UDMH from their dilute aqueous solutions could be prohibitively high.

The currently employed nitramine process is providing UDMH of specification grade but the overall cost is high. Also, the process cannot be modified for the production of MMH or hydrazine and the intermediate is corrosive.

The Nitrosamine process certainly has disadvantages because of the well known carcinogenicity of the nitrosamine. Also, this method cannot be employed for the production of MMH or hydrazine.

The urea process is suitable for the manufacture of hydrazine, but its applicability for the laboratory scale production of MMH and UDMH is yet to be explored.

The Sisler process appears to have several advantages for manufacturing the hydrazine fuels. This process has no known biologically unacceptable waste or by-products, and has indications of being an economically attractive method of synthesis for hydrazine UDMH and MMH. Furthermore, these products can be obtained either anhydrous or in aqueous solutions.

Besides the above methods there are several other methods reported in the literature for the preparation of hydrazines, but they have not been industrically developed.

ACKNOWLEDGEMENT

The authors gratefully acknowledge the support of the research by the Air Force Office of Scientific Research through a grant to the University of Florida.

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Paper No 2

POTENTIAL OF A HYDRAZINE-TYPE FUEL SPILL OR EMISSION DURING MOVEMENT FROM SUPPLIER TO USER

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INTRODUCTION

As an introduction I would like to describe how the Directorate of Energy Management (SF) is involved in hydrazine fuels support. SF has the responsibility to supply all DOD and NASA facilities with the various hydrazine fuels. We provide the many services - inventory management, quality control, procurement, transportation, and packaging - to insure that the user receives specification material. SF controls all of the transportation of the hydrazine fuels between the suppliers and DOD or NASA users.

TRANSPORT EQUIPMENT

First, let's outline the type of equipment used to transport the hydrazine fuels. The Code of Federal Regulation Title 49 lists the type of equipment that can be used. We are using aluminum tank cars and stainless steel tank trailers for hydrazine and hydrazine/UDMH mix (Table 1). UDMH is moved in carbon steel tank cars and stainless steel tank trailers (Table 2). MMH is currently only moved in stainless steel equipment (Table 3). We also have stainless steel and aluminum drums for the fuels. Most of the transportation equipment

TABLE 1. EQUIPMENT USED TO TRANSPORT HYDRAZINE AND UDMH/HYDRAZINE MIXTURE

	DOT Spec	Metal	Capacity
Trailer	MC 311	304 Stainless Steel	40,000 pounds
Rail Car	103AALW	Aluminum	50,000 pounds
Drums	5C	Stainless Steel	440 pounds (N_2H_4)
	42C	Aluminum	375 pounds (Mix)

TABLE 2. EQUIPMENT USED TO TRANSPORT UNSYMMETRICAL DIMETHYL HYDRAZINE (UDMH)

	DOT Spec	Metal	Capacity
Trailer	MC 311	304 Stainless Steel	40,000 pounds
Rail Car	105A300W	Carbon Steel	68,000 pounds
Drums	5C	Stainless Steel	335 pounds
	17C	Carbon Steel	335 pounds

TABLE 3. EQUIPMENT USED TO TRANSPORT MONOMETHYLHYDRAZINE (MMH)

	DOT Spec	Metal	Capacity
Trailer*	MC 312	304 Stainless Steel	40,000 pounds
Rail Car*	103CW	430 Stainless Steel	70,000 pounds
Drum	5C	Stainless Steel	375 pounds

*Commercial Equipment

is in dedicated service for the hydrazine fuels; however, in some cases common carrier's equipment is used when dedicated equipment is not available. Our average annual movement of the fuels is shown in Table 4.

TABLE 4. AVERAGE ANNUAL MOVEMENT OF HYDRAZINE FUELS

1.3 Million Pounds of Hydrazine
.5 Million Pounds of MMH
1.4 Million Pounds of UDMH
2.0 Million Pounds of UDMH/N_2H_4 Mix

SHIPPING ROUTES

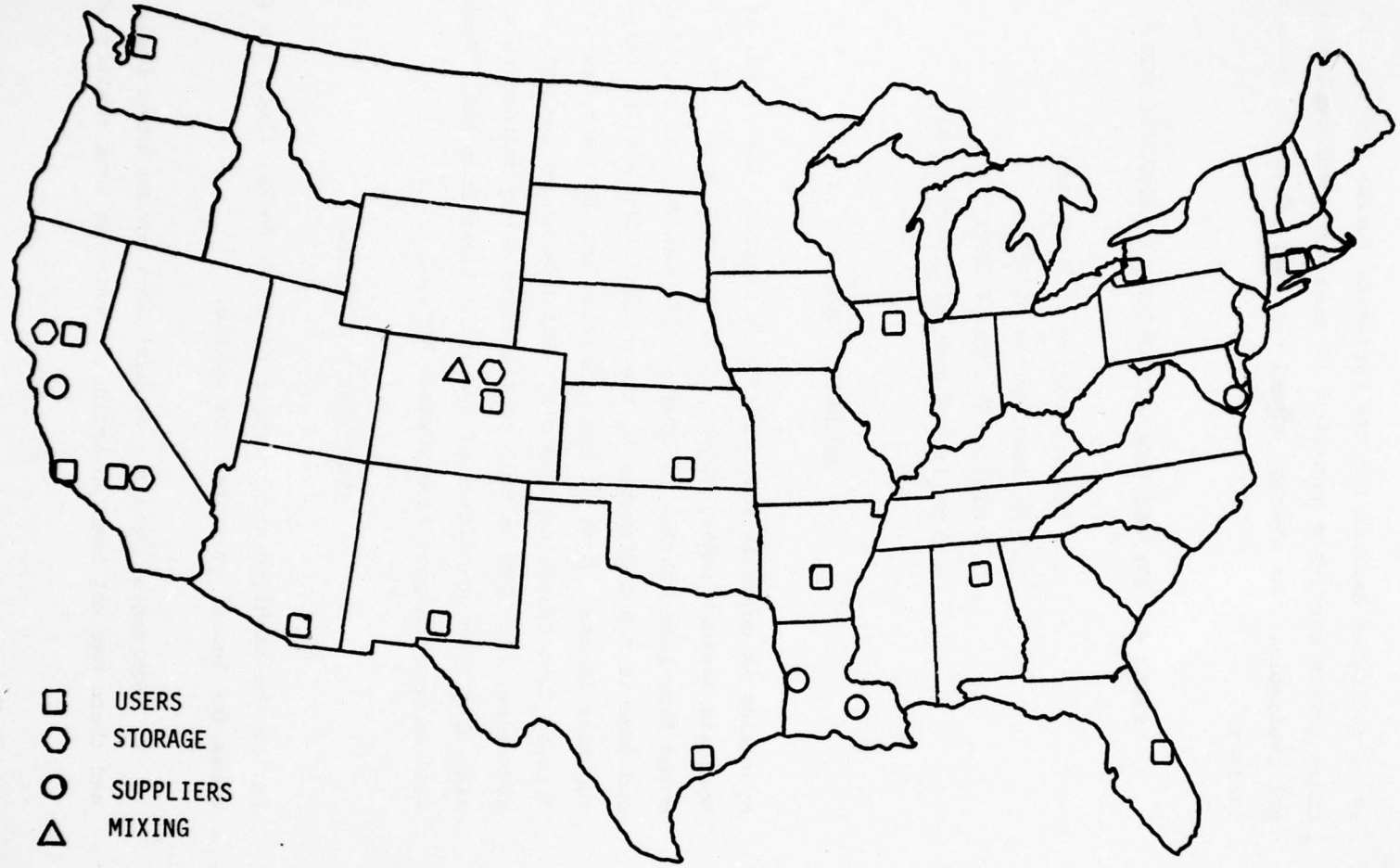
Hydrazine is normally moved from Lake Charles, Louisiana, to Rocky Mountain Arsenal (RMA), Denver, Colorado (Figure 1). Bulk MMH is moved from Lake Charles to Edwards AFB, California, for storage and some is moved directly to the users. UDMH will be shipped from supplier to RMA. Most of the hydrazine and UDMH shipped to RMA is blended into Hydrazine/UDMH mix. RMA transships the mix, pure hydrazine, and UDMH in bulk to the users or to storage points. We also ship drum quantities of hydrazine fuels from RMA. Bulk MMH will be transshipped from Edwards AFB CA.

POTENTIAL FOR SPILLS

During the handling and movement of these fuels, there are potential areas for leaks, emissions, or spills.

a. Accidental Spills - We have been moving these fuels since 1961 and there has not been an accident involving tank trailer or tank car

Figure 1. Locations of Hydrazine Fuels Facilities



shipments. The accident rate for this type of carrier is about five per million miles which includes all types of accidents.

b. Transfer Operations - The greatest potential for spills or leaks is during coupling or uncoupling of the hoses for loading or unloading of tankers.

c. Sampling - Each shipping container requires sampling before it leaves the plant after loading. This can present problems with the disposal of the purged liquid and the residual sample.

d. "Empties" - The so-called "empty" trailer is a potential source of emission. Many people tend to forget that the empty trailer contains residual material and they do not handle the vessel as carefully as a full vessel. There is also the problem that vessels are not totally off-loaded when they should have been.

e. Storage Quantity - The requirement to maintain a two-year supply of each fuel is introducing additional sources of spills and leaks due to the extra handling and shipping.

f. Equipment Cleaning - The biggest problem we currently have is due to the DOT requirements to hydrostatically test each rail car or trailer at a defined interval. Normally this test frequency is five to ten years. However, because of the age of our aluminum tank cars, DOT requires they be tested annually. This requires that the residual hydrazine or mix be removed from the car by washing before going to a shop for testing. The disposal of these washings can become a problem.

In the past we have had problems with a few leaking drums. These leaks were fixed on the spot or the fuel was disposed of. The only potential major spill that we know about happened several years ago

at RMA when the fire sprinkler system went off and floated a storage tank. In the future we expect a shift to MMH because of the space shuttle program and the number of shipments to increase. The introduction of aircraft using hydrazine systems will create more problems and increase the chances of an emission or spill due to the number of locations requiring hydrazine.

SUMMARY

In summary there are many areas that are potential sources of an accidental release of these fuels. A specific number cannot be given on the probability of an accidental release of hydrazine fuels to the environment during its transportation and handling. Each year there are about 5.2 million pounds of various hydrazine fuels moved by tank trailers, tank cars, and drums, over about 200,000 miles of public highway. Also the directorate is developing sufficient storage capacity for a two-year supply of each fuel. We currently have storage for 2.5 million pounds. With this large quantity of fuels being moved, handled, or stored, there is a potential for an accidental release to the environment.

Paper No 3

HYDRAZINE EVAPORATION

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INTRODUCTION

Hydrazine is used as a reducing agent in rocket fuel and for emergency power production in the F-16. Since the F-16 will also be used by the NATO countries, it will be distributed throughout the world. This will require that the hydrazine used in the airplane be similarly distributed with its allied handling problems.

As hydrazine is a potential carcinogen with current ambient air working limits set at 0.1 ppm, it is necessary to protect personnel and the environment from this potentially dangerous chemical. This study was initiated to determine evaporation rates for hydrazine.

EXPERIMENTAL METHODS

The experiments were broken into two broad categories. The first series of experiments were conducted outside under varying environmental conditions. The second group of experiments were conducted in the laboratory where temperature and air velocity were controlled.

Studies conducted outside consisted of placing known quantities of hydrazine fuel in glass Petri dishes of 9.0 cm diameter. These were placed outside in the prevailing weather conditions. Samples were weighed prior to introduction to the environment. At different time intervals the samples were returned to the laboratory and analyzed for N_2H_4 concentration and density.

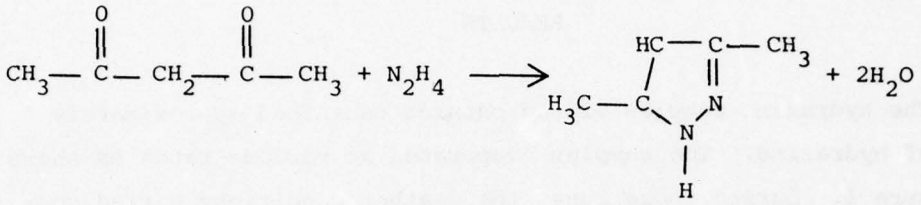
The studies performed inside duplicated those outside except that the temperature, humidity, and air velocity were controlled. All studies were performed in a hood where the air velocity at evaporating surface was measured at 63.5 cm/sec. The temperature was 21 $\pm$ 1°C and the relative humidity ranged from 68-82%. Again, Petri dishes were filled with various concentrations of hydrazine and allowed to evaporate. During the evaporation period, samples were weighed and aliquots removed for analysis.

The hydrazine concentration was determined by two methods. The first method uses potassium iodate (KIO_3) as a standard oxidant (Reference 1). The reaction is shown in equation 1.

$$IO_3^- + N_2H_4 + 2H^+ + Cl^- \longrightarrow ICl + N_2 + 3H_2O \qquad (1)$$

A standard 0.025M solution was prepared by drying reagent grade KIO_3 for one hour at 100°C and equilibrating to room temperature in a desiccator. Exactly 5.350 g KIO_3 were dissolved in 1.00ℓ of distilled water. A mixture of 30 ml of concentrated hydrochloric acid, 20 ml of distilled water, and 5 ml of chloroform were added to the sample aliquot and titrated with the standard KIO_3 solution. The solution was stoppered and shaken between KIO_3 additions. The titration was continued until the organic layer was decolorized. The organic layer changes from a deep wine red to colorless at the end point of the titration.

The second method for determining hydrazine was by pyrazole derivative gas chromatographic analysis (Reference 2). In this method, hydrazine is reacted with 2,4-pentanedione to form dimethyl pyrazole as shown in equation 2.



(2)

The pH of the samples was adjusted to between 6 and 9, diluted to 100 ml, and 100 µl of 2,4-pentanedione added. The mixture was allowed to stand for at least one hour before chromatography. The sample was then chromatographed on a Tracor Model 222 Gas Chromatograph (GC) equipped with dual flame ionization detectors. The column was a 1.83 m, 0.635 cm outside diameter glass U-tube. It was packed with a 30% load of a mixture containing 83% Apiezon L and 17% Amine 220. Nitrogen carrier gas was 30 mls per minute. The injector was operated at 225°C, the detector 240°C, and the column 140°C isothermal. A sample size of 2.0 µl was used for all studies.

Quantitative recovery was checked by preparing standard solutions of hydrazine sulfate and treating with 2,4-pentanedione. These samples were chromatographed and peak heights obtained. Standards were also prepared directly from 3,5-dimethylpyrazole, m.p. 107.5-108.5°C, and chromatographed to obtain peak heights. There was no difference in peak height between similar standards prepared by either method.

Total sample weights were measured on a Mettler P1200 balance and weights recorded to one hundredth of a gram. Sample densities were determined by weighing a known volume of sample on a Mettler Model H-51 with weights recorded to one hundredth of a milligram.

RESULTS

The hydrazine samples placed outside contained approximately 10 g of hydrazine. The samples evaporated at various rates as shown in Figure 1. During these runs, the weather conditions varied considerably. Temperatures ranged from 15-27^{o}C. The winds were generally mild from several kilometers per hour (kph) to approximately 24 kph. The relative humidity ranged from 60-80%. There were both overcast and sunny days. The most rapid decrease observed was a loss of 9.4 g of hydrazine in 180 mins or 96% of the total amount. The slowest run lost 6.1 g in 180 mins or 62% of the total.

Two runs were made in the shade and the results are shown in Figure 2. Since the evaporation rate appears slower, a check was conducted to determine whether the hydrazine was being photochemically oxidized or degraded. A glass stoppered bottle of hydrazine was placed in the sun and one in the shade. After several hours both samples were returned to the laboratory for analysis. The hydrazine concentration was the same in the two bottles and had not changed from the original concentration. In 180 mins 4.2 g of hydrazine or 43% of the total had evaporated in the shade.

Figure 3 shows two runs of hydrazine fuel evaporation conducted inside. This figure shows that the hydrazine mass decreased from 19 g to 11.4 g in 180 mins, a loss of 40%. After another 2460 mins (41 hr) there was approximately 8 g of hydrazine remaining. Even thougn the hydrazine continued to evaporate over the entire period, the actual

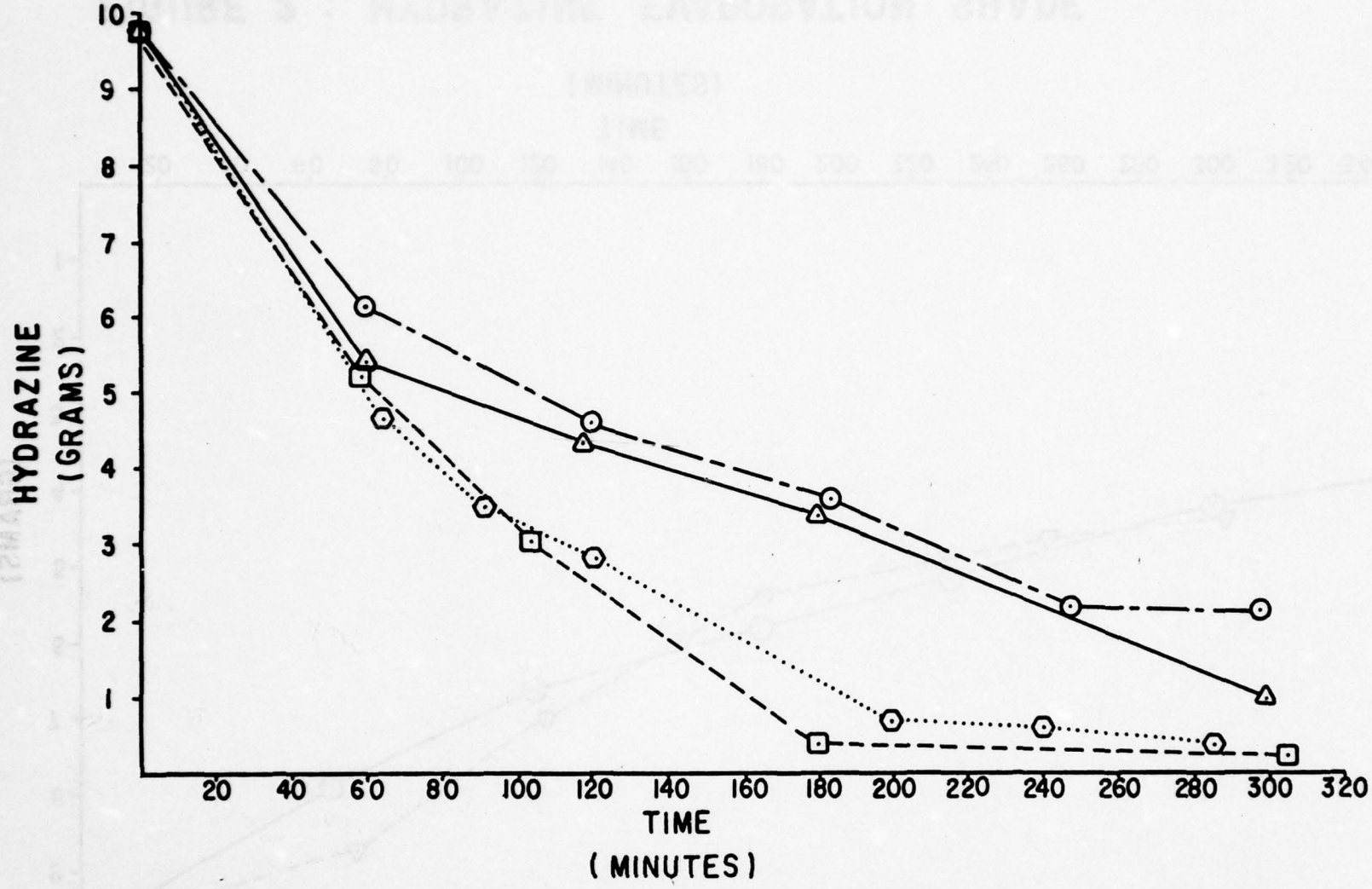


FIGURE 1 : HYDRAZINE EVAPORATION OUTSIDE

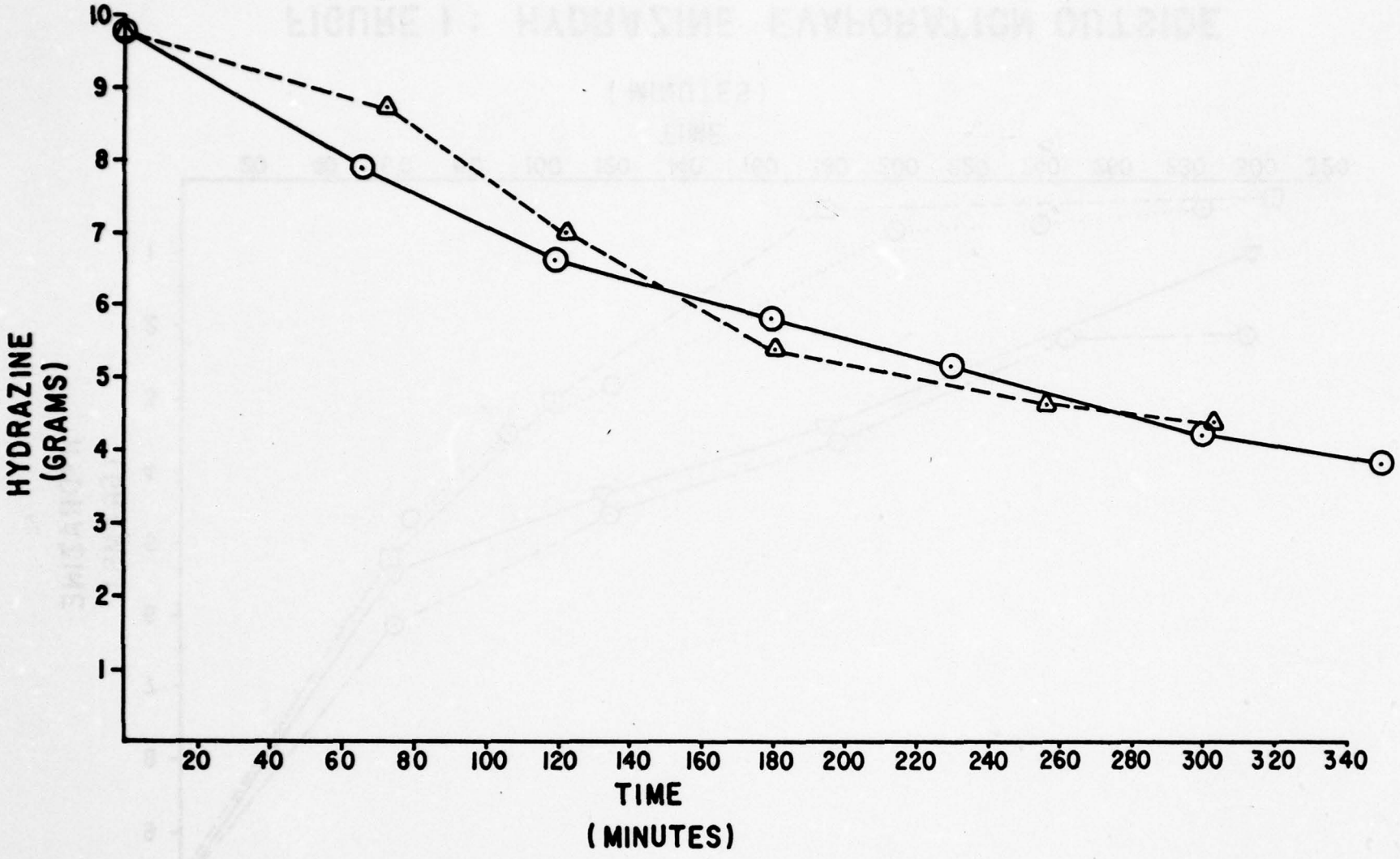


FIGURE 2 : HYDRAZINE EVAPORATION SHADE

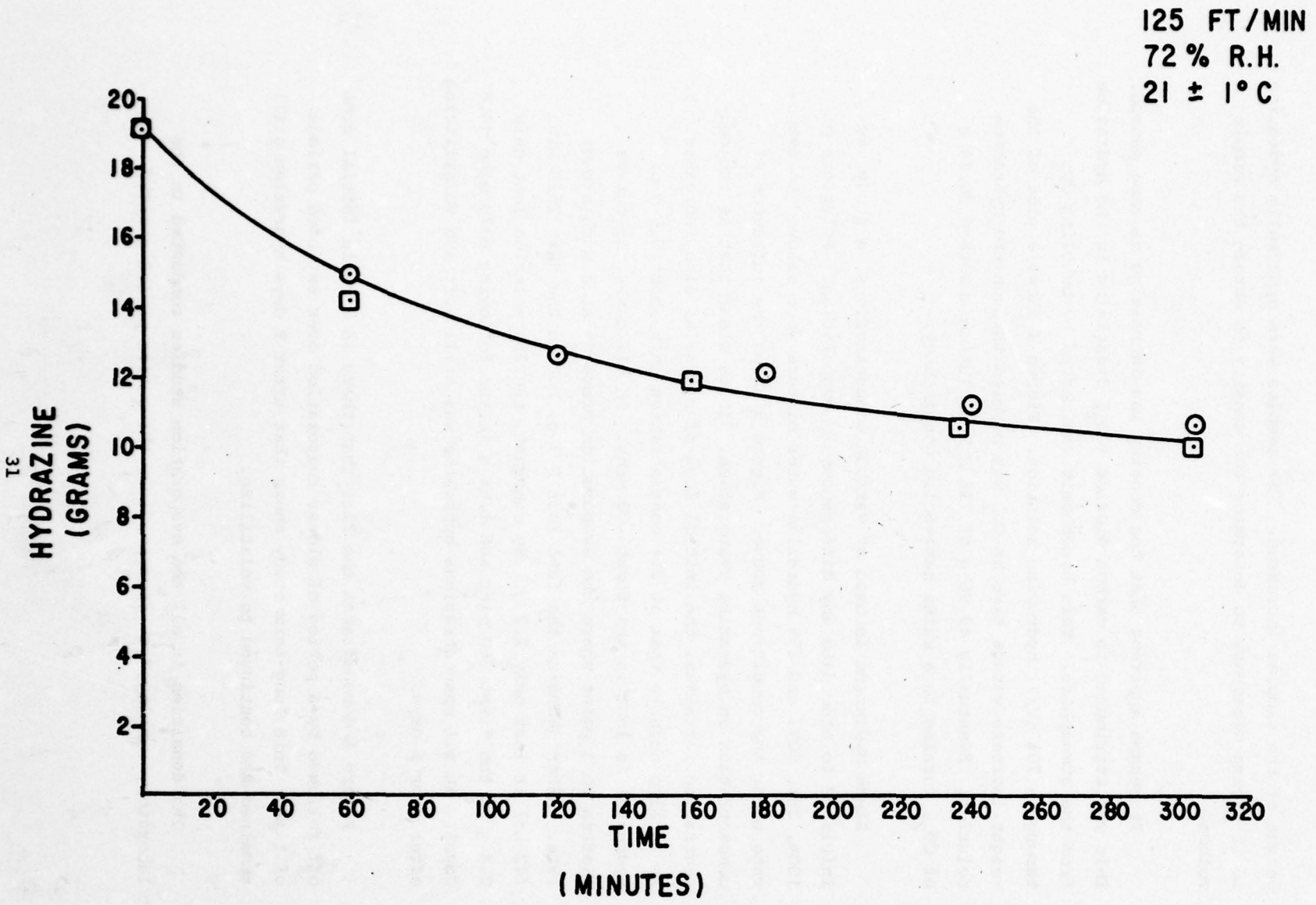


FIGURE 3 : HYDRAZINE FUEL EVAPORATION

weight of the samples increased. The samples were apparently hydrating so it became necessary to determine the density to obtain the sample volume.

It became apparent that the density was increasing as time passed. This was attributed to carbon dioxide (CO_2) dissolving in the hydrazine from the atmosphere. This hypothesis was tested by bubbling CO_2 through a 70% (V/V) hydrazine solution. Figure 4 shows a plot of the weight increase versus time as CO_2 was bubbled through the hydrazine solution. Eventually 49.96 g of 70% N_2H_4 solution absorbed 30.14 g of CO_2, turning to a white semi-solid consistency.

Since hydrazine is used at various concentrations, a study was initiated to elucidate any differences in evaporation. Solutions of 100%, 75%, 50%, and 25% hydrazine-water mixture were allowed to evaporate under the conditions above. Figure 5 shows the influence of concentration on hydrazine evaporation. It is clear that as the concentration increases, the initial loss of hydrazine also increases. It is also notable that at 25% concentration only about 0.5 g of hydrazine is lost in the first 400 mins. In all cases the curves flatten to a point where the evaporation proceeds at a much slower rate. After 360 mins the fuel lost 8.7 g, but in the next 2520 mins (42 hr) it lost only 2.2 g. By contrast, the 25% solution lost only 0.4 g in the first 360 mins and 1.65 g in the following 6870 mins (4.8 days). At all concentrations hydrazine was still left and volatilizing after 4 or 5 days.

Figure 6 demonstrates the fact that there is a rapid initial drop off followed by a period of slower evaporation over extended periods of time. This long-term study shows that after 9 days hydrazine still remained and continued to volatilize.

The densities in all the evaporation studies conducted in the laboratory continued to increase over the entire period studied. No

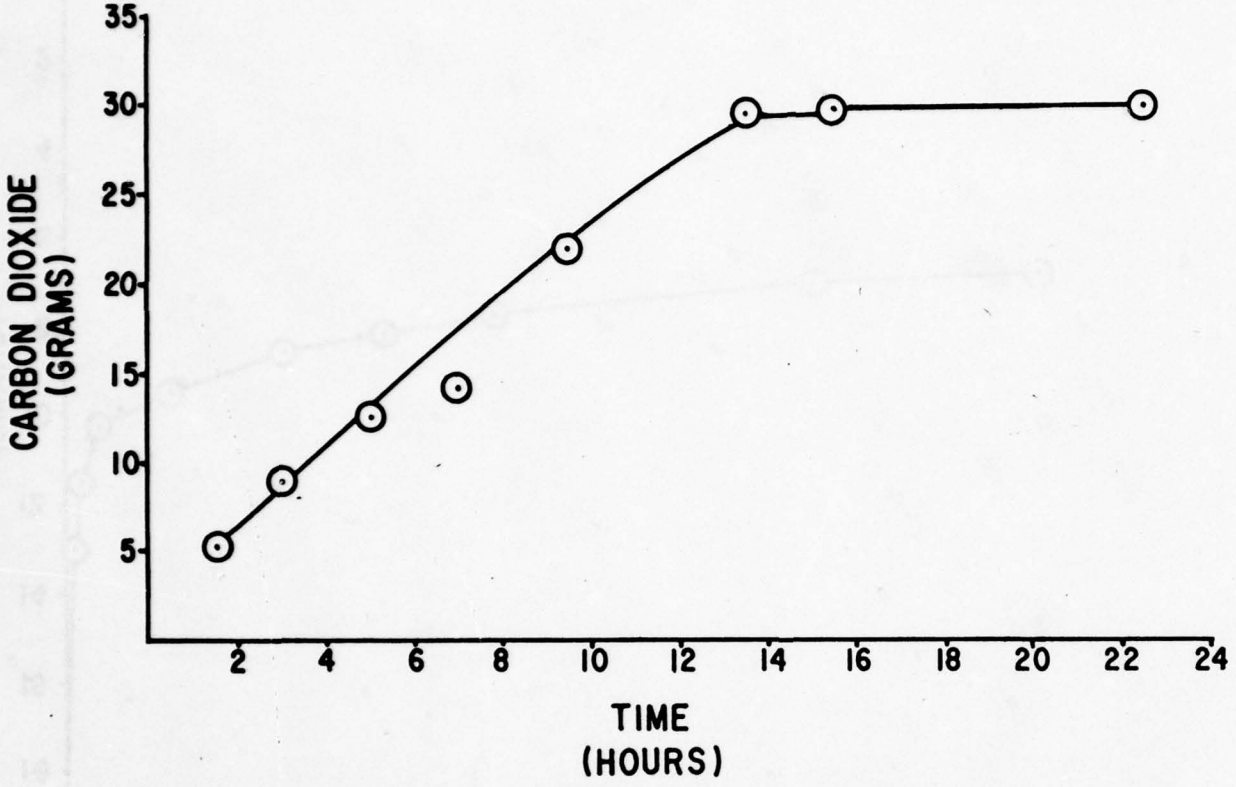


FIGURE 4 : CARBON DIOXIDE ABSORPTION BY 70 % (V/V) HYDRAZINE SOLUTION

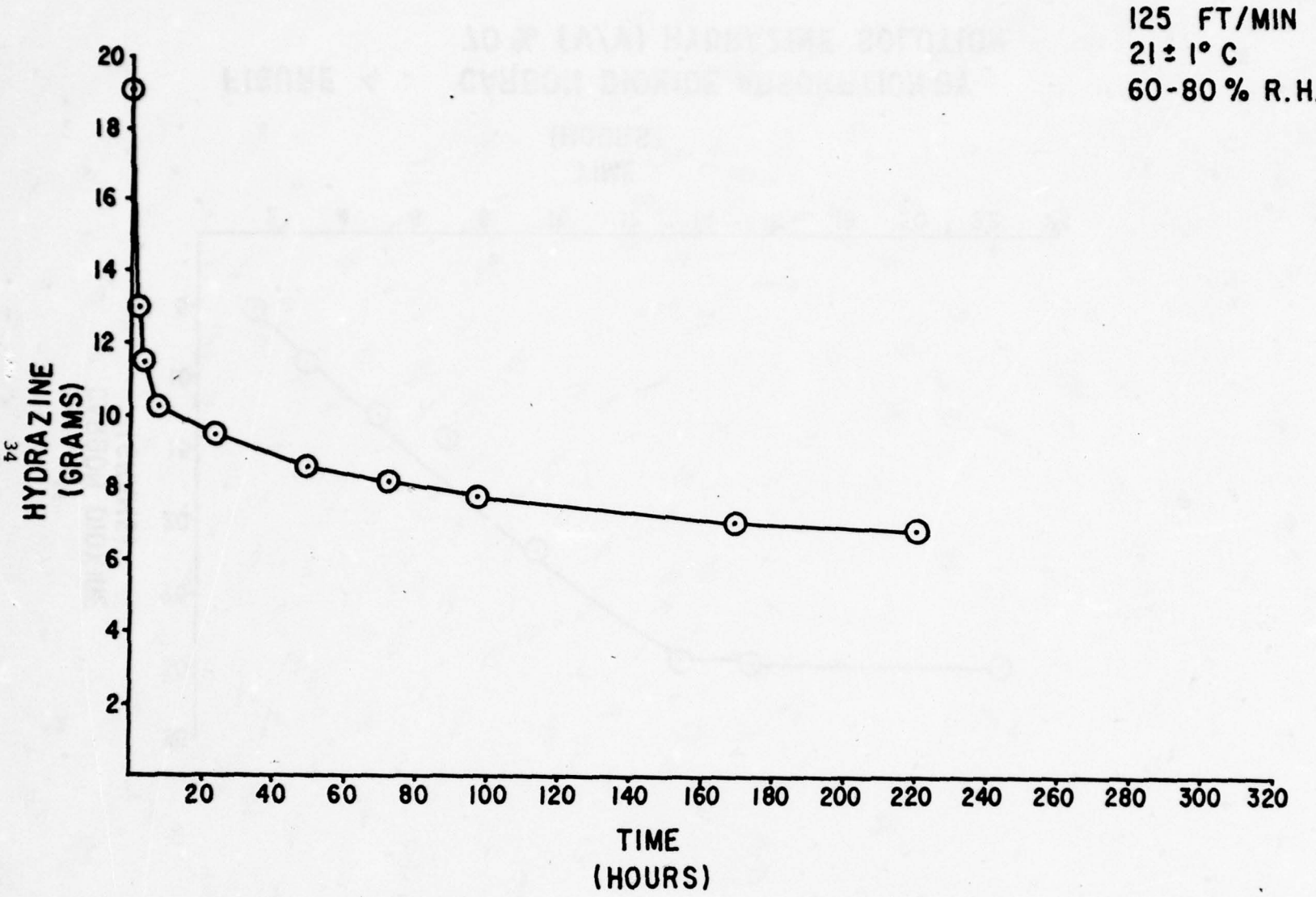


FIGURE 5 : LONGTERM EVAPORATION OF HYDRAZINE FUEL

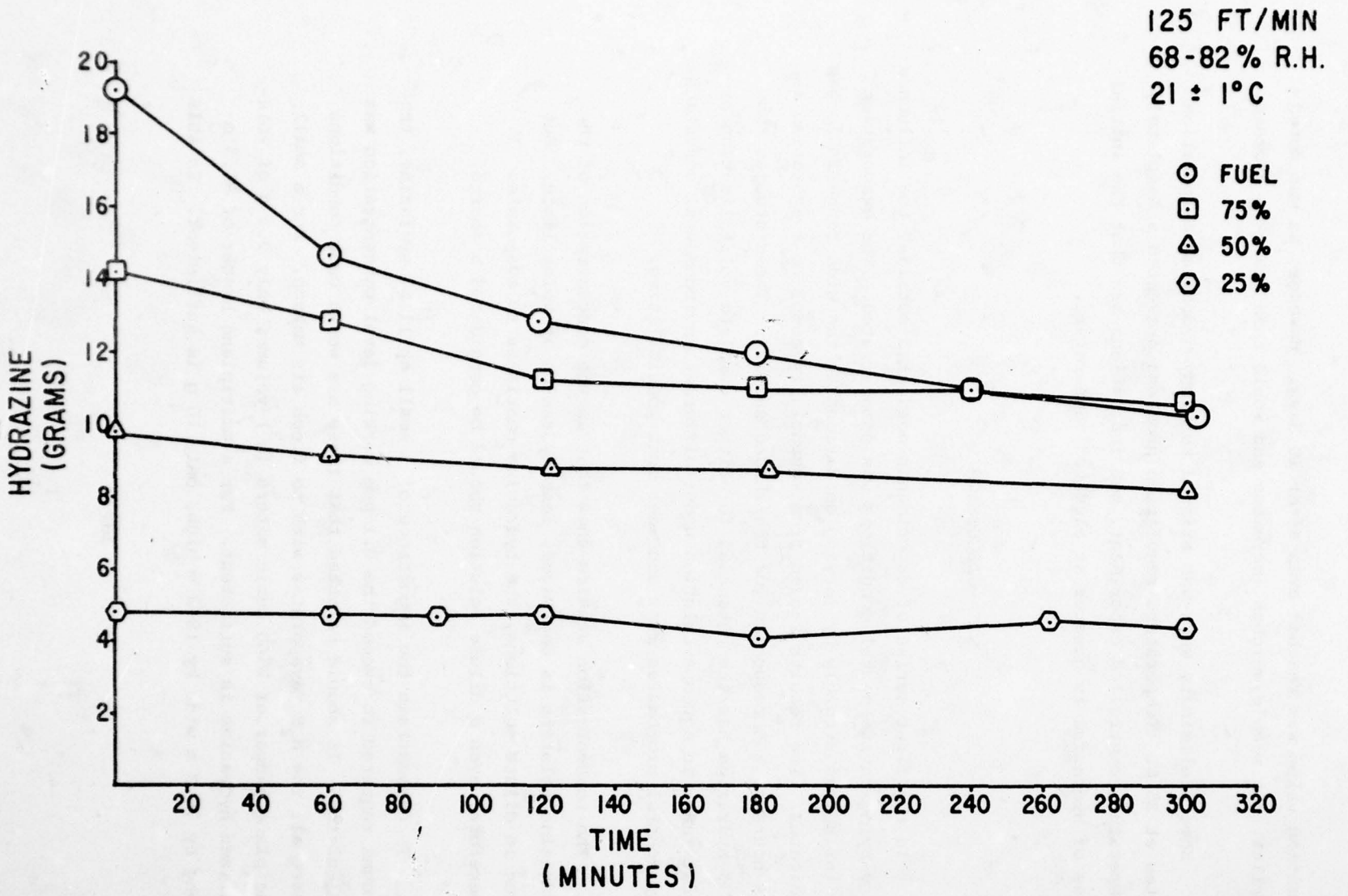


FIGURE 6: INFLUENCE OF CONCENTRATION ON HYDRAZINE EVAPORATION

limiting value was reached even after 10 days. However, as was noted earlier, the sample weights increased and would then start to decrease.

Some preliminary work was started to study hydrazine evaporation rates at 35°C. Temperature regulation problems prevented a completely temperature controlled experiment, but indications are that the initial loss of hydrazine is greater at elevated temperature.

DISCUSSION

In the first series of experiments conducted outside, the influence of varying environmental conditions was demonstrated. The evaporation is influenced strongly by varying conditions as the wide range in losses indicates. The results ranged from essentially complete evaporation in six hours to 60% reduction for the shaded samples. These studies show that hydrazine has the potential for either complete volatilization or persistance in aqueous solution under different environmental conditions. Any control procedures must consider both possibilities.

The concentration studies show that as the concentration of the hydrazine solution is decreased, less hydrazine is volatilized. But even in dilute solutions, the hydrazine continues to evaporate. Therefore, even a dilute solution should be considered a source.

To demonstrate the importance of a small spill of hydrazine, the amount required to exceed the 0.1 ppm working level concentration was calculated. It should be noted that these are worst case conditions where all the N_2H_4 evaporates with no fresh air makeup. For a small one plane hangar of 2560 cubic meters (m^3) volume, only 0.3 g of volatilized hydrazine is sufficient. For a multiplane hangar of 91.5 m long by 76.2 m wide by 12.2 m high, only 10 g is sufficient. In this

study, approximately 20 mls of 75% hydrazine solution, which approximates the 70% solution used in the F-16, volatilized 3.2 g of hydrazine in 180 mins (3 hr). Therefore, even small indoor spills require cleanup.

The continual increase in density of the evaporating samples is attributed to the absorption of CO_2. It was shown that bubbling CO_2 through the hydrazine formed a semi-solid substance. Placing this compound in an acid solution produced a colorless, odorless gas. This compound is assumed to be carbazic acid, Equation 3.

$$N_2H_4 + CO_2 \longrightarrow H_2NNH-\overset{\overset{O}{\|}}{C}-OH \qquad (3)$$

However, in our study the stoichiometry was 1.0 moles N_2H_4 to 0.634 moles CO_2; not the 1:1 relation as predicted. It is felt that the formation of this acid may stabilize the hydrazine, thereby retarding its volatilization rate. Experiments are currently underway to prove or disprove this assumption.

SUMMARY

The present studies have shown that environmental factors greatly influence the evaporation of hydrazine. Differences in experiments conducted in sunshine and shade are not due to photochemical effects, but probably to temperature changes. Concentration of the evaporating solution affects the evaporation rate. Over extended time periods, hydrazine solutions hydrate and then lose the additional water. Densities of evaporating solutions increase probably due to the absorption of carbon dioxide which may stabilize these solutions. Hydrazine

volatilizes rapidly enough to require that any small spill indoors should be cleaned up and neutralized for personnel protection. Over periods of up to ten days, aqueous hydrazine solutions continued to slowly volatilize, therefore necessitating some type of cleanup procedure.

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Paper No 4

DESIGN OF AN EMISSION CONTROL SYSTEM FOR HYDRAZINE VAPORS

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INTRODUCTION

Large amounts of hydrazine fuels were utilized in space propulsion systems in the Apollo/Saturn space vehicles and even larger amounts will be used in the space propulsion systems of the Space Shuttle which is now approaching operational status.

Meanwhile, the toxicity classification and ecological constraints for hydrazine continue to become more and more severe as knowledge of the material increases. Health and safety measures which were considered satisfactory a few years ago are no longer acceptable.

VAPOR CONTROL SYSTEMS

In 1973, it was determined that KSC Design Engineering should pursue a suitable program to define the various methods being used in the United States and Free World for hypergolic propellants vapor and liquid waste disposal, the compatibility of those methods with current ecology constraints, and to advance the state-of-the-art in this regard, if necessary.

Consequently, in August of 1973, a study contract was awarded by KSC to Florida Institute of Technology (FIT), and the task was begun.

Phase One of the FIT study comprised a survey and tabulation of the disposal methods in the United States and free world.

Phase Two comprised evaluation of each disposal method under current ecology control measures and trend.

Phase Three defined the areas needing improvement and described theoretical concepts which might accomplish this.

Subsequent phases included laboratory scale testing, data evaluation, prototype development and related tasks leading toward workable design concepts for actual hardware with major emphasis on efficiency, economy, simplicity and flexibility.

The leading concept for hypergol vapor disposal began to emerge as an advanced type of closed-circuit water scrubber with chemicals in the water to trap and neutralize the hypergol vapor.

Concurrently, in 1974, this concept for vapor scrubbers was incorporated in KSC Design Engineering planning for Space Shuttle facilities and in mid-1975 the Design Engineering support contractor, Planning Research Corporation (PRC), was given a work order to develop preliminary design concepts for the unit, designated the "S70-1094 Hypergol Fuel Vapor Scrubber."

This preliminary engineering was incorporated into a formal Technical Specification (A79K08492) in November 1976, and in January 1977 a contract was awarded to Martin Marietta Corp (MMC), Denver, Colorado, to develop final design/fabricate/test and deliver four (4) S70-1094 units for installation at KSC Launch Pad LC-39A and the Hypergol Maintenance Facility (HMF).

The MMC design (F79K10055) for the S701094 unit comprises a package approximately 6.5' x 8' x 11' high weighing approximately 6000 pounds dry and 7400 pounds wet.

The closed circuit water solution subsystem contains 150 gallons of water/citric acid (15% solution) in a 30" dia. x 6'3" long sump tank. This is circulated through two packed towers (in parallel) by a 100 gpm, 5 hp electric centrifugal pump. The packed towers are each 30" dia. x 7'3" high and the bed depth is 4'0". The packed bed material is ceramic saddles. The water flow is downward through the packed bed from a spray nozzle in the top of each tower.

The contaminated gas flow ("0" to 400 scfm) is upward through the two packed beds, in series (not parallel). The first tower removes about 99.5 to 99.8% of the hydrazine vapor from the vent gas stream and the second tower removes about 0.1 to 0.2%. The output contamination level runs about 0.5 to 3.0 ppm as measured by wet chemistry and "no trace" as measured by MSA sample tubes.

More sophisticated measurement methods (than wet chemistry or MSA tubes) will be necessary to more precisely determine the ppm of hydrazine in the output gas stream. The MSA tubes were not sensitive enough at these low levels and the wet chemistry measurements were too variable to elicit confidence. Output analysis will continue at KSC (during normal operations) to further refine the output ppm characteristic.

During the "inoperative mode" (when the pump is off) the contaminated gas flow is directed to a perforated pipe submerged in the sump solution and bubbles up through the solution to achieve partial scrubbing. This feature accommodates unplanned flows from relief valves on hydrazine storage tanks, etc. The scrubbing efficiency in this mode appears to be somewhat less than the "operative" mode, perhaps only about 90% efficiency at high flow rates (400 scfm).

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Paper No 5

MONITORING HYDRAZINE FUEL VAPORS IN AIR

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INTRODUCTION

Hydrazines of interest to the Air Force are hydrazine (H) itself, monomethylhydrazine (MMH), and unsymmetrical-dimethylhydrazine (UDMH). These hydrazines are used as rocket motor propellants either pure or in mixtures such as aerozine-50 (50% H - 50% UDMH). Developments are underway to further utilize these fuels for aircraft starting cartridges and auxiliary power systems. During use and handling, quantities of the highly toxic hydrazines can be released into the environment causing safety and health problems. The toxicity of the hydrazines is evident from knowledge of present threshold limit values (TLVs) for an eight-hour working day exposure which are 0.1 ppm (H), 0.2 ppm (MMH), and 0.5 ppm (UDMH).

Detection and measurement techniques for the hydrazines in air can be classified according to purpose as area and personal. Area monitoring is usually done by instruments located at specific sampling points and is conducted either continuously or intermittently, preferably in real time or without significant delay. Personal monitoring usually involves wearable lightweight devices with measurement of contaminant concentrations delayed until the end of the day. Both area and personal

monitors are required in most operations. Area monitors provide real-time information for area entry or warning to evacuate. Personal monitors can provide a warning of localized problems but are used primarily to provide a record of an individual's exposure over a specific period of time.

EXISTING MONITORING EQUIPMENT

Presently-used area instrumental methods for the continuous measurement and detection of the hydrazine fuels in air are the "Billionaire," an MSA product which operates on an ionization principle, and the "Olfacton," an electrochemical analyzer sold under the Teledyne name. Both of these instruments have proven inadequate in many situations because of problems with sensitivity, stability, specificity, and/or reliability. A non-instrumental area method now in use is based on pulling a known volume of air through a "detector tube" containing a reactive dye on an inert support. A color is produced whose intensity or length of stain is proportional to the hydrazine concentration. These tubes are all subject to interference and require verification of positive results by other methods.

The only routine personal monitoring of hydrazines in air by industry and government that we are aware of uses a portable pump which draws sample air through a miniature sulfuric acid impinger. The impinger liquid is analyzed colorimetrically at the end of the day.

CURRENT RESEARCH ON AREA MONITORS

Four area monitors now under development are based on chemiluminescence, electrochemical, tape-colorimetric, and gas filter correlation spectroscopic techniques. The chemiluminescence technique

depends on measurement of the intensity of light emitted by the reaction between in-situ generated ozone and the hydrazine contained in a sample air stream. Sensitivities on the order of 0.1 ppm have been demonstrated for all three hydrazines, with an on-going evaluation of sensitivity and specificity of a breadboard model. The electrochemical approach uses oxidation at a controlled potential after selective transport of the hydrazines across a semi-permeable membrane. Sensitivities are again said to be on the order of 0.1 ppm with minimal interference by potential contaminants. Electrochemical prototypes are now being evaluated by the Naval Research Laboratory for NASA use in space shuttle operations. An area monitor based on continuously-moving impregnated paper tape technique has been developed and evaluated by MDA Scientific, Inc. The MDA monitor is claimed to work in the 0-2 ppm range for all hydrazines without interference by "normally" present industrial gas atmospheres. To our knowledge no independent evaluation of this instrument for hydrazine measurement has been made by industry or government. A fourth development, gas filter correlation spectroscopy, is a nondispersive infrared method that can be used to measure airborne contaminant concentrations in a remote mode. Interferences are minimized using a masking (correlation) technique. Major problems of concern appear to be sensitivity and cost.

CURRENT RESEARCH ON PERSONAL MONITORS

On-going programs in the search for personal monitors are centered around detector tube, diffusion, and tape techniques. Detector tubes containing an absorbent such as sulfuric acid on silica gel are worn on the person. A miniature pump is used to pull air from the surrounding environment through the tube. The tube is analyzed at the end of the day colorimetrically, gas chromatographically after derivatization, or with selective electrode systems. Diffusion dosimeters are based on passage of the hydrazine across a semi-permeable membrane with collection

and storage on an absorption medium. The hydrazine is measured by a method of choice at the end of the day. The two techniques just discussed give only an integrated response. A miniaturized version of the MDA area monitor could give both integrated and point-in-time measurement. A small battery-operated cassette dosimeter would pull air through a moving impregnated tape at a constant rate. Development of the tape after use should give an estimate of hydrazine vapor exposure at specific times.

Paper No. 6

MONITORING AND ANALYSIS OF PERSONNEL EXPOSURES TO HYDRAZINES AT A ROCKET PROPELLANT PLANT

Lary R. Cook, Robert E. Glenn, Maj, MSC, George E. Podolak

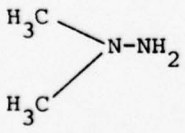
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INTRODUCTION

The potential carcinogenic activity of hydrazines, coupled with the proposed lowering of their threshold limit values (TLV), (Reference 1) spawned a new concern over potential industrial exposures. This placed additional demands on the sampling and analytical methods for determining their concentrations in working atmospheres and on the adequacy of available personal protective equipment. In the interest of worker's health, the US Army adopted the 1976 proposed TLV values (Table 1) and conducted extensive monitoring of personnel exposures to hydrazine compounds at a rocket propellant facility. In addition to the monitoring, a thorough evaluation of the respiratory protective devices namely, full facepiece gas masks, was made.

TABLE I

Threshold Limit Values for Hydrazines

Compound and Chemical Formula	Time Weighted Average (TWA) ppm	Short Term Exposure Limit (STEL) ppm
1,1-Dimethylhydrazine 	0.5	1.0
Hydrazine* H_2N-NH_2	0.1	0.3

*1976 proposed.

PLANT AND PRACTICES

In 1971 it was estimated that 1.4 million kilograms (3.1 million pounds) of hydrazine were marketed in the United States and it was estimated that the United States' production of 1,1-dimethylhydrazine (UDMH) in 1973, amounted to approximately 0.5 million kilograms (1.1 million pounds), (Reference 2). The UDMH produced in the United States is used almost entirely for rocket propellant, while hydrazine, in addition to rocketry, finds wide commercial application.

The facility which was evaluated is a bulk rocket propellant handling plant. Operations at this facility consisted of off-loading shipments of hydrazines from railcars, storing the material in above ground storage tanks, blending of hydrazine and UDMH into Aerozine 50 (approximately 50 percent hydrazine and 50 percent UDMH), and loading of the hydrazines for shipment to the customer. Containers used for shipment included: railcars, truck tankers, and 242 liter (55 gallon) stainless steel drums. The Aerozine 50 production at this facility during the period of 1972-1975 averaged approximately 900,000 kilograms (1.98 million pounds) yearly. Total process figures for unblended hydrazine or UDMH were not available, however, only small quantities of the hydrazines are shipped unblended (Reference 3).

The surveyed facility was operated by four workers. Operation of the facility required two of the personnel to be involved directly with the handling of hydrazines while the other two performed supervisory and ancillary tasks. However, all four workers were rotated between the various tasks and all were potentially exposed. The personnel directly involved in handling the hydrazines wore Mine Safety Appliance Company (MSA) Rocket Propellant Masks. This consisted of the Ultravue facepiece, 92372 GM-SSW Canister, and a 71 centimeter (28 inch) breathing tube. Neither the National Institute for Safety and Health or Mining Enforcement Safety Administration (NIOSH/MESA) have established performance requirements for testing and approving this gas mask. The manufacturer's data sheet

limits the use of the device to oxygen supportive atmospheres and those having concentrations less than two percent rocket fuel vapors (Reference 4). Personnel within the work area but not directly involved in handling the hydrazines were the M9 protective gas mask with M11A1 canister. This is a full face piece military gas mask and the M11A1 canister contains approximately 150 grams of activated charcoal in combination with a High Efficiency Particle Attraction filter. The mask and canister are designed to protect the respiratory tract from particulates and vapors.

PROCEDURES

Sampling. From the outset of this investigation, it was decided to adapt the sampling and analytical method of Wood and Anderson (Reference 5). This technique, besides the sensitivity, provided a convenient means of collecting samples from inside the respiratory protective equipment.

In each test calibrated, MSA Model G, personnel pumps, adjusted to a flow of approximately 1 liter per minute through the collection media were attached to the operating personnel. One sampling tube was placed outside the protective mask and approximately 35 liter samples were collected (Figure 1). The MSA mask was modified to allow collection of a simultaneous sample from within the mask. This was achieved by inserting a gas-tight sampling port on the right side of the facepiece at the nose level of the wearer (Figure 2). The M9, military, general purpose gas mask with the M11A1 charcoal canister was modified in a similar manner. To insure the gas-tight integrity of the masks had not been compromised by the modification, the sampling ports were plugged and the devices were leak tested to 203 millimeters (8 inches) of water gage using a bench type DOP (dioctyl phthalate) test to indicate leakage.

Analytical. The analytical scheme consisted of trapping hydrazines in sulfuric acid coated silica gel contained in a glass sampling tube; aqueous sample solutions were made and the derivatives formed by addition

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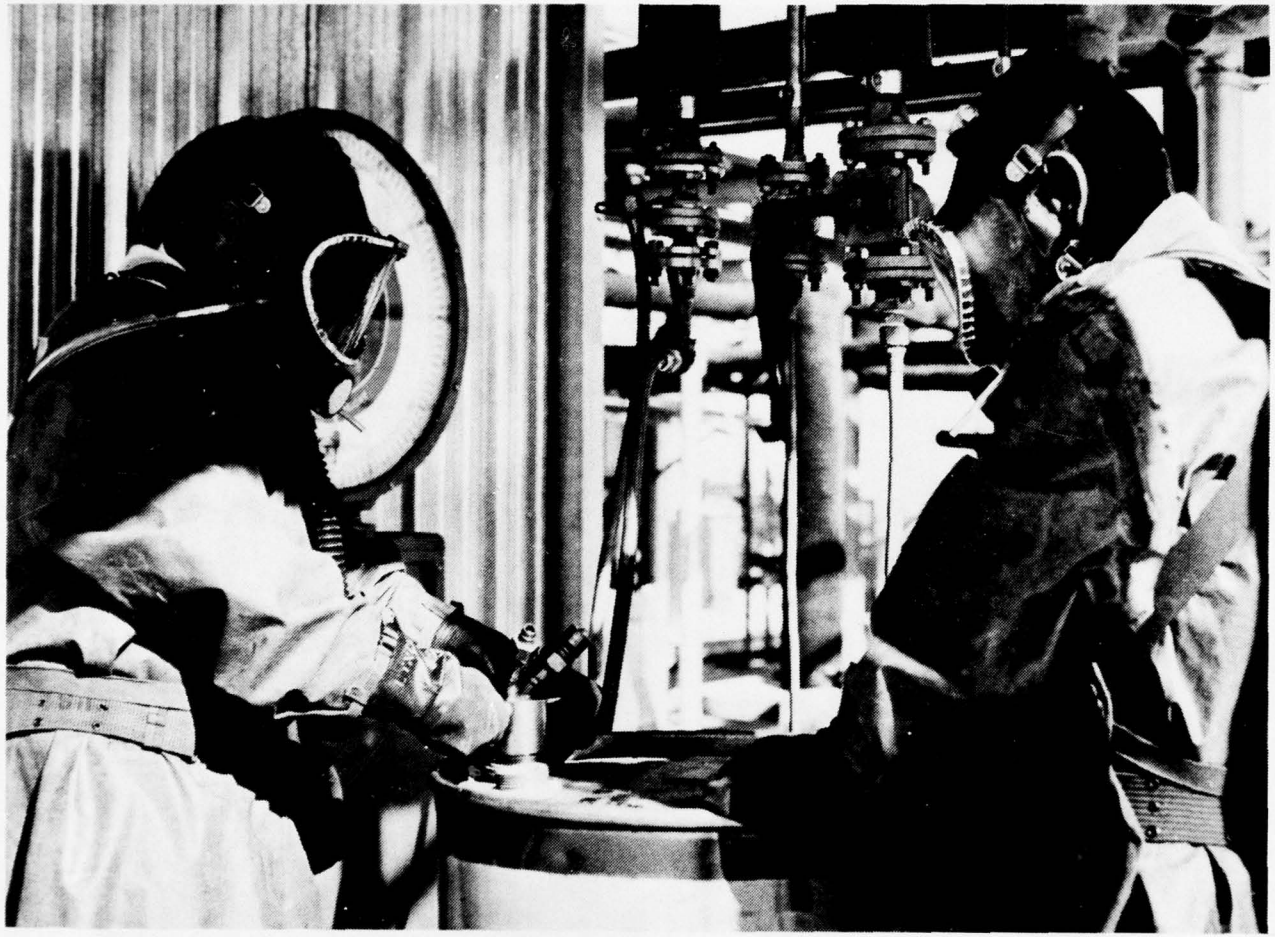


Figure 1. Sampling and Personal Protective Gear

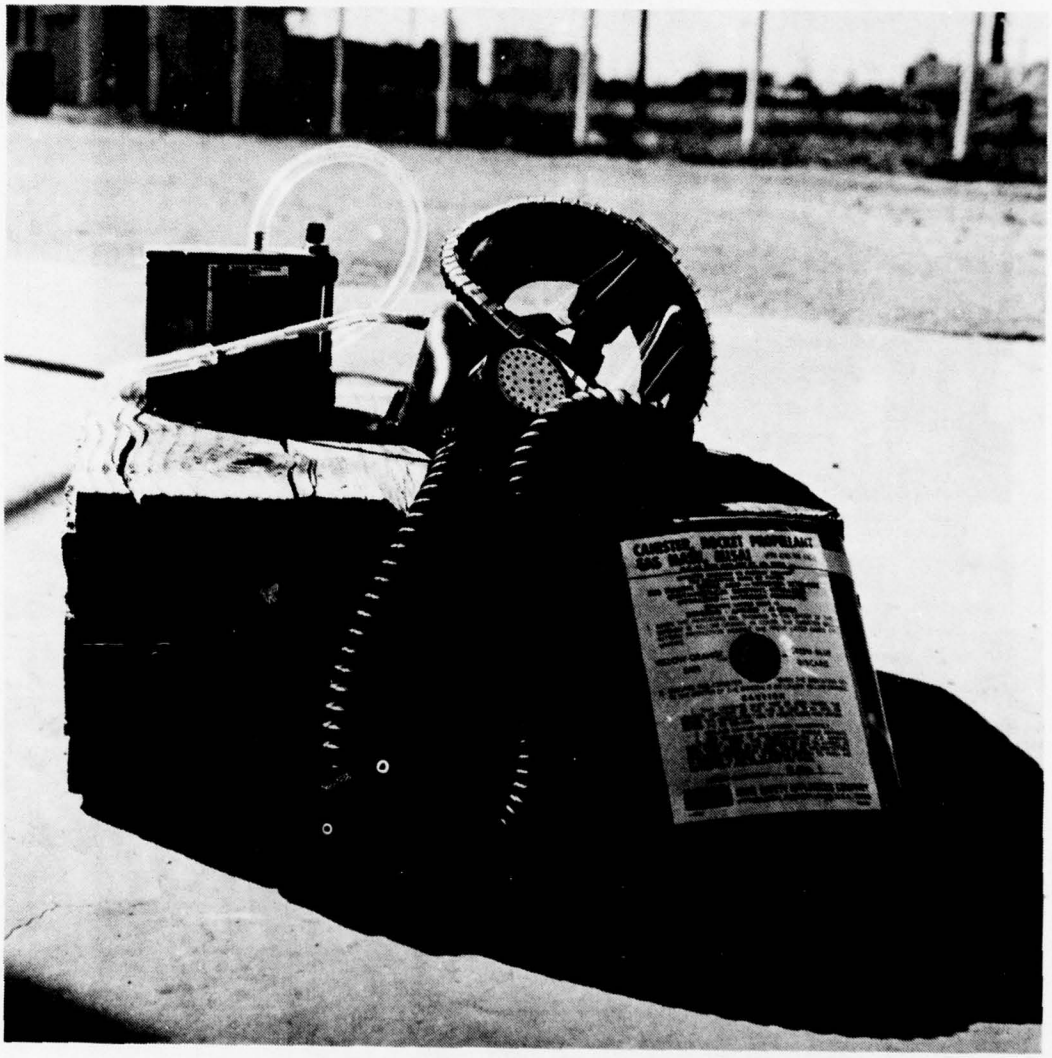


Figure 2. Modified MSA Mask

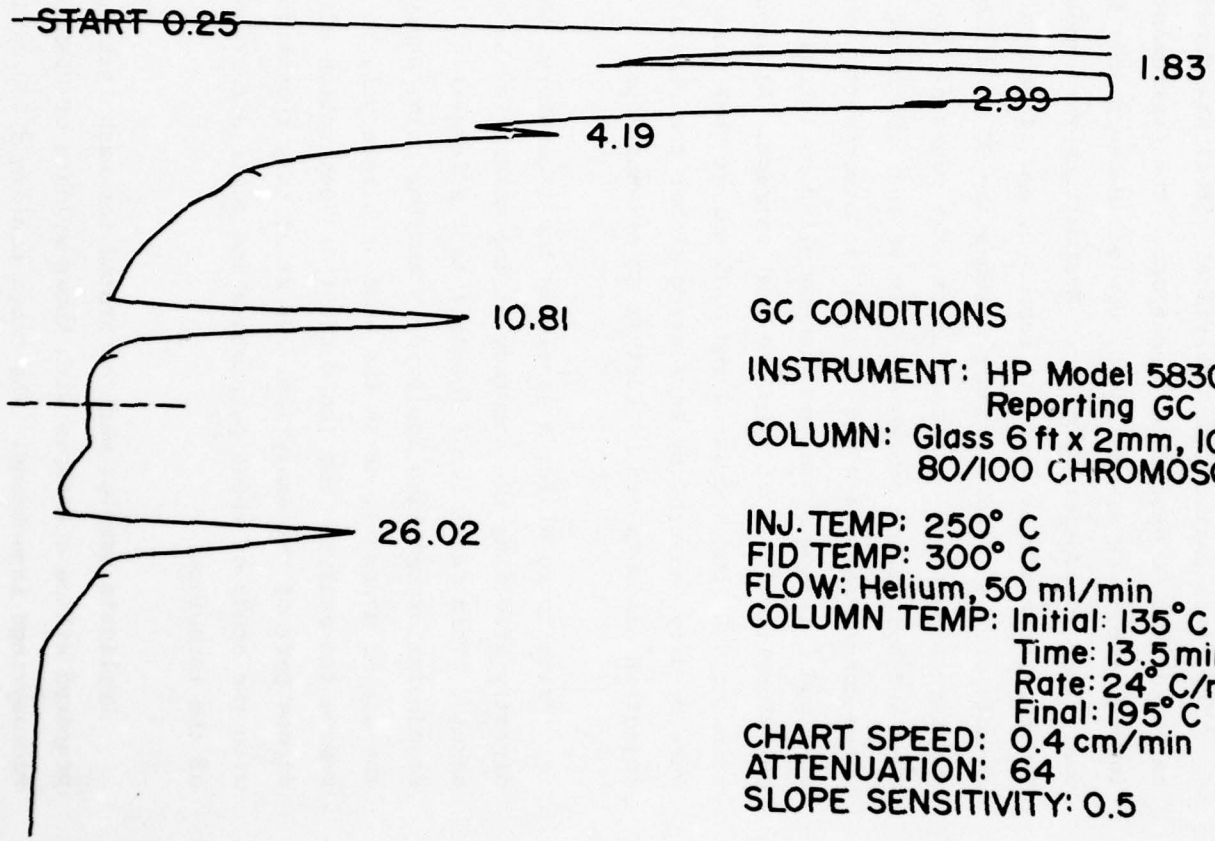
of 2-furaldehyde in sodium solution; the derivatives in turn, were extracted into ethyl acetate and measured by gas chromatography (GC).

The first part of the analytical effort was directed at optimization of the GC operating conditions. The instrument used in the investigation was a model 5800, Hewlett Packard (HP) GC, equipped with dual flame ionization detector. Evaluations were made of detection limits, linearity of detector response, and of general quantitative aspects of the method. Figure 3 shows the GC conditions in the temperature programmed mode and dipicts the peaks of the derivatives of UDMH and hydrazine, representing 19.56 and 5.05 nanograms, respectively. These concentrations would be equal to atmospheres containing 0.23 ppm UDMH and 0.11 ppm hydrazine when sampling 35 liters of air and injecting one microliter aliquot from the 1 ml extract. Atmospheric concentrations of 0.01 ppm hydrazine and 0.05 ppm of UDMH (one tenth the TLVs) were readily measured by increasing either the sampling time and/or the injection aliquots and by further GC attenuations.

Prior to receiving a sample in the laboratory, the major variable directly affecting the accuracy of the method is the stability of the sample. This facet is of interest to the industrial hygienist from the standpoint of sampling logistics. Another prime analytical variable in the use of sorbents, as in the case of silica gel, is the ability to remove the analyte from the sorbent or "desorption efficiency." The second part of the analytical effort of this investigation was concerned with the study of these parameters and their effects on the reliability of the technique.

Replicate samples were generated for each test by spiking uniformly prepared silica gel tubes with known weights of UDMH and hydrazine by microsyringe injections. The tubes contained 400 milligrams of sulfuric acid coated silica gel sorbent in one section (20% by weight concentrated

10.81 Min UDMH - 19.56 NANOGRAMS
26.02 Min HYDRAZINE - 5.05 NANOGRAMS



GC CONDITIONS

INSTRUMENT: HP Model 5830 A, Dual FID, Reporting GC
COLUMN: Glass 6 ft x 2mm, 10% OV-7on 80/100 CHROMOSORB GHP

INJ. TEMP: 250° C
FID TEMP: 300° C
FLOW: Helium, 50 ml/min
COLUMN TEMP: Initial: 135°C
Time: 13.5 min
Rate: 24° C/min
Final: 195° C
CHART SPEED: 0.4 cm/min
ATTENUATION: 64
SLOPE SENSITIVITY: 0.5

Figure 3. Chromatogram of UDMH and Hydrazine Derivatives

H_2SO_4 on 40/60 mesh activated silica gel). In each run, two samples were analyzed immediately, while others were split into pairs and were stored in a freezer compartment of a refigerator for 1, 2, or 3 days. Table II shows the results of two runs of stability testing.

Looking at the percent recoveries, it became evident that samples in this form do not lend themselves to storage or transportation for any reasonable length of time even when frozen. The negative storage factor can be circumvented by performing sample elutions immediately, and refrigerating the eluted solutions. Table III shows the percent recoveries when applying this type of procedure. In this investigation, almost instantaneous elutions and immediate analyses were adhered to.

In an effort to determine desorption efficiencies and to ascertain overall percent recoveries, samples were prepared in the same manner as previously described only with varying loadings and immediately analyzed. A total of 36 samples containing hydrazine and UDMH together, or each one separately were generated by our laboratory. For quality assurance 20 speciments containing unknown quantitites of the hydrazines were obtained from the Analytical Reference and Quality Assurance Division of USAEHA. The results of these 56 standards were statistically analyzed and are presented in Table IV.

TABLE II
Stability Testing

Sample Storage Time (hr)	UDMH			Hydrazine		
	Theoretical Value (µg)	Mean Observed Value (µg)	Mean Percent Recovery (%)	Theoretical Value (µg)	Mean Observed Value (µg)	Mean Percent Recovery (%)
0	39.20	37.25	95.0	5.05	4.75	94.0
24	39.20	24.75	61.9	5.05	1.90	37.6
48	39.20	17.07	43.5	5.05	1.60	31.7
72	39.20	6.42	16.4	5.05	.57	11.3

TABLE III
Recoveries of Samples When Eluted and Stored in Refrigerator for Approximately Four Days

Test Number	UDMH			Hydrazine		
	Theoretical Value (µg)	Mean Observed Value (µg)	Mean Percent Recovery (%)	Theoretical Value (µg)	Mean Observed Value (µg)	Mean Percent Recovery (%)
1	15.59	13.86	88.9	5.05	4.32	85.5
2	39.18	35.02	89.4	10.10	8.89	88.0
3	--	--	--	15.15	13.25	87.5

TABLE IV
Percent Recoveries of Hydrazines

Number of Sample & Source (N)	Compound	Theoretical Value (µg)	Mean Observed Value (µg)	Mean Percent Recovery (%)	Relative Standard Deviation (%)
36 Samples generated in our lab	UDMH	19.59	17.90	91.4	1.7
		39.18	36.13	92.2	3.4
		58.77	54.76	93.2	2.8
	Hydrazine	5.05	4.48	88.7	4.8
		10.10	9.09	90.0	2.7
		15.15	13.21	87.2	1.8
20 samples from Quality Assurance Division of USAEHA	UDMH	11.8	3.6	31*	12
		19.6	18.2	93	13
		39.2	40.8	104	13
	Hydrazine	1.19	1.09	92	4.2
		2.38	2.33	98	6.4
		4.36	4.34	99	12

*These low recoveries were attributed to the improper slope sensitivity setting on the computer type integrator which caused only part of the GC peak to be integrated.

Monitoring. The evaluation of the propellant facility was undertaken upon verification of the analytical techniques in the laboratory. During two visits to the plant, sampling and analysis were conducted in the field, and atmospheric concentrations of the hydrazines were determined throughout the work area of the plant. Table V shows the concentrations observed during typical operations. Depending on the type of operation being performed, the concentrations of the hydrazines in the proximity of the workers' breathing zone (outside the protective mask) ranged from 0.23 ppm to 4.61 ppm for UDMH and from 0.22 ppm to 1.6 ppm for hydrazine.

To determine the adequacy of the respiratory protective equipment, simultaneous samples were collected from inside of each workers' protective mask and compared to the results obtained outside the mask. Operations typical of the surveyed facility varied in duration from 0.5 to 3 hours. As need arose the workers rotated from one operation to another, but wore the same mask throughout the length of each day of testing. Data from the simultaneous sampling on the outside and inside of the masks are presented in Table V. In one instance a low concentration of UDMH was found inside one mask. This was attributed to breaking the face seal on the mask, and not to canister depletion, because no hydrazines were detected in subsequent samples taken from inside the mask with the same canister.

TABLE V

Hydrazine Concentrations Outside and Inside the Masks

Operation	UDMH (ppm)		Hydrazine (ppm)	
Compound	Outside Mask	Inside Mask	Outside Mask	Inside Mask
UDMH	1.10*	ND**		
	.28	"		
	.45	"		
	.56	"		
	4.61	.03		
	2.95	ND		
	.23	"		
	.36	"		
	3.46	"		
Hydrazine			1.15	ND
			1.64	"
			.22	"
			1.98	"
Aerozine 50	1.61	ND	1.60	ND
	1.71	"	.71	"
	1.33	"	.99	"
	.40	"	.22	"
	.30*	"	.31*	"

* M-9 Military Mask.

** None deteced.

CONCLUSIONS

The sampling train discussed in this report has been found adequate within the limits imposed by the degree of analytical sensitivity. This type of sampling train may be adapted to other exposures where it is desirable to obtain data of this type, i.e., determination of the protection afforded individuals by respiratory protective equipment.

The analytical method of derivatizing hydrazines and analysis by GC was extensively tested in the laboratory and proved satisfactory in the field tests. The percent mean recoveries and relative standard deviations were determined on the basis of analyses of 56 UDMH and hydrazine specimens. However, it is necessary to have a field laboratory located at the sampling site, because it was found imperative to run analyses immediately after sample collections.

The respiratory protective equipment used afforded adequate protection to prevent inhalation exposures of the workers.

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Paper No 7

SORPTION TUBE SAMPLING TECHNIQUE FOR ANALYSIS OF DIMETHYLNITROSAMINE

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INTRODUCTION

The industrial synthesis of Unsymmetrical Dimethylhydrazine (UDMH) involves nitrosation of Dimethylamine (DMA) to N-Nitrosodimethylamine (NDMA), with subsequent chemical reduction to UDMH. The large scale manufacture, transfer and temporary storage of UDMH and its intermediates have recently been of concern to the United States Environmental Protection Agency (EPA) as a potential source for atmospheric nitrosamines.[1] Independent studies in October 1975 showed evidence of NDMA in ambient air samples taken in Baltimore, Maryland, downwind of a UDMH production facility. In order to pinpoint the nitrosamine source, an EPA sampling study was conducted in close proximity to the UDMH manufacturing facility in November 1975. The USAF School of Aerospace Medicine participated with the EPA in this study and found that cryogenic trapping of ambient air was logistically cumbersome.

This report describes a sorbent tube sampling technique developed to augment a cryosampling procedure employed in early field trials.[2] The sorption tube atmospheric sampling system was developed and employed to reduce the size of the collection unit, increase sensitivity, and simplify the analytical procedure. The sorbent tube unit has since been used to monitor UDMH storage facilities, caustic waste processing plants and a salt recovery facility.

METHODS

A Tenax-GC (2,6-diphenyl-p-phenylene oxide polymer) sorption tube atmospheric sampling system consists of three subsystems, pump and flowmeter, sample tube, and thermal desorption block. The system is described in Air Force Invention 12,052.

The sample tube was a 1.27 cm diameter x 15.24 cm long x 0.89 mm wall stainless steel tube (Fig 1), and contained 2.5 grams of 35/60 mesh Tenax-GC. The interior wall of the stainless steel tube was electropolished to reduce any surface effects of the metal. The Tenax-GC was held in place by double stainless steel screens at each end of the tube. The ends of the tube were connected to a Swagelok SS-810-C Cap which was centrally drilled to accept a Cajon VCR Vacuum Coupling consisting of a 4VCR-3-A-SS gland and a center welded 4VCR-1SS female nut. The tube was sealed by a special Nylon plug and a Teflon washer.

Sample collection was accomplished by connecting the sample tube to the pump and flowmeter portion of the system (Figure 2). The air stream after passing through the sorption media passed through a ball valve. The gas then passed through a 7 micron filter which prevents the pump (Metal Bellows Model MB-155) from being contaminated with Tenax-GC dust. A needle valve (Whitey SS-21RS4) was used for flow control. The flow rate was measured with a Fisher and Porter 10A3665S flowmeter and vented to the ambient atmosphere. A flow of one liter per minute was maintained through the system. The sorbent tube was sealed by means of the Nylon plugs immediately upon completion of sample collection.

Hydrocarbon analysis of the collected sorbent tubes was accomplished with a coupled Gas Chromatograph(Varian 1400 Model)-Mass Spectrometer(DuPont Model 21-491)-Data Acquisition(DuPont 21-094 and Hewlett Packard 3352B) (GC-MS-DS) system (Figure 3). The chromatograph column was a 3-meter-long (0.7 mm I.D.) stainless steel tube packed with Porapak Q (120-150 mesh). This column with temperature programing from -100 to 250^{o}C has proven adequate for separation of compounds ranging from ethane to the C10

aliphatic and aromatic oxygenates. The chromatographic effluent (Figure 4) was split 1/3 to the Flame Ionization Detector (FID), and 2/3 to the mass spectrometers via jet separator. Compound quantitation was from the FID signal by digital integration with the Hewlett-Packard 3352B system.[3] Compound identification is done by selecting appropriate scans (fracture patterns) for the peaks of interest (Figure 5) and comparing those to fracture patterns contained in the computer library.[4] NDMA standards prepared in water established an absolute minimum sensitivity for the GC-MS-DS of 0.17 µg. Samples of 240 liters were collected from the area being sampled. This size sample combined with the sensitivity of the analysis system gives an ability to detect concentrations of NDMA in excess of 0.7 ug/m^3.

$$\frac{0.17 \text{ ug (absolute sensitivity of GC-MS-DS)}}{240 \text{ liters (sample size)}} \cdot \frac{1000 \text{ Liters}}{m3} = 0.7 ug/m^3$$

RESULTS AND DISCUSSION

The sorbent tube method has been used to monitor UDMH storage facilities, caustic waste storage, a caustic waste recovery facility, and UDMH Production Sites. This monitoring was established to insure that as a result of fuel production, NDMA was not released into the environment.

Samples were collected from the atmosphere near a UDMH storage facility. Samples from upwind of the unloading point (Figure 6) were obtained to insure that NDMA was not present in the ambient atmosphere. If NDMA were found in the downwind sample, it would be the result of leakage into the atmosphere from the offload point.

The system has been effective in monitoring production and storage facilities associated with UDMH. The source of NDMA atmospheric contamination was located when local micro-meteorology was combined with NDMA concentrations. Figure 7 shows the mini-weather collection devices used to obtain data as the sample was being collected. At a plant where the caustic waste UDMH production (containing NDMA) was processed to obtain an innocuous material, samples were collected in an area of the evaporator frequented by employees. This sample was obtained to insure that the employees were not exposed to high concentrations of nitrogen containing compounds (Figure 8). Application of this system to collect samples other than those associated with NDMA and UDMH has shown a great deal of promise considering the limitations of the sorbent.

List of Illustrations

Figure 1. Sorption tube of atmospheric sampling system.

Figure 2. Atmospheric sampling system.

Figure 3. Gas Chromatograph-Mass Spectrometer-Data Acquisition System.

Figure 4. Schematic of analysis system.

Figure 5. Ion Chromatogram.

Figure 6. Sample obtained upwind of tank car offload area.

Figure 7. Sample collection unit and devices for obtaining local weather conditions.

Figure 8. Second level of caustic waste evaporator frequented by plant operators.

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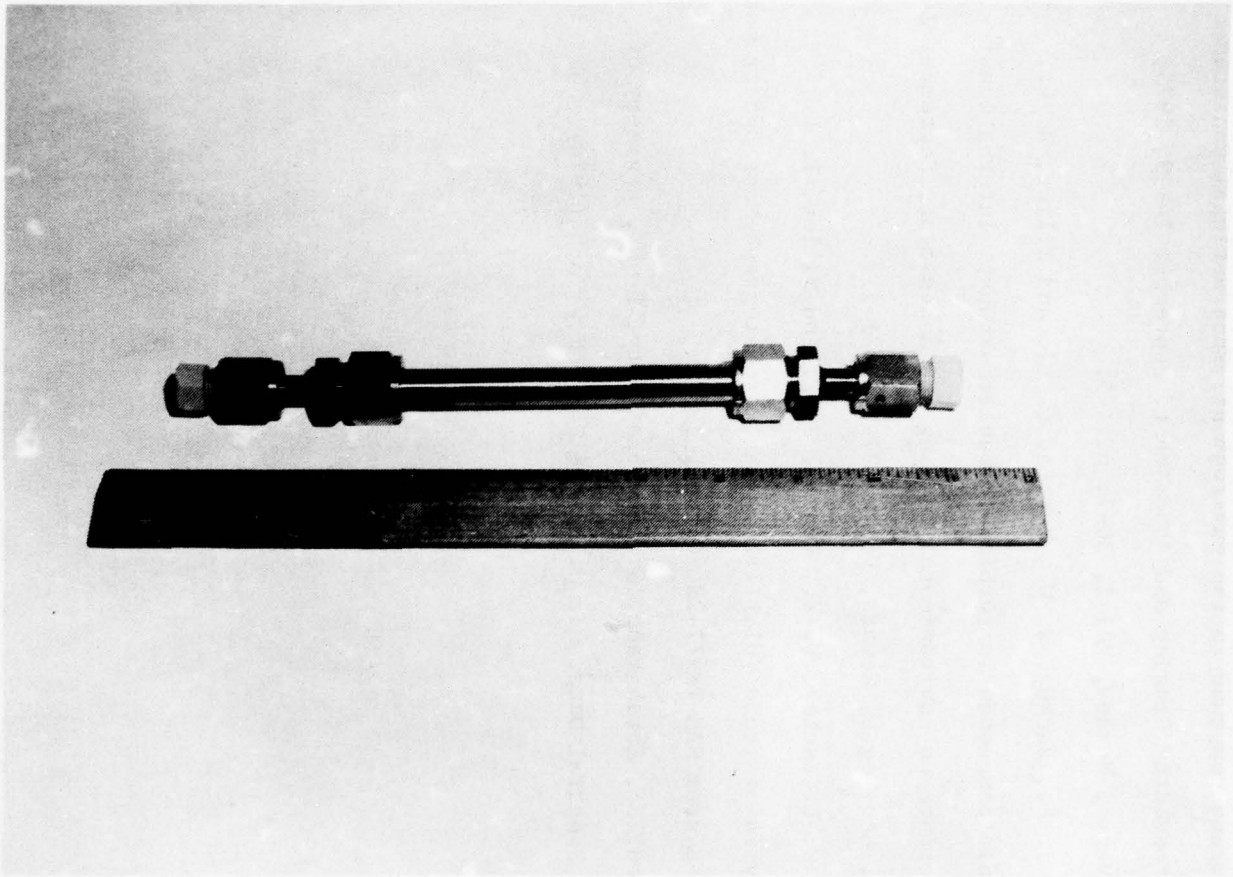


Figure 1. Sorption Tube of Atmospheric Sampling System

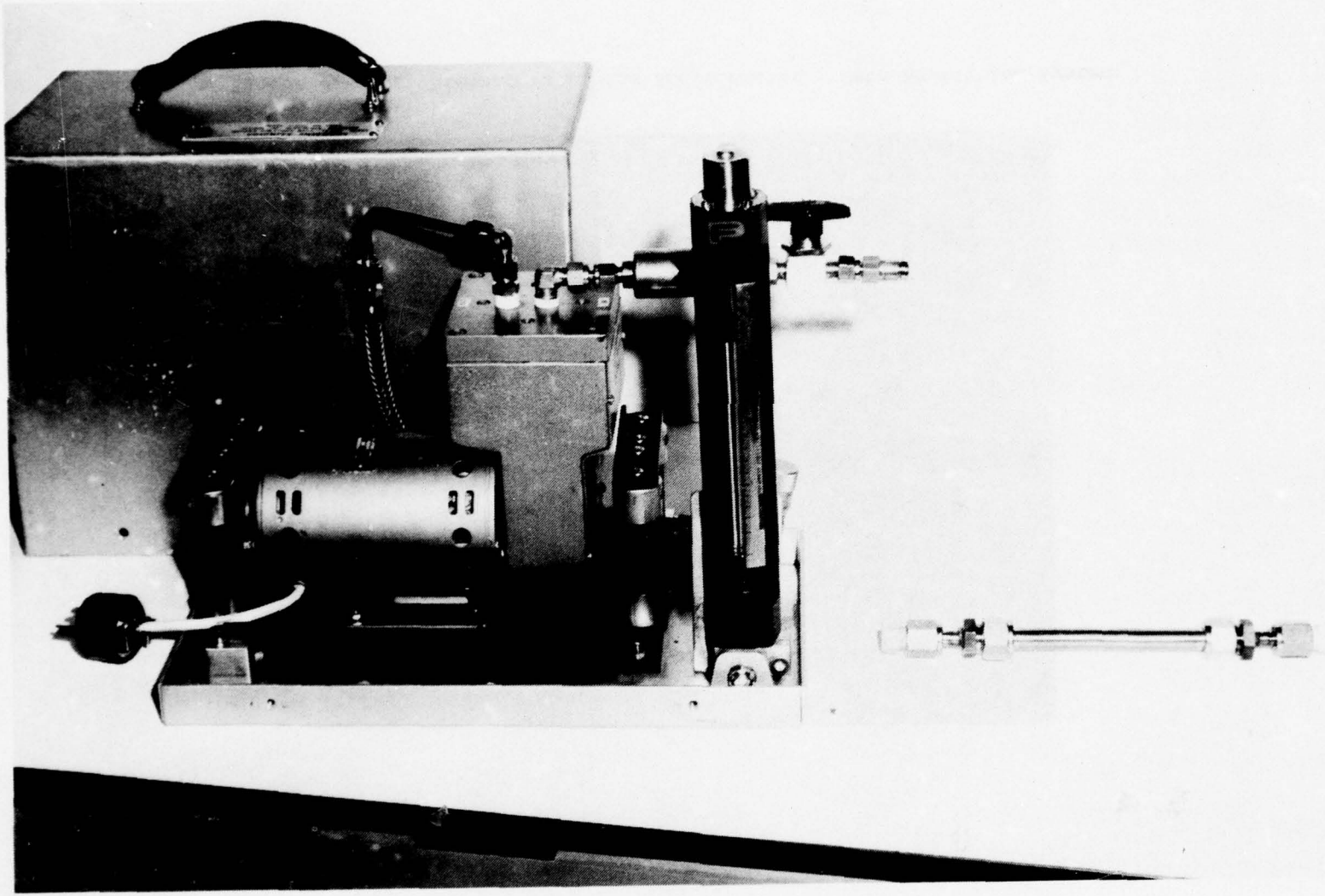


Figure 2. Atmospheric Sampling System



Figure 3. Gas Chromatograph/Mass Spectrometer - Data Aquisition System

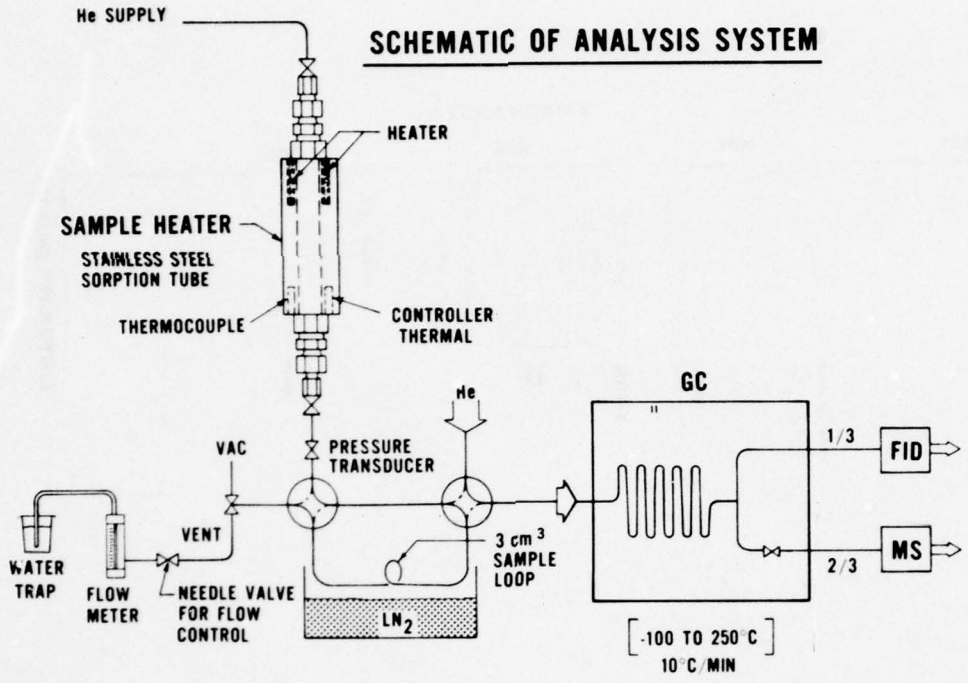


Figure 4. Schematic of Analysis System

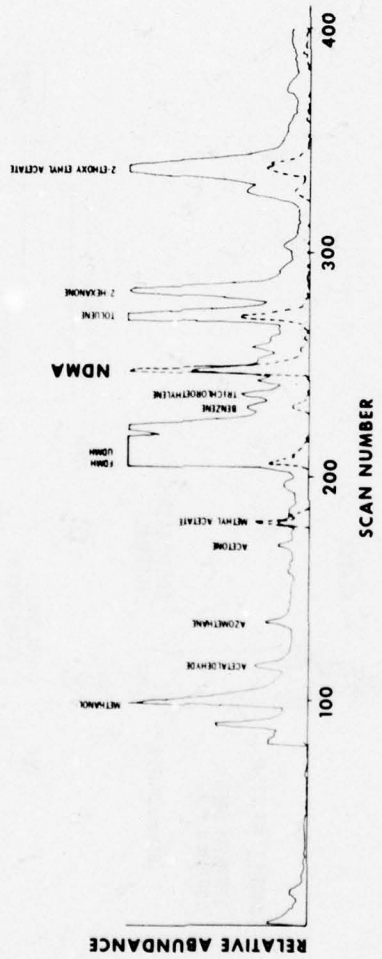


Figure 5. Ion Chromatogram

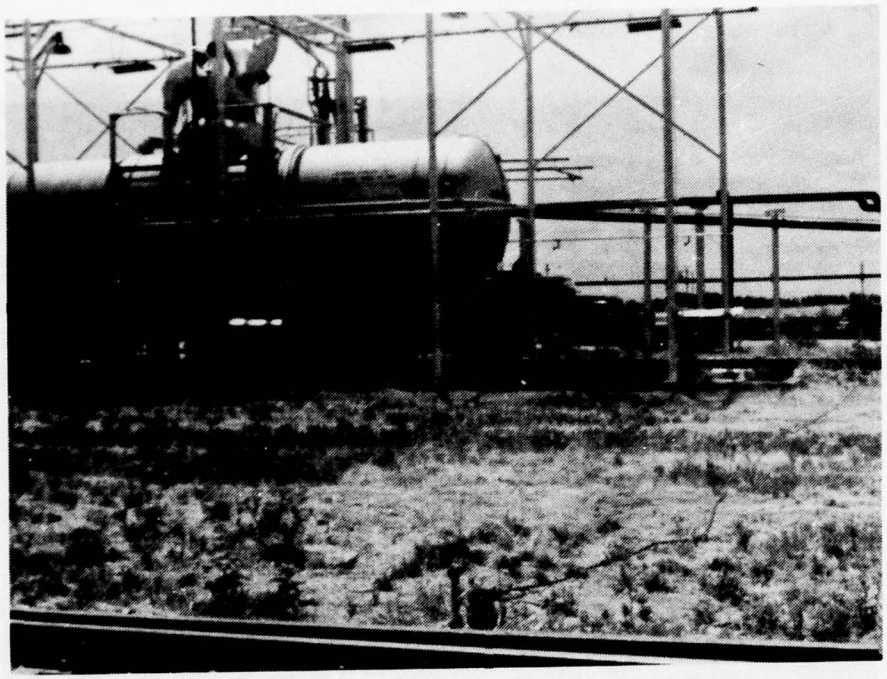


Figure 6. Sample Obtained Upwind of Tank Car Offload Area

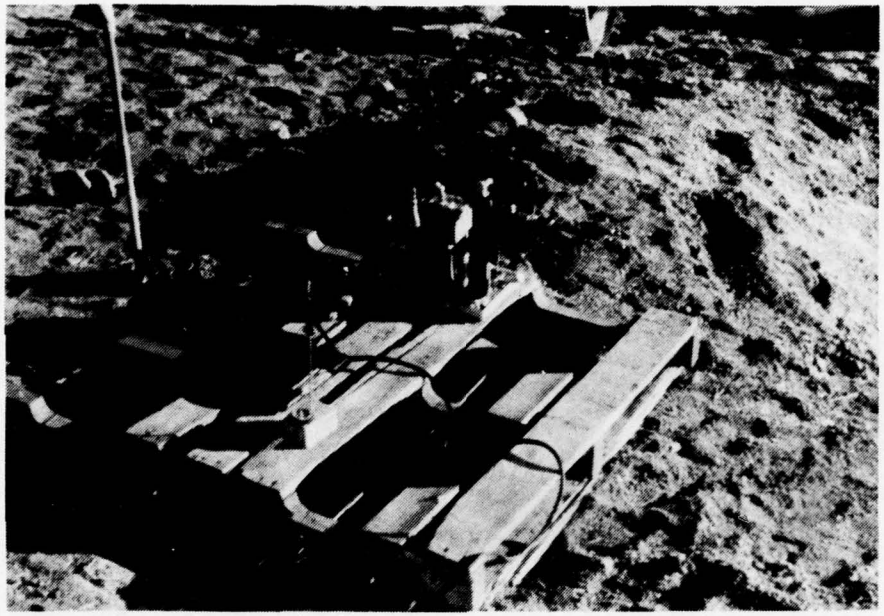


Figure 7. Sample Collection Unit and Device for Obtaining Local Weather Conditions

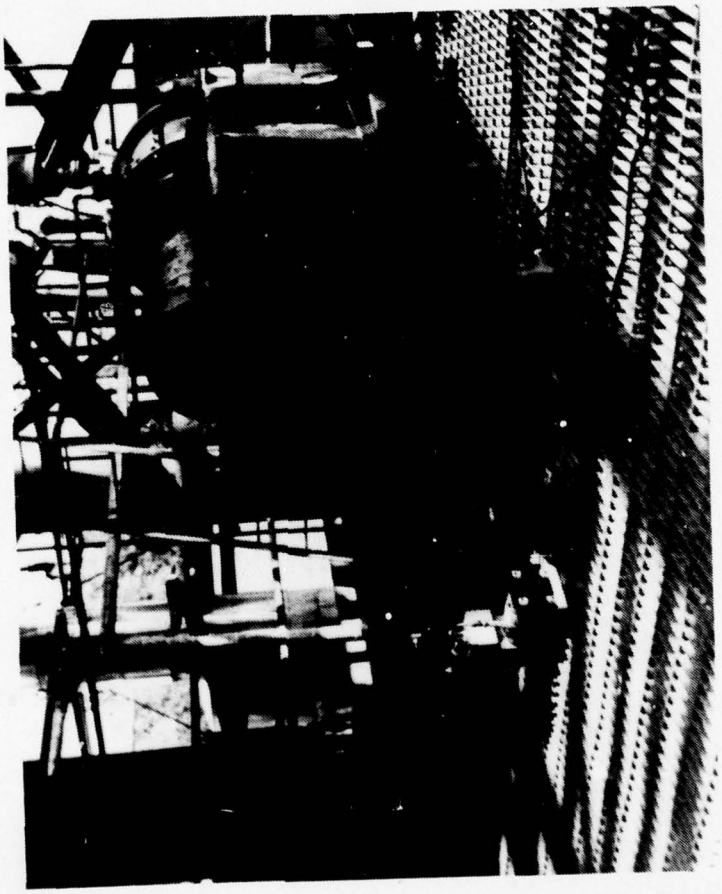


Figure 8. Second Level of Caustic Waste Evaporator Frequented by Plant Operators

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Paper No 8

THE ANALYSIS OF HYDRAZINE, MONOMETHYL HYDRAZINE AND 1,1-DIMETHYL HYDRAZINE USING WCOT/GC TECHNIQUES

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INTRODUCTION

The quantitative analysis of hydrazine and its methyl derivatives by gas chromatographic procedures has been previously reported by Dee and Webb (1) and by Dee (2) as well as other workers (3,4,5). While the procedures proposed by Dee offered improvements over previous analytical techniques in reducing the effect of interfering materials and decreasing analysis times the procedure advanced was not without drawbacks.

The direct analysis procedure outlined by Dee and Webb did not provide sufficient sensitivity for many analytical problems and column life times were very short. In addition, sample stability prior to analysis and in the G.C. injection port was a problem. The use of 2,4-pentanedione advanced by Dee (2) to form pyrazole derivatives of HZ and MMH prior to G.C. analysis improved the sensitivity (3), reduced many of the interfering materials and reduced problems of sample stability in the G.C. But this analysis procedure cannot be used to analyze two important methyl derivatives; sym- and unsym-dimethylhydrazine (SMDH and UMDH), and the sensitivity and recovery were dependent on reaction conditions such as pH and reaction time. In addition, because reaction mixtures were directly injected into the G.C. column, life times were reduced.

The analysis procedure outlined in this report is basically a modification of Dee's (2) procedure in which the derivatizing reagent is changed, the derivative is extracted with organic solvents and glass capillary columns are used for the chromatography. A variety of reagents, including benzal-

*Now located at Waters Associates, Milford MA

dehyde and cyclohexanone as well as acetone, were studied. Several extraction solvents including hexane, benzene, pentane, $CHCl_3$ and CH_2Cl_2 were tried; and a variety of columns and column conditions used (these included OV-101, SE-30, OV-17 and CW20M). The analysis procedure outlined in this report was found to be the most satisfactory combination of conditions and reagents for the analysis of HZ, MMH and UMDH. The analysis of SMDH was not found to be possible by derivatization and must be run independently.

EXPERIMENTAL

Instrumentation. A Hewlett Packard 5840 series gas chromatograph equipped with both flame ionization and N-P detectors and modified for capillary columns was used to perform the analysis. Each detector has independent gas feeds and can be calibrated and operated independently from the G.C. console.

The FID was used for all analyses presented in the report unless otherwise indicated. The carrier gas was helium. Nitrogen was used for the makeup gas. The instrument was equipped with a Hewlett Packard model 18824A auto injection system, and all routine analyses were performed using this injector.

The instrument modifications made to adapt the system for use with glass capillary (WCOT) columns are shown in Figures 1 and 2. The general instrument configuration is given in Figure 1. All seals between the column and injection liner are made with graphite ferrules. The split adjust configuration allows one fine metering valve to be used to balance the column at a low split ratio. The second valve (routed in parallel through an on/off valve) can be set to produce a second higher split ratio with the same column flow. The column flow and split ratios are column head pressure dependent so a single stage regulator is placed on the carrier gas input line. By using this regulator and the splitter metering valves the proper column flow and split can be achieved. The column flow is routed through the instrument's flow sensor, but the flow controller is bypassed. The

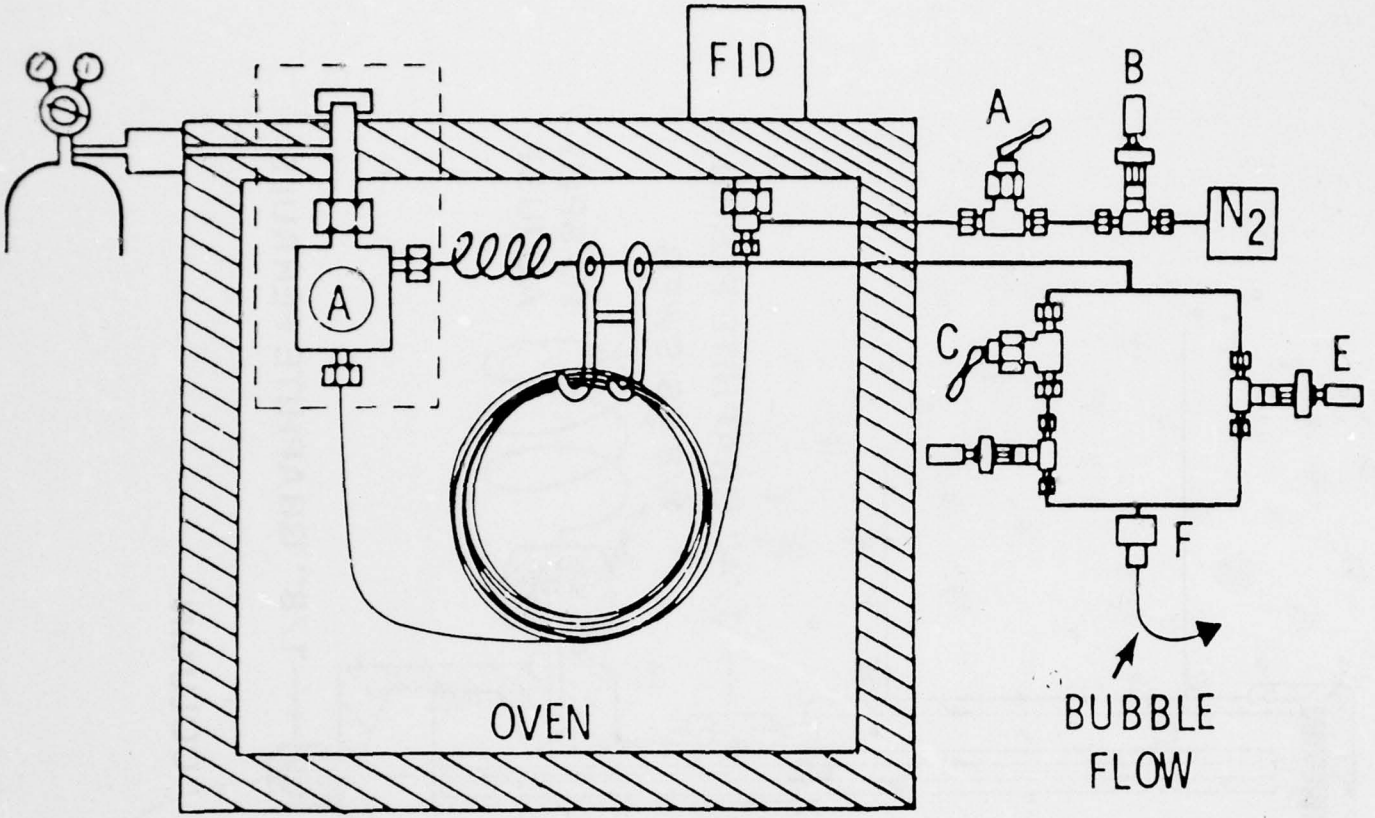


Figure 1

INSTRUMENT CONFIGURATION FOR USE WITH GLASS CAPILLARY COLUMNS

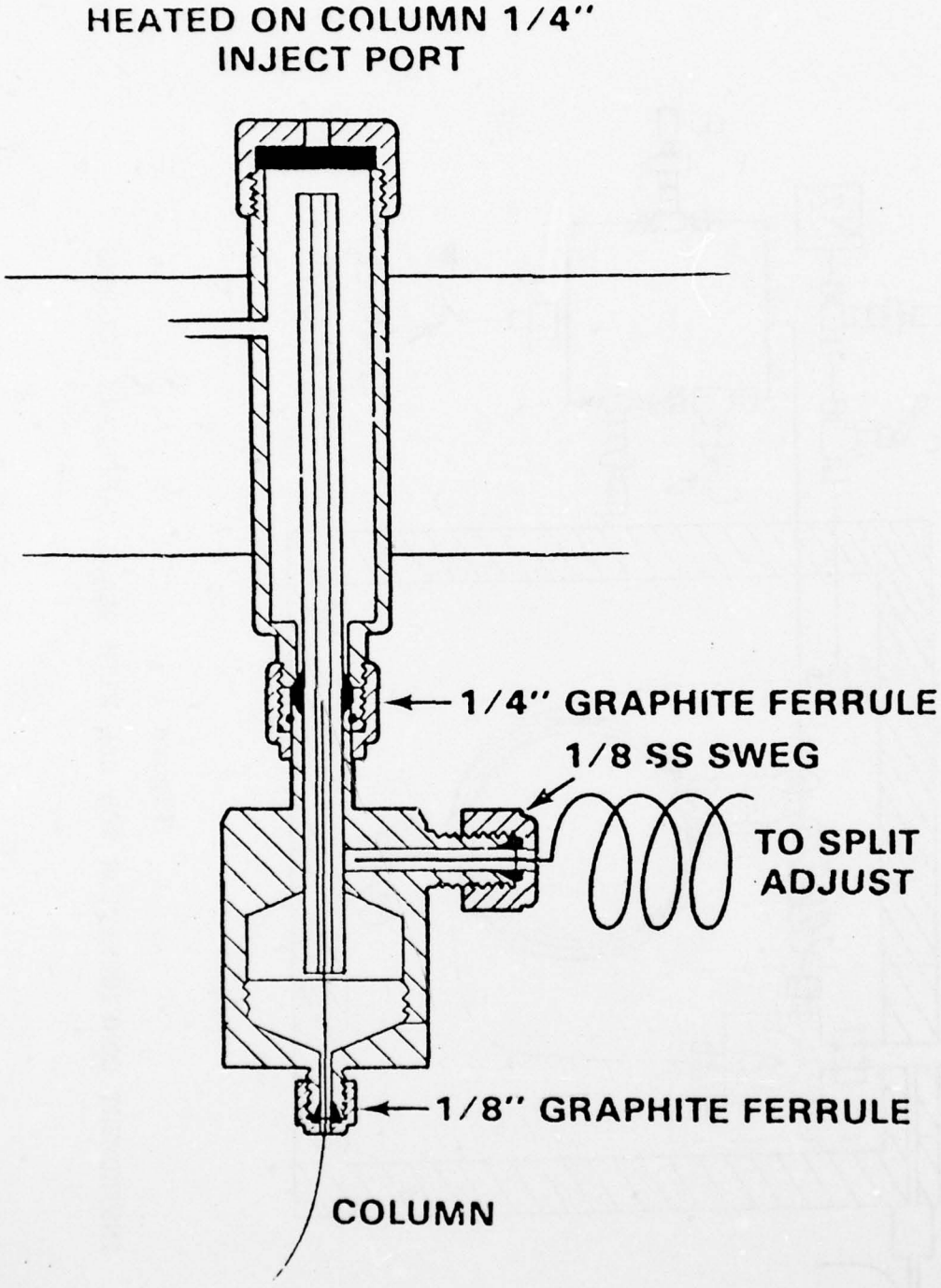


Figure 2

INJECTION PORT CONFIGURATION
FOR USE WITH GLASS CAPILLARY COLUMNS

makeup gas is plumbed through both the flow sensor and flow controller. This configuration allows both critical flows, the makeup gas and the splitter flow, to be continuously monitored at the console. The total carrier flow is the sum of the splitter flow and the column flow (plus any peaks), but since the column flow is in the 0.5 to 1.5 ml/min range the flow sensor reading can be used to measure the splitter flow which is at least a factor of 10 higher. This system also allows the instrument to be leak tested, i.e., if the measured column flow and splitter flow do not equal the flow reading the system has a leak. The splitter body shown in Figure 2 was obtained from J & W Scientific (Orangevale CA 95662) and is based on the design reported by Jennings et. al. (6). The splitter uses a ¼" O.D. glass liner. The I.D. of the liner and the liner packing used is dependent on the total splitter flow. For split ratios of less than 15:1, a 2 mm I.D. liner is used and it is packed with coated glass beads. For higher split ratios a 4 mm liner is used and packed with glass wool. The liners have a restriction at the point where the capillary column is placed to insure proper sample loading on the column. These liners can be obtained from A.A. Pesce Co. (Kennett Sq PA 19348).

The glass capillary columns were obtained from J & W Scientific (Orangevale CA 95662). The reported analysis was performed on a 60 meter OV-101 column (J&W number G100-0V-101, cost $275.00). Analysis of the HZ and MMH acetone derivatives were also performed on a 18 meter CW20M column obtained from the same source, but the UMDH derivative could not be resolved from the solvent peak.

Reagents. All solvents used were Burdick and Jackson high-purity solvents. The acetone was Baker reagent grade. The hydrocarbon standards were obtained from Poly Science Corp. (Kit No. 21A). The MMH and UDMH were obtained from Aldrich Chemical Co. and the HZ from Baker Chemical Co.

Derivatization and Extraction Procedures. The hydrazone standards were prepared by reacting a known amount of each hydrazine (UMDH, MMH and HZ) with a five-fold excess of acetone in methylene chloride. Completeness of reaction was checked at three concentration levels (100 ug/ml, 1000 ug/ml

and 10,000 ug/ml). Each solution was monitored by G.C. at 15, 30, 60, 120 minutes and 4, 24 and 48 hours to determine completeness of reaction. The reaction products are stable for the 0.1 and 1.0 mg/ml concentrations at 15 minutes and are stable at 30 minutes for the 10 mg/ml concentration. The area response for each hydrazine compound was based on the area response of the resulting hydrazine product from this reaction. Extraction standards were prepared by adding known amounts of each hydrazine (UMDH, MMH, and HZ) to distilled water and to a simulated reaction mixture (3M NaCl, 3M NaHP04 and 1.0M NaOH).

A three-fold excess of acetone was added and the mixture was shaken on a wrist arm shaker for 15 minutes (30 minutes for concentrations over 5.0 mg/ml). These samples were either assayed directly or extracted.

The extractions were performed following adjustment of the reaction solution to pH 9.0. A known amount of the reaction mixture (5 mls) was quantitatively transferred to a screw cap vial and twice this volume of CH_2Cl_2 was added. The desired amount of internal standards were also added (octane and nonane for FID) and the mixture was shaken for 15 minutes. The organic layer was removed and the extraction repeated a second time without the addition of the standards. The extracts were combined and assayed on the G.C. If the N-P detector is used, benzene or hexene are used for the extraction solvents and nicotine or pyrazol were used as internal standards. The reaction mixtures were derivatized and extracted as described above except water was added to make the acetone miscible when the mixture contained a very high salt content. For samples where the concentration levels of the products were not known one ml of acetone was added to every two mls of sample. This was extracted twice using an amount of solvent double the total volume of sample plus acetone.

Gas Chromatographic Analysis. The G.C. analysis conditions for use with the 60 meter OV-101 column were as follows:

TEMP 1	240*	105**	105
TIME 1	0.50		

RATE	5.00		
TEMP 2	240*	195	
TIME 2	10.00		
INJ TEMP	350*	250	250
FID TEMP	400*	300	300
AUX TEMP	350*	300	300
CHT SPD	0.50		
ZERO	10.0		
ATTN 2	7		
FID SGNL	+B		
SLP SENS	1.00		
AREA REJ		100	
FLOW A	30.00	30.0 (Makeup)	
FLOW B	38.1	38.9 (injector)	

Time Function	Value
3.00 RATE	25.00
8.00 ATTN 2	4
12.00 STOP	

*Temperature Limits

**Temperature Set Points

(The hydrogen flow was 40 mls/min and the air flow was 240 mls/min).

The 5840A is processor controlled and all major functions can be time programmed. Therefore, the slope sensitivity (SLP SENS) and temperature programming rates were adjusted periodically to produce the best resolution and most reproducible integration for each sample series.

The quantitative analysis of the components was accomplished using the 5840 integrator. Two internal standards (ISTDS) normally octane (Cn-8) and nonane (Cn-9) were used at all times. Slope sensitivities that yielded the most reproducible peak integrations were set using standard mixtures of all

components. The relative area response factors for the hydrazone derivatives and the ISTDS were periodically recalculated and were checked each day with the standard mixtures.

The primary quantitation was accomplished using the Cn-8 standard. Measurements of the Cn-9 standard provided a check on the standards and the analysis. The response of the standards and of the sample extracts were found to be stable for up to 30 days without special handling and longer if kept cool and out of the light.

RESULTS

Extraction Procedure. Chromatograms of a standard mixtures and extracts of aqueous reaction standards of the UDMH, MMH and HZ derivatives and the Cn-8 and Cn-9 internal standards are given in Figure 3A and B, and Figure 4 shows a chromatogram of a typical reaction sample. The column and analysis conditions used produced a Neff* = 32,000 at a partition ratio (k) = 2.3 and a Neff = 18,000 (k) = 2.5 for the Cn-8 and hydrazine derivatives respectively. By optimizing analysis conditions these can be increased by a factor of three. All peaks are symmetrical when the system is operating properly. Some tailing will occur following extensive use due to sample residue build-up in the injection port liner. When tailing is observed the liner should be cleaned. Some tailing is also observed if the glass column ends that are straightened during mounting are not deactivated with a 5% CW20M/CH_2Cl_2 solution. The column and analysis conditions did produce adequate resolution in all cases for identification and quantitation of the components under investigation.

The area response data for each component under investigation is given in Table 1. The maximum area that can be quantitatively measured (at signal to noise ratio of 3:1) is approximately 30 A_u. The area responses are linear over the concentrations spanded by each split ratio. In practice samples in similar concentration ranges are grouped and the split and analysis conditions are optimized for that concentration range. For mixtures where the individual components are in widely varying concentrations

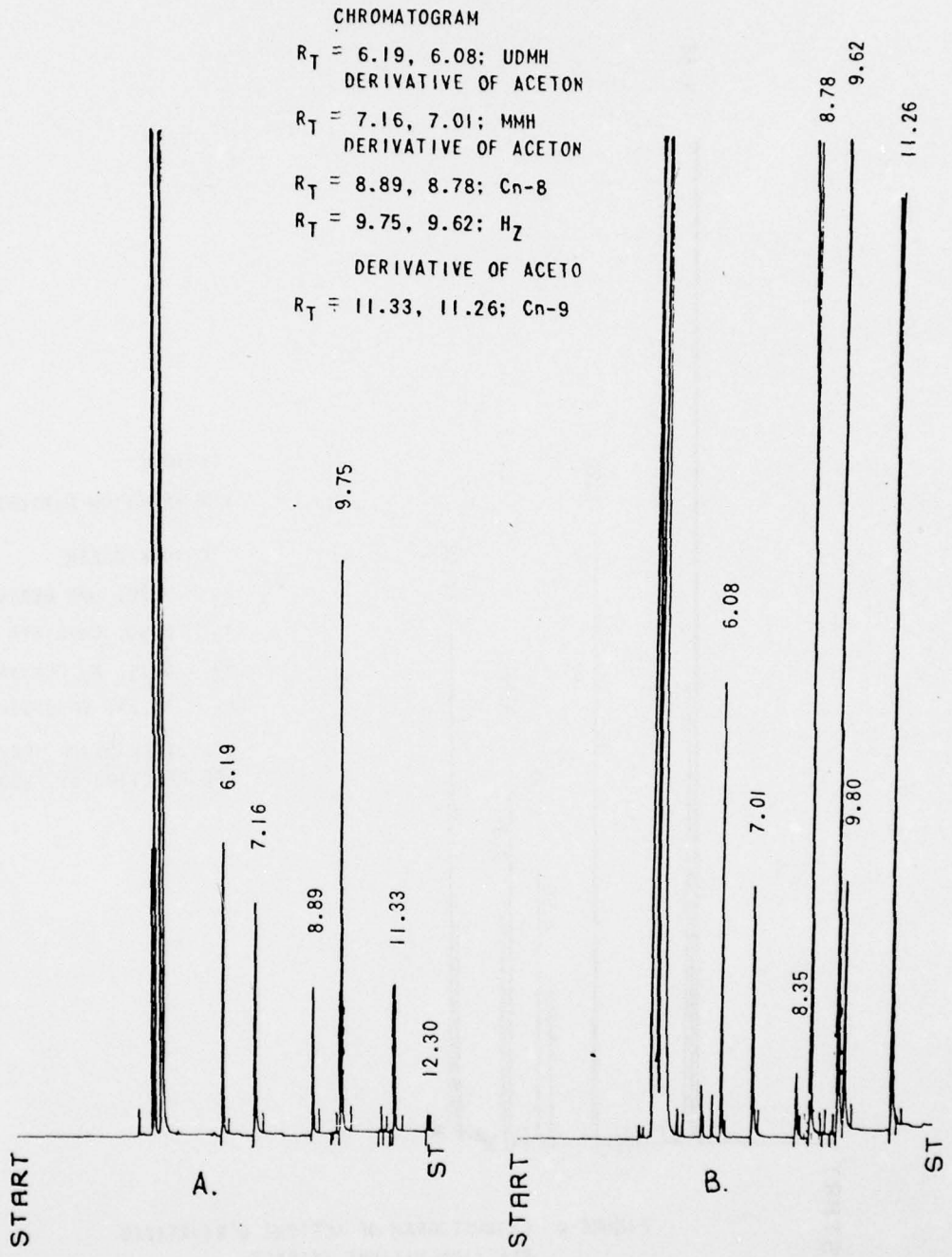
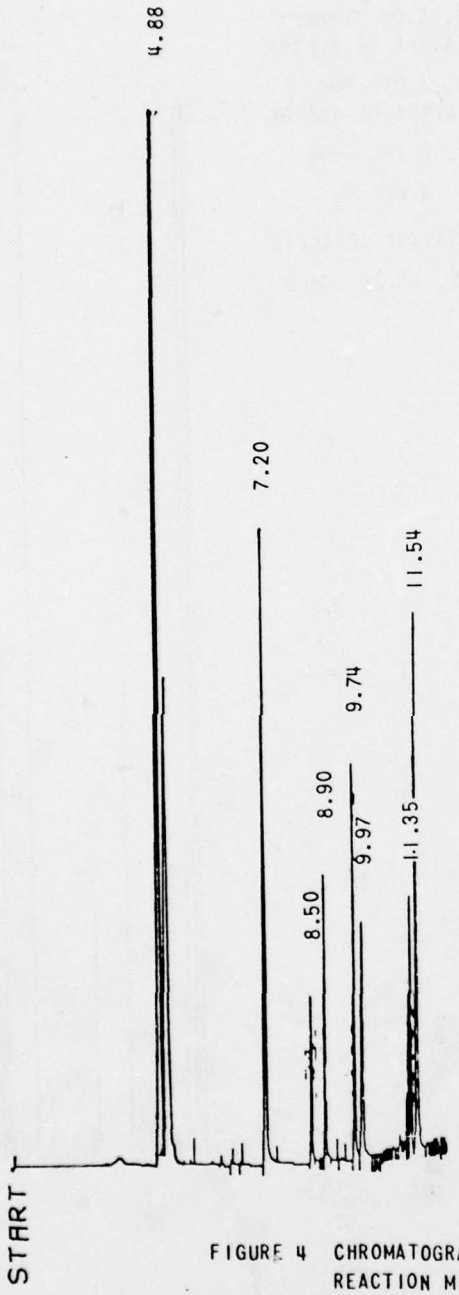


FIGURE 3 A & B CHROMATOGRAMS OF HYDRAZONE PRODUCTS OF UDMH, MMH AND H_Z

A.) ACETONE DERIVATIVES OF UDMH, MMH AND H_Z IN CH_2Cl_2

B.) EXTRACT OF ACETONE DERIVATIZATION OF UDMH, MMH AND H_Z FROM SIMULATED REACTIM MIXTURE



SAMPLE

MMH REACTION MIXTURE

CHROMATOGRAM

R_T = 7.20; MMH DERIVATIVE

R_T = 8.90; Cn-8 STD

R_T = 9.74; H_Z DERIVATIVE

R_T = 11.54; Cn-9 STD

ALL OTHER MAJOR PEAKS
ARE REACTION BY PRODUCTS

FIGURE 4 CHROMATOGRAM OF ACETONE DERIVATIZED REACTION MIXTURE EXTRACT

TABLE 1. AREA RESPONSE FOR ACETONE DERIVATIVES OF UDMH, MMH AND HZ

Solution Conc. of hydrazine compound (ug/ml)	Capillary splitter rato (split flow column flow)	area for UDMH hydrazone derivative (Area units) m=5	area for MMH hydrazone derivative (Area units) n=5	area for HZ hydrazone derivatives (Area units) n=5
1.0	10:1	$7.8 \pm 1.6 \times 10^{1}$	$7.6 \pm 1.6 \times 10^{1}$	$1.8 \pm .5 \times 10^{2}$
5.0	10:1	$4.1 \pm .5 \times 10^{2}$	$4.0 \pm .5 \times 10^{2}$	$9.3 \pm .4 \times 10^{2}$
10.0	10:1	$8.3 \pm .6 \times 10^{2}$	$8.1 \pm .4 \times 10^{2}$	$18.8 \pm .4 \times 10^{3}$
50.0	10:1	$4.4 \pm .6 \times 10^{3}$	$4.5 \pm .3 \times 10^{3}$	$9.7 \pm .5 \times 10^{3}$
100.0	10:1	$9.1 \pm .5 \times 10^{3}$	$8.7 \pm .3 \times 10^{3}$	$20.0 \pm .4 \times 10^{3}$
500.0	30:1	$1.7 \pm .3 \times 10^{4}$	$1.5 \pm .1 \times 10^{4}$	$3.6 \pm .2 \times 10^{4}$
1000.0	30:1	$3.5 \pm .2 \times 10^{4}$	$3.2 \pm .2 \times 10^{4}$	$7.4 \pm .2 \times 10^{4}$
1500.0	30:1	$5.2 \pm .3 \times 10^{4}$	$4.9 \pm .2 \times 10^{4}$	$10.1 \pm .3 \times 10^{4}$
2500.0	30:1	$9.1 \pm .4 \times 10^{4}$	$8.9 \pm .2 \times 10^{4}$	$19.8 \pm .4 \times 10^{4}$
5000.0	30:1	$18.2 \pm .4 \times 10^{4}$	$17.7 \pm .3 \times 10^{4}$	$39.2 \pm .3 \times 10^{4}$
5000.0	60:1	$10.8 \pm .3 \times 10^{4}$	$9.4 \pm .1 \times 10^{4}$	$20.0 \pm .3 \times 10^{4}$
7500.0	60:1	$16.0 \pm .4 \times 10^{4}$	$14.5 \pm .2 \times 10^{4}$	$30.1 \pm .3 \times 10^{4}$
10,000.0	60:1	$21.7 \pm .3 \times 10^{4}$	$19.2 \pm .2 \times 10^{4}$	$39.2 \pm .2 \times 10^{4}$

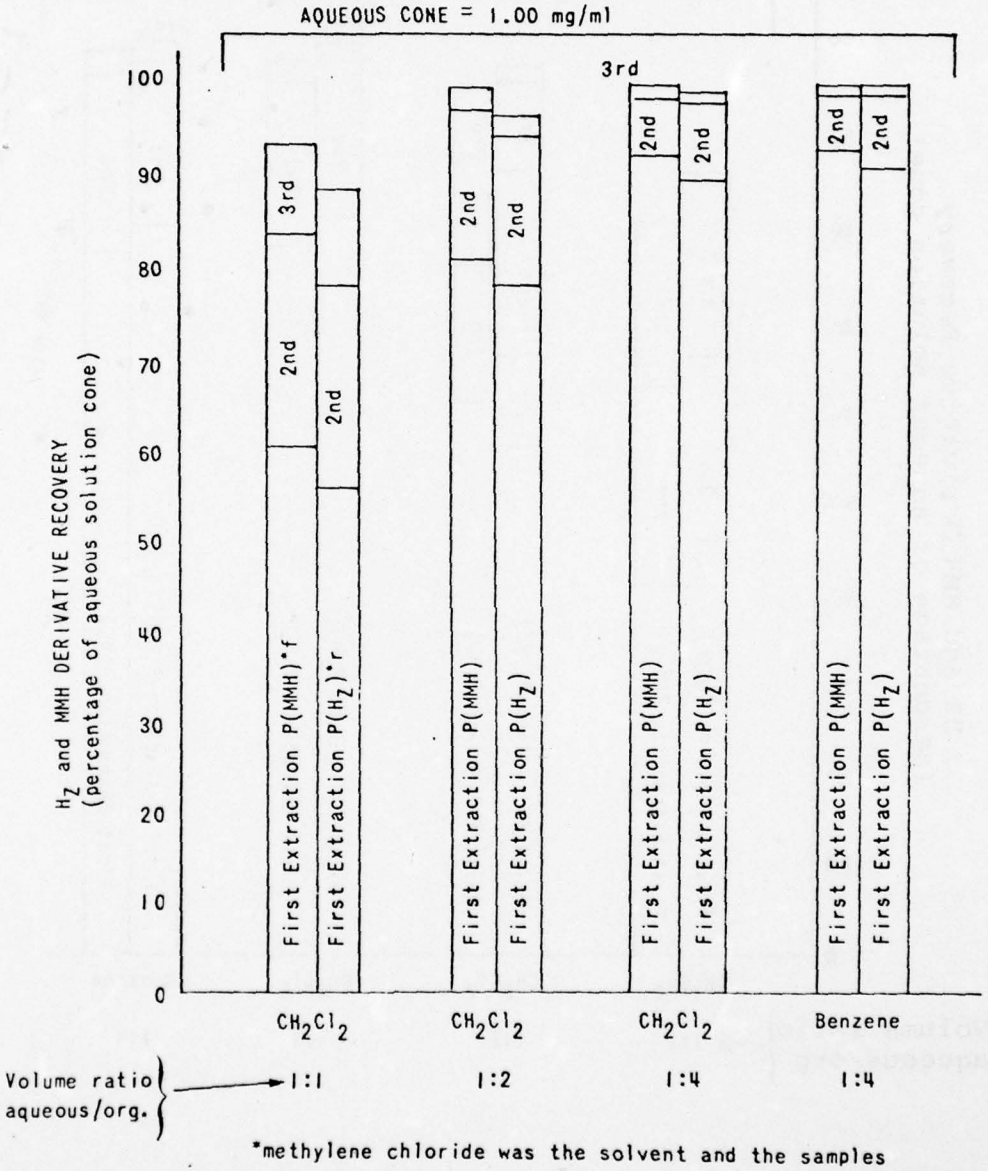
the split is set to provide the necessary sensitivity for the lowest concentration component. The integration conditions are then adjusted to accommodate the overload tailing that results in the high concentration components. Standards reflecting this concentration variation are also used.

The recoveries for samples at 0.10 mg/ml and 1.00 mg/ml are 98.3 $\pm$ .5 (n=10) for monomethylhydrazine, 96.2 $\pm$ 1.2% for hydrazine and 97.7 $\pm$ 1.2% for unsym-dimethylhydrazine. The recoveries using two extractions for samples at 10.0 mg/ml are 96.3 $\pm$ 1.5 (n=10) for MMH, 93.0 $\pm$ for HZ and 91.8 $\pm$ 2.1 for UDMH. The use of a third extraction increases the recoveries for all components to 98 $\pm$ 1%. The recoveries of the three components were the same for both H_2O and the simulated reaction media. The data presented in Figure 5 illustrates the effect that the organic to aqueous ratios and the number of extractions has on recovery of the MMH and HZ derivatives from the simulated reaction media.

G.C. Analysis. The maximum sensitivity was achieved at a 5:1 split ratio with a 2 μl injection using peak height for quantitation instead of integrated area. The lowest detectable concentration (a signal to noise ratio of 3) was approximately 0.5 μg/ml for UDMH and MMH and 0.2 μg/ml for HZ.

The integrator reproducibility for repeated (autosampler) injections of the same sample was better than 1%. The reproducibility of the overall analysis procedure was better than 2.5% based on the analysis of 30 blind pairs of reaction samples and on the analysis of ten pooled standard samples where sample component concentrations are greater than 100 ug/ml. The greatest error in the overall analysis procedure was the measurement of the total reaction mixture volume and the sample aliquot volume. These generally had a 5-10% error factor. Thus the G.C. analysis procedure was not the limiting factor in the accuracy and reproducibility of the reaction mixture analysis.

The direct analysis of the reaction mixture or hydrazine solutions following derivatization with acetone was also accomplished using the OV-101



*methylene chloride was the solvent and the samples were shook for 10min. at each extraction

FIGURE 5a. ACETONE REACTION PRODUCT RECOVERIES

**P(MMH)=MMH/ACETONE REACTION PRODUCT

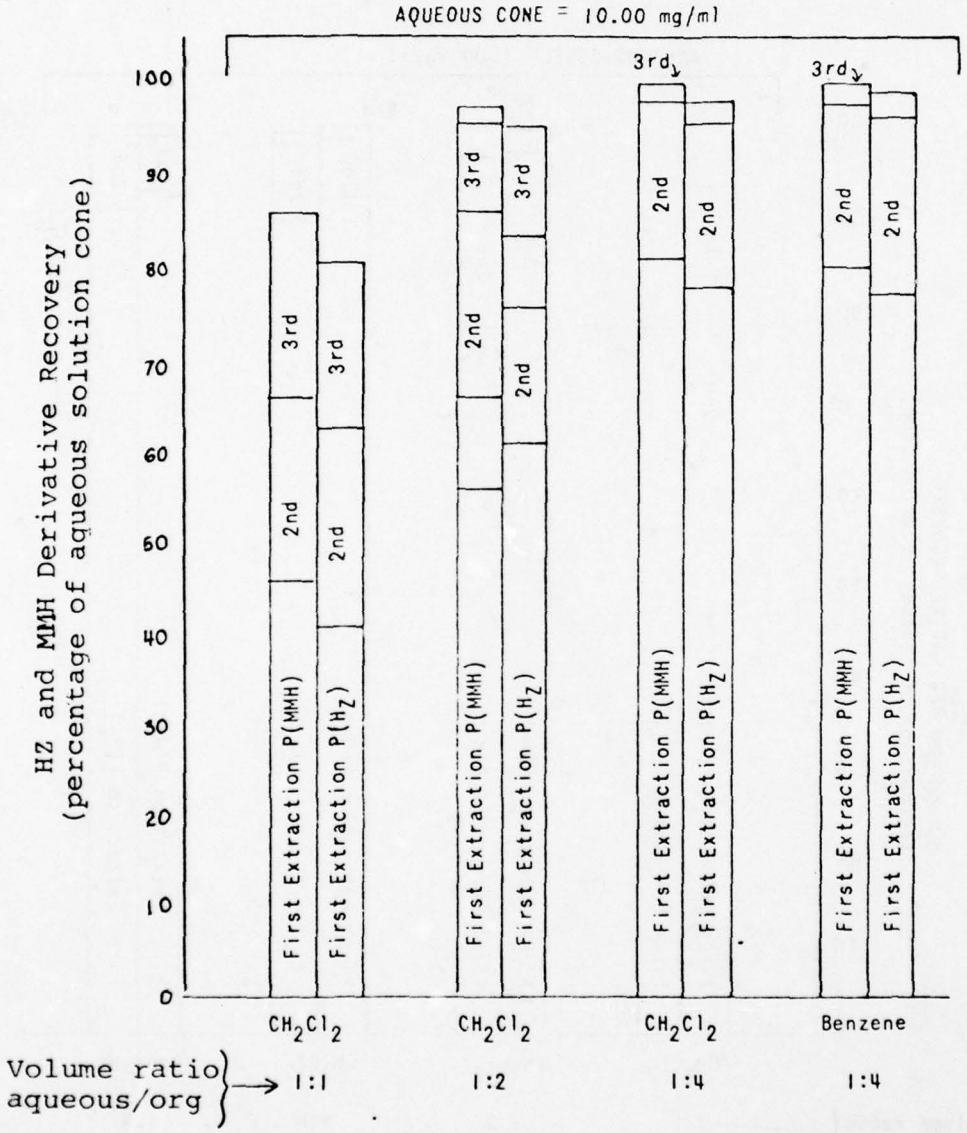


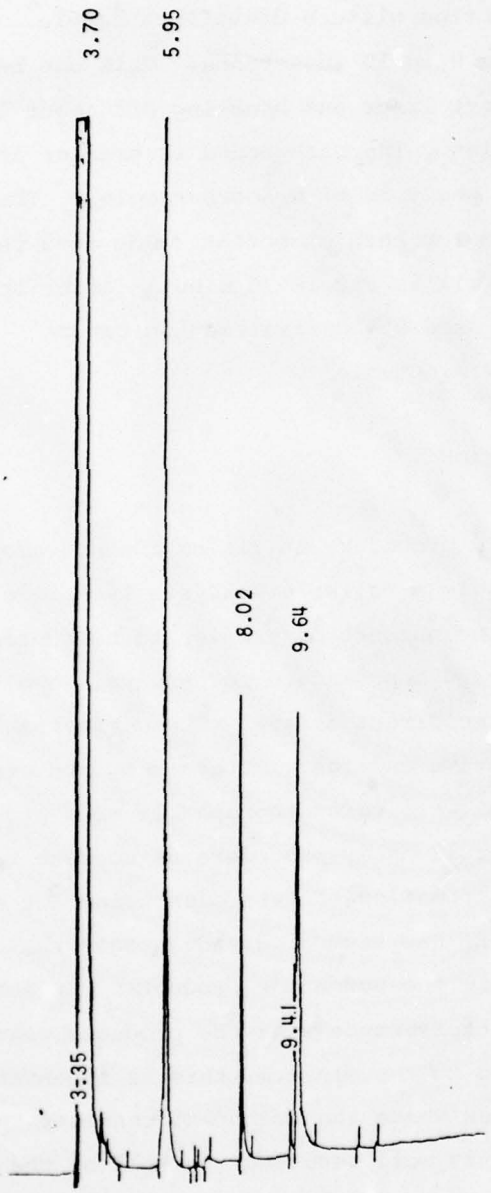
FIGURE 5b. ACETONE REACTION PRODUCT RECOVERIES

**P(MMH) = MMH ACETONE REACTION PRODUCT

WCOT column (which is water stable). Figure 6 shows a chromatogram of a direct injection of a derivatized reaction mixture distillate sample. Peak tailing begins to occur following 8 to 10 injections. This can be corrected by changing the injector port liner and breaking off about 0.5 meters of the column every 20-30 samples. The background is greater and the FID less sensitive for the direct analysis of aqueous samples. The lower detectable limit is about 50 ppm for each component. The area response for standard solutions (1.0 mg/ml) is stable 30 minutes after the addition of acetone. If mild heat is used 95% derivatization can be effected in five minutes and 98% in 10 minutes.

DISCUSSION

The gas chromatographic glass capillary procedure utilizing the hydrazone derivatives of UDMH, MMH, and HZ provides a reliable analysis technique for use in situations that require large numbers of samples to be routinely assayed (the extraction procedure) and a procedure for analysis applications that require quick turnaround (the direct assay). The derivatization reaction utilizing acetone is quantitative and fast. Other reagents were tried and usable reactive products that were chromatographable were produced but none provided as good an overall assay procedure as acetone for all components being considered. The formation of Pyrazoles using 2.4 - pentanedione (AA) as outlined by DEE (2) has several disadvantages that can be overcome by using acetone to form the hydrazone products. Excess AA will produce some chromatographic interference with the products requiring that the amount of AA added be held to the minimum, this is inconvenient for large scale analysis of samples where the component concentrates are not known. Since the acetone peak is well resolved from all of the hydrazone products, excess acetone does not present a problem. UDMH cannot be assayed using the AA procedure since a derivative is not formed. Acetone produces a hydrazone derivative with UMDH that is well resolved from the MMH and HZ products allowing a single standard procedure to be used for all three compounds. The acetone reaction does not require pH control and the hydrazone products can be easily and quantitatively extracted from the aqueous reaction mixtures with a variety of solvents. The AA reaction is slower



ANALYSIS CONDITIONS

TEMP 1 = 75°

TIME 1 = 6.00

RATE = 7.50°/MIN

TEMP 2 = 190°

TIME 2 = 5.0 MIN

STOP @ 15 MIN

SPLIT = 35:1

INJ = 1.2

SAMPLE

0.56 mg/ml H_Z

0.83 mg/ml MMH

1.50 mg/ml UMDH

100 mg/ml ACETONE

SOLVENT - WATER

CHROMATOGRAM

R_T = 5.95; UDMH DERIVATIVE

R_T = 8.02; MMH DERIVATIVE

R_T = 9.64; H_Z DERIVATIVE

FIGURE 6 CHROMATOGRAPH OF DIRECT INJECTION OF ACETONE DERIVATIZED REACTION MIXTURE

and the pyrazoles are not as early extracted requiring larger solvent volumes, longer shaking time and more careful pH control to obtain reproducible, quantitative recoveries. The advantages of using the acetone derivatives are restricted to the WCOT/G.C. tecnhique in that the hydrazone products are very difficult to resolve using packed columns. Thus, if WCOT columns are not available, the technique of Dee (2) modified by using organic extraction procedures to increase column life and decrease tailing would still provide the best assay technique for MMH and HZ. The direct G.C. analysis of the derivatized aqueous reaction mixture or reaction mixture distillate can provide very quick sample turnaround time if that is desired. But the salts deposited in the injection port and glass liner surface reactions produced by the direct injections make injection port cleaning every 15-25 samples mandatory. The effort required to perform the sample extractions is less than this instrument maintenance, thus the direct analysis does not produce an overall cost reduction. In addition, the FID response is better when organic solvents are used and since N-P detectors cannot be used with direct water injections the extraction procedure will allow increased sensitivity to be obtained if desired by going to the N-P detector system. The advantage of the direct injection system is that it can provide sample turnaround of less than 20 minutes. The sample can be derivatized in 5 minutes and the chromatogram can be supressed to as little as 3.5 minutes for MMH and UDMH and six minutes for HZ without compromising the analysis. Because of the resolution power of the WCOT columns, reactive products other than UMDH, MMH and HZ could also be monitored if desired. This would increase the G.C. analysis time as many of the by-products are in the lower boiling ranges that require longer columns, lower temperatures and slower temperature programming rates to achieve peak resolution. Some potential does exist for the direct analysis of the reactive mixture extracts using the N-P detector that would allow SDMH to be assayed also.

APPENDIX A. ANALYSIS PROCEDURE FOR UMDH, MMH, AND HZ

1. Sample Preparation

a. Place 2.5 mls of sample (volumetrically) in a 20 ml screw cap vial, and add 1.0 ml of acetone. (If salt level is high, add H_2O until solution is miscible).

b. Let set for 20 minutes (5 minutes with mild heat).

c. Add 5.0 mls of CH_2Cl_2 (or benzene) and ISTDs (1.0 mg of Cn-8 and Cn-9).

d. Add 0.5 mls of 3N NaOH (make pH 9.0).

e. Shake on a wrist arm shaker for 10 minutes with sufficient agitation to make the resolution homogeneous.

f. Allow the layers to separate and remove the organic layer to a prelabeled vial.

g. Add 5.0 mls of CH_2CL_2 (or benzene) and repeat steps e. and f.

h. Analyze on G.C. set up with 60 meter OV-101 WCOT column. Base quantitation on Cn-8 STD. (Use Cn-9 STD as an internal check).

2. G.C. Procedure

a. The instrument analysis conditions are:

	Max	Setting	Reading
TEMP 1	250	75	75
TIME 1	6.00		
RATE	7.50		

TEMP 2	250	240	
TIME	20.00		
INJ TEMP	350	200	200
FID TEMP	400	300	300
AUX TEMP	350	250	250
CHT SPT	0.50		
ZERO	10.0		
ATTN 2	6		
FID SGNL	+B		
SLP SENS	40.00		
AREA REJ		100	
FLOW A	30.00	30.0	(madeup gas)
FLOW B	78.3	74.3	(70 to 1 split)

Time Function	Value
6.00 SLP SENS	0.25
8.50 RATE	30.00
8.75 SLP SENS	0.10
9.50 SLP SENS	0.25
12.50 STOP	
13.60 IFN	10
13.65 SLP SENS	1.00
15.00 STOP	

2. For quantitation the area response factors are calculated using the appropriate standards.

The absolute values for the area response are dependent on the split, but the relative response factors used to calculate sample values when ISDs are used are not.

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Paper No. 9

ANALYSIS OF SIDE PRODUCTS OF CHLORAMINATIONS OF MONO- AND DI-METHYLAMINES

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INTRODUCTION

Side product determination is an integral part of development of a process for the production of unsym-dimethylhydrazine (UDMH) and monomethylhydrazine (MMH) by the reaction of chloramine (CA) with dimethylamine (DMA) and monomethylamine (MMA), respectively. In a pilot or full-scale production plant, side products must be eliminated from waste streams to prevent environmental hazards and from product streams so that fuels produced by this process meet military specifications. If reactants such as amines and ammonia are recycled in this process, contaminants in recycle streams must be eliminated to prevent buildup of potentially hazardous materials in the system after continuous recycle. In addition, many side products react with CA. Finally, some side products could have economic value and therefore, should be isolated. To facilitate elimination of undesirable side products as well as isolation of potentially valuable side products, it is essential to identify as many side products as possible in process solutions.

SIDE PRODUCT FORMATION

In the process being developed at Martin Marietta Corp., anhydrous CA, produced by the reaction of ammonia and chlorine, is added to a contactor through which flows DMA or MMA in aqueous sodium hydroxide.

For UDMH production:

$$(CH_3)_2NH + NH_2Cl \longrightarrow (CH_3)_2NNH_2.HCl$$

DMA CA UDMH . HCl

$$(CH_3)_2NNH_2.HCl + OH^- \longrightarrow (CH_3)_2NNH_2 + Cl^- + H_2O$$

UDMH.HCl UDMH

For MMH production:

$$CH_3NH_2 + NH_2Cl \longrightarrow CH_3NHNH_2.HCl$$

MMA CA MMH.HCl

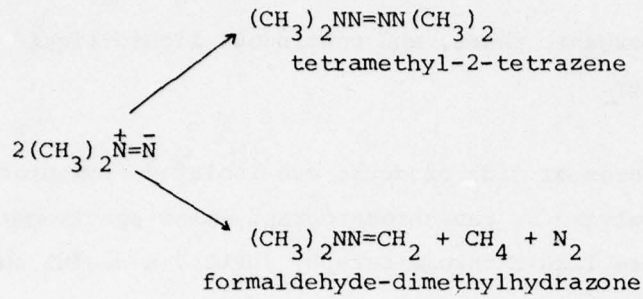
$$CH_3NHNH_2.HCl + OH^- \longrightarrow CH_3NHNH_2 + Cl^- + H_2O$$

MMH.HCl MMH

Side products are formed in these processes primarily because CA can react with MMH and UDMH either by addition of an $-NH_2$ group or oxidation by abstraction of hydrogen atoms.

Both types of reactions are known to occur when UDMH is treated with CA. CA adds to UDMH to form 2,2-dimethyltriazanium chloride (TCl), a diamino analog to quaternary ammonium salts (Reference 1). In the MMA process TCl is not an expected product because it is unstable in aqueous base (Reference 2). CA can also react with UDMH to form oxidation products which we believed to proceed through the intermediate 1,1-dimethyldiazene ($(CH_3)_2\overset{+}{N}=\overline{N}$) (Reference 3).

$$(CH_3)_2N\text{-}NH_2 + NH_2Cl \longrightarrow (CH_3)_2\overset{+}{N}=\overline{N}$$



In addition to these products, it is possible that 1,1-dimethyl-diazene undergoes intramolecular rearrangment to form formaldehyde-monomethylhydrazone ($CH_3NHN=CH_2$).

Studies on the chloramination of MMH have not been undertaken. Attempts to form a triazanium salt of MMH were unsuccessful; it is not expected that this product would be stable if formed, because it would not contain a quaternary nitrogen. Possible products of hydrogen abstraction of MMH by CA include a monomethyl analog ($CH_3\overset{+}{N}H=\overset{-}{N}$) of 1,1-dimethyladiazene, methyl diazene, ($CH_3N=NH$) a reported oxidation product of MMH, and formaldehyde hydrazone ($CH_2=NNH_2$) formed by a mechanism similar to that of the formation of formaldehyde-dimethylhydrazone by the chloramination of trimethylhydrazine (Reference 4). In addition, some of the side products which could be formed by chloramination of MMH are likely to be unstable and are likely to undergo further reaction by loss of N_2, dimerization (Reference 5), rearrangement or hydrolysis (Reference 6).

SIDE PRODUCT IDENTIFICATION

In order to identify side products, it is essential to separate them from the volatile, caustic process solutions in which side products are present in low concentrations. Methods of separation include distillation of process solutions using an eight-foot packed vacuum jacketed column, addition of sodium hydroxide to process solutions to concentrate side

products in an organic phase, and continuous liquid-liquid extraction with diethylether.

After mixtures of side products are isolated from process solutions they will be analyzed by gas-chromatography-mass spectrometry (GC/MS) and high pressure liquid chromatography (HPLC), a useful complement of GC/MS for the following reasons:

1. HPLC provides a means of separating components not readily separable by GC/MS.

2. High-boiling or thermally unstable compounds not analyzable by GC/MS could be analyzed by HPLC which does not require high temperatures to effect separation.

3. HPLC can be used to isolate pure samples of compounds of chemical or toxicological interest. Pure compounds thus obtained could be further analyzed by infrared or nuclear magnetic resonance spectroscopy.

If investigation of mechanisms of formation and side products is desired, UDMH or MMH or other compounds of interest could be chloraminated on a laboratory scale CA generator and suspected intermediates in side product formation could be treated with simulated process solutions.

To date GC/MS analysis of MMH and UDMH process solutions have been undertaken using a Hewlett-Packard 5992A gas chromatograph -mass spectrometer equipped with a six-foot column packed with Carbowax 20M or Carbopak B. Components of UDMH and MMH process solutions are listed in Tables I and II, respectively.

TABLE I

SIGNIFICANT GC/MS PEAKS IN UDMH PROCESS SOLUTIONS

	Retention Times (Min.)	Major Mass Fragments	Compound
1.	1.3	45, 44, 42, 28	$(CH_3)_2NH$
2.	4.2	60, 59, 45, 53, 42	$(CH_3)_2NNH_2$
3.	5.4	58, 57, 43, 32, 30, 28	$CH_3-N=N-CH_3$ or $CH_3NHN=CH_2$
4.	8.2	72, 71, 57, 42, 30	$(CH_3)_2NH=CH_2$
5.	12.8	96, 93, 71, 44, 42	$C_4H_{10}N_2$
6.	13.1	73, 44, 42, 28	$C_2H_7N_3$

TABLE II

SIGNIFICANT GC/MS PEAKS IN MMH PROCESS SOLUTIONS

	Retention Times (Min.)	Major Mass Fragments	Compound
1.	0.6	31, 30, 28	CH_3NH_2
2.	2.1	44, 43, 42, 29, 28	$CH_3-N=N-H$ or $CH_2=N-NH_2$
3.	2.7	46, 45, 31, 29, 28	$(CH_3)HNNH_2$
4.	4.3	60, 59, 45, 43, 42, 32	$(CH_3)_2NNH_2$
5.	5.4	58, 57, 43, 30, 28	$CH_3-N=N-CH_3$ or $(CH_3)HNN=CH_2$
6.	8.3	72, 71, 57, 42, 32, 20	$(CH_3)_2N-N=CH_2$

Carbowax 20M has been found to be unsuitable for further GC/MS investigation because of bleed of column constituents onto the detector, instability of Carbowax to injection of water and indefinite retention of some compounds (such as tetramethyl-2-tetrazene) on carbowax. It is anticipated that use of "Tenax," a porous polymer, during later GC/MS investigations will provide better results and permit better identification of suspected side products.

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Paper No 10

DETECTION OF N-NITROSODIMETHYLAMINE BY GAS CHROMATOGRAPHY-METHANE CHEMICAL IONIZATION MASS SPECTROMETRY WITH SINGLE ION MONITORING *

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INTRODUCTION

Since the discovery that N-nitrosodimethylamine (NDMA) and other N-nitroso compounds are carcinogenic,[1-4] there has been a great deal of concern over their effects on cancer epidemiology.[5] Nitrosamines occur in cured foods such as fried bacon[6, 7] and fish meal[8] and are thought to be formed by the reaction of nitrite preservatives with naturally occurring amines. Atmospheric NDMA can be produced by the gas-phase nitrosation of dimethylamine by nitrous acid.[9]

Several recent developments in NDMA analysis have centered around gas chromatographic techniques, using the Coulson[10] and alkali flame ionization[11] detectors that show enhanced response to nitrogen-containing compounds. Gas chromatography-mass spectrometry (GC-MS) with single ion monitoring has extended the detection limit for NDMA to the subnanogram region.[12]

Another development has been the thermal energy analyzer pioneered by Fine and co-workers.[13-17] This device is specific for N-nitroso

* This paper to be published in Analytical Letters 11(1), 1978

compounds.[15] Coupled to a gas chromatograph, it can detect approximately 50 pg of sample injected.

In this study, we report the detection of NDMA at ca. 25-50 pg (injected) using GC-MS with methane chemical ionization and single ion (m/e 75) monitoring.

EXPERIMENTAL

Samples were analyzed on a Finnigan 3200 GC-MS with the 6000 Data System. Gas chromatography was performed at 95°C on a silanized 1.5m x 2mm i.d. glass "U" column packed with 10% Carbowax 20M-TPA on 80-100 Chromosorb W/AW (Supelco, Inc.). The injector was heated to 150°C, and the GC-MS interface was kept at 125°C. Methane carrier gas (20 ml/min) also served as the chemical ionization reagent gas; the total column effluent was routed to the MS source where a pressure of 1.0 torr was maintained.

The MS monitored the 75.0 ion, the protonated NDMA parent ion, MH^+. Other parameters were - electron multiplier (continuous dynode): -2100 V; electron energy: 100eV; preamplifier 10^{-9} a/V; 1 second per scan.

Standard solutions of NDMA in deionized water were prepared by dilution from a 1% aqueous stock solution.

RESULTS AND DISCUSSION

The results of the NDMA sensitivity tests are shown in Figure 1. At these very low levels, ghost (memory) effects are severe, and care must be taken to clean up the column/injector prior to each analysis.

Ghost peaks are most prominent when going from high to low levels of NDMA. Column clean-up was accomplished by injecting 1.0 µl shots of water until no more NDMA was eluted. The MS filament is turned on approximately 38 seconds after injection to avoid the hot filament seeing large quantities of water. This water accounts for the tailing baseline prior to the NDMA peak.

At very low levels of NDMA, the instrument response is not linear, probably because of irreversible adsorption and/or decomposition during GC analysis. Figure 1a shows the response to 100 pg of NDMA. Halving the amount of NDMA injected (Figures 1b and 1c) gives peaks of variable height, while at 25 pg injected (Figures 1d and 1e) the NDMA is just barely detectable. A water blank (Figures 1f and 1g) shows no traces of NDMA.

Another series of runs was done with the NDMA dissolved in hexane to see whether the interaction of water with the GC packing has an adverse effect on sensitivity. It was found that NDMA/hexane showed a detection limit of 25-50 pg, the same as for NDMA/water.

Lower detection limits for NDMA in various samples are, of course, possible using clean-up and concentration procedures.[18] The advantages of GC-MS over less sensitive methods is that many liquid samples containing NDMA at the ppb level can be analyzed directly, obviating the attendant errors resulting from incomplete extraction, irreversible adsorption, and nitrosamine decomposition. The combination of a specific GC retention time and a specific MS protonated parent ion serves to separate NDMA from potential interferences with the same retention time and a different MS ion, and <u>vice versa</u>.

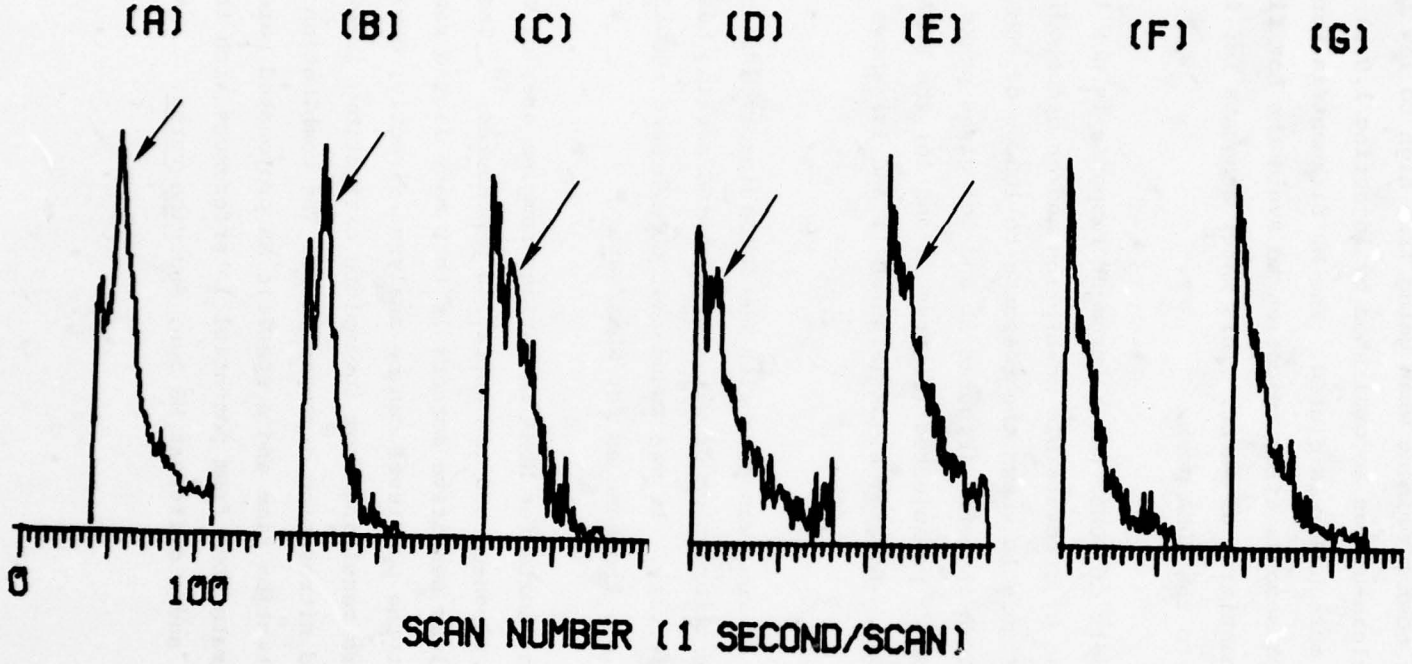


Figure 1. N-Nitrosodimethylamine Detection by GC-MS with Single Ion Monitoring at m/e 75. (a) 100 pg (b), (c) 50 pg, (d), (e) 25 pg, (f), (g) water blank. NDMA peaks indicated by arrows.

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Paper No. 11

ENVIRONMENTAL DEGRADATION OF 1, 1-DIMETHYL-HYDRAZINE

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The studies reported here were conducted under a contract with the Air Force Office of Scientific Research in which we are investigating the fate of 1,1-dimethyl-hydrazine (missile propellant) and N-phenyl-1-napthylamine (lubricant additive) in the aquatic environment.

INTRODUCTION

The objectives of the study for the first year are twofold: (1) to study the degradation of 1,1-dimethyl-hydrazine (UDMH) by naturally occurring microbial communities in lake and river water and to determine the kinetics of the process, and (2) to identify the products resulting from microbial degradation. Early in the project we observed that aqueous solutions of UDMH decomposed on standing, and consequently we decided to study this chemical reaction in some detail as a prelude to the microbial experiments. This progress report describes work completed up to August 15, and includes (i) data on the kinetics of oxidation of UDMH by dissolved oxygen in distilled and lake water, and (ii) preliminary data on the products of chemical and microbiological degradation.

OXIDATION OF UDMH IN DISTILLED WATER

Spectroscopic Studies

In preliminary experiments it was observed that oxygenation of basified UDMH solutions containing trace amounts of copper sulfate results in violet or yellow solutions which absorb in the U.V. at approximately 326 nm. The absorption reversibly moves to longer wavelengths (356 nm.) on acidification, and the pK_a for the ionization lies between 8 and 9. Figure 1 illustrates the spectra obtained in a typical experiment upon oxidation of a UDMH/$CuSO_4$

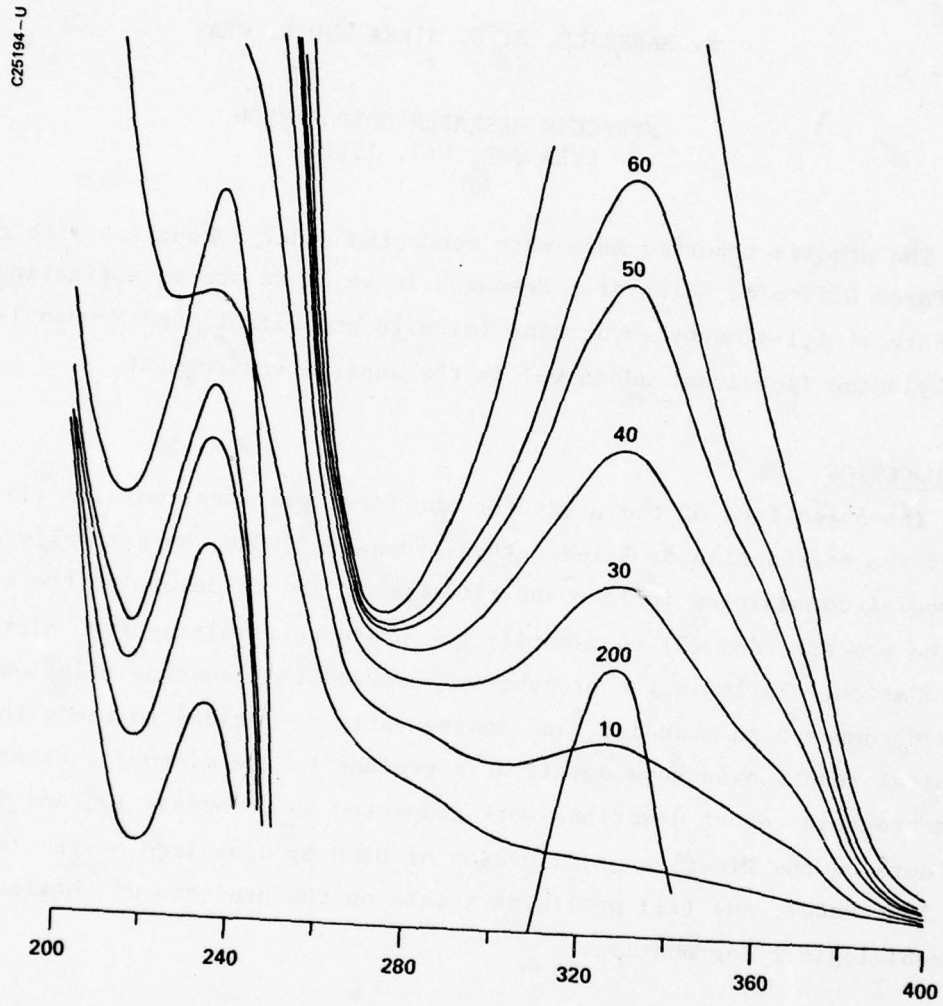


Figure 1. Oxygenation of a 3.44×10^{-4}M solution of UDMH in a borate buffer of pH 9.12 containing 1.55×10^{-4}M $CuSO_4$. The numbers indicate oxygenation time in minutes.

solution in a borate buffer of pH 9.12. The progressive increase of the two peaks with time indicates the formation of a conjugated product (or products). At higher UDMH concentrations (3.34×10^{-3}M), the presence of tetrazene is observed as verified by U.V. spectrophotometry and gas chromatography.

Attempts to extract the compound corresponding to the long wavelength U.V. absorption into ether failed, not surprisingly, since the compound appears to be polar and capable of salt formation. Hence, the oxidation was studied by p.m.r. in order to monitor the formation of products in situ. UDMH.HCl ($\approx$ 30 mg.) in 0.5 mls. of D_2O containing a crystal of $CuSO_4$ was oxygenated over a period of 5 hours. The spectrum recorded after 5 hours is illustrated in Figure 2. The solution was then basified, and the resulting spectrum is recorded in Figure 3. It is difficult at this point to interpret these spectra without suitable reference compounds. The large number of high field resonances, however, indicates the formation of several products. The low field singlet in Fig. 2 corresponds to formic acid, as suggested by the peak enhancement observed upon addition of authentic material. Significantly, N,N-dimethyl-nitrosamine is not present to an observable extent unless isotope exchange with solvent occurs rapidly.

Since it appeared unlikely that the product corresponding to the long U.V. absorption could be extracted and isolated from the reaction mixtures, we explored the possibility of preparing it with other oxidizing agents. It has previously been reported (McBride and Kruse, 1957) that alkali halates and halogens oxidize UDMH to 1,1-dimethyl-diazene which is oxidized to undetermined products. We considered it likely that one of the oxidation products of the diazene would correspond to our unknown U.V. absorbing material, and we investigated the bromination of UDMH as a possible synthetic route.

The bromination of UDMH was studied initially by a titration method in which aliquots of a standard bromine solution were added to a UDMH solution, and U.V. spectra of the resulting solutions were recorded. In a typical experiment, aliquots of a 4.45×10^{-2}M bromine water solution were added to 25 mls. of a 3.54×10^{-3}M UDMH.HCl solution, spectra being traced after each addition with appropriate dilutions when necessary (Fig. 4). A plot of A_{356} vs. $[Br_2]/[UDMH]$ is illustrated in Fig. 5. It is evident that the increase in absorbance at 356 nm. occurs primarily after the addition of

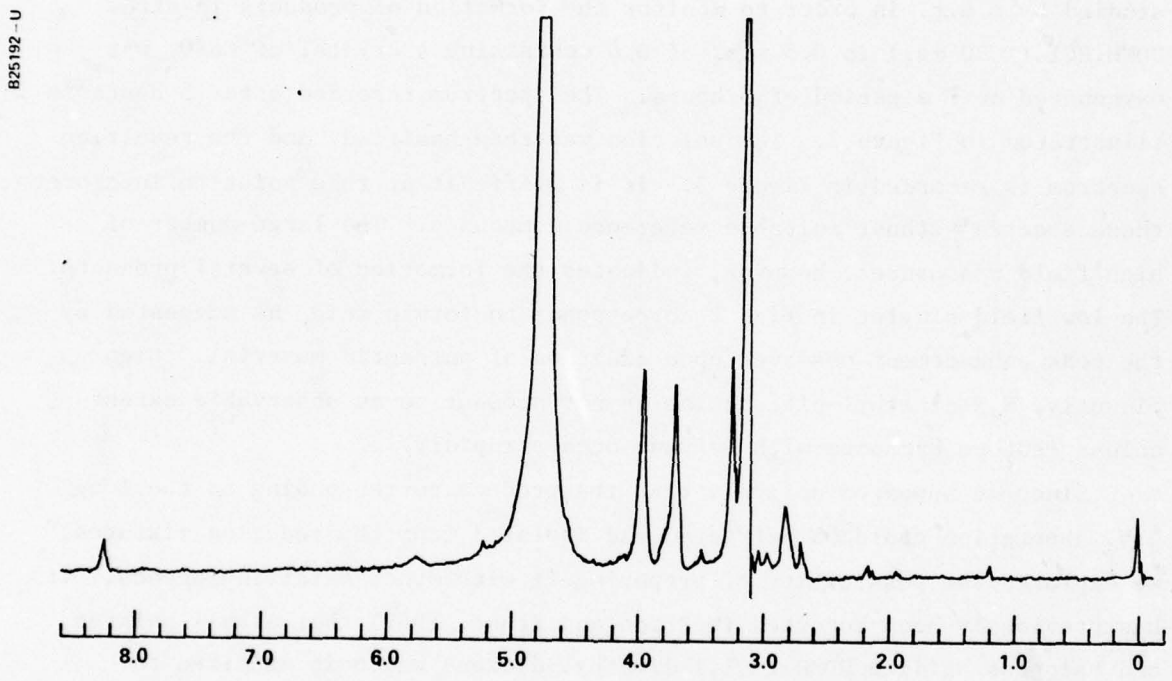


Figure 2. Spectrum obtained on oxygenation of a UDMH/$CuSO_4$ solution in D_2O for 5 hours.

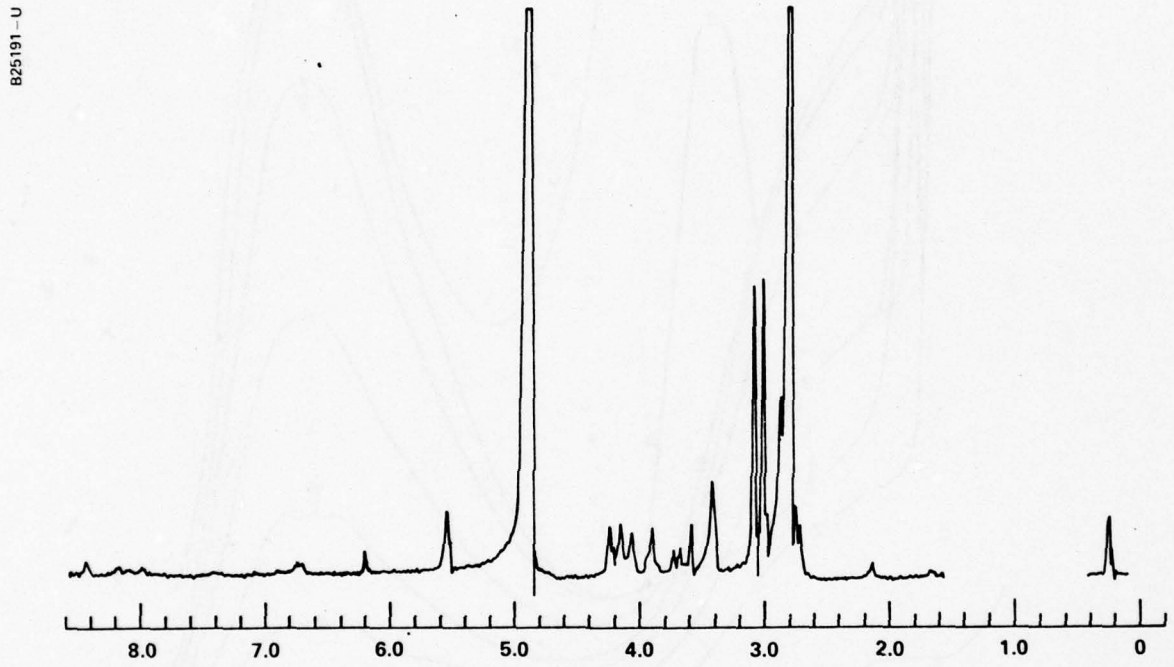


Figure 3. Spectrum obtained on oxygenation of a UDMH/$CuSO_4$ solution in D_2O for five hours followed by basification with solid NaOH.

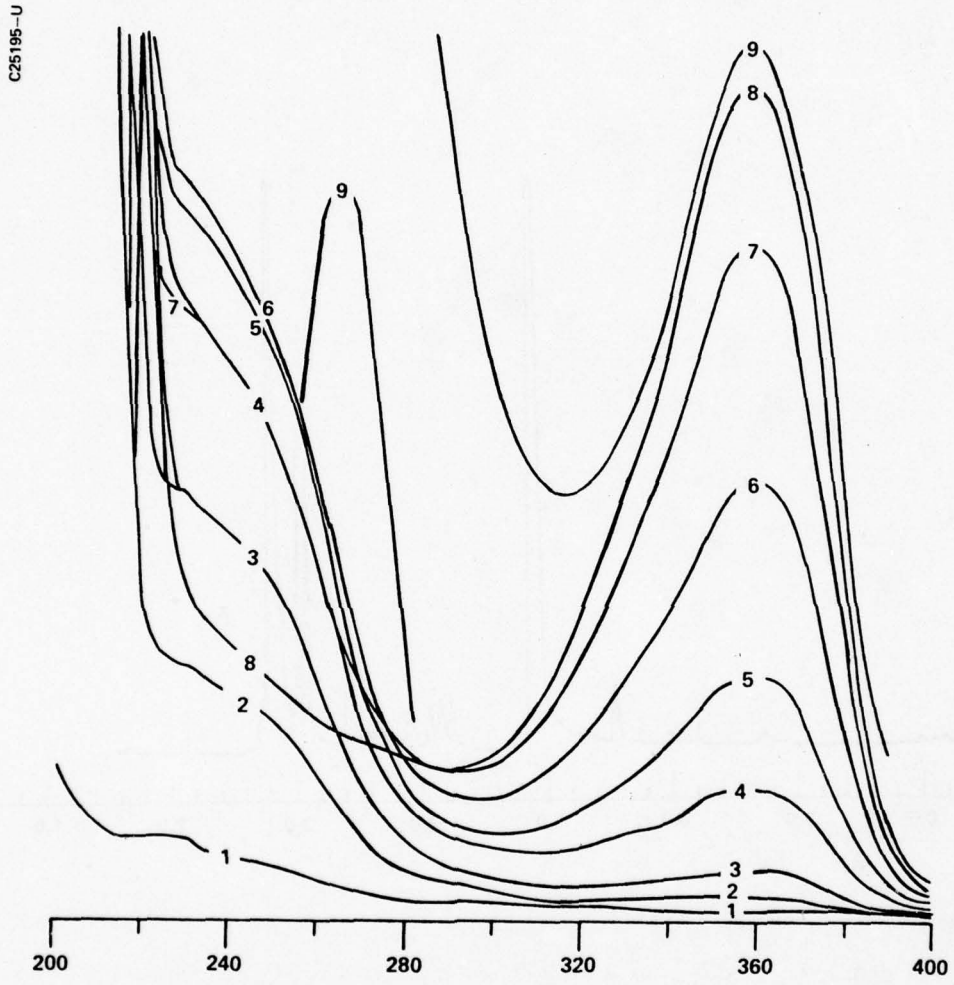


Figure 4. Spectra obtained on bromination of UDMH. Spectra 1-9 represent the following $[Br_2]$:[UDMH] ratios: (1) 0.41, (2) 0.80, (3) 1.23, (4) 1.62, (5) 2.04, (6) 2.45, (7) 2.86, (8) 3.27, (9) 3.67.

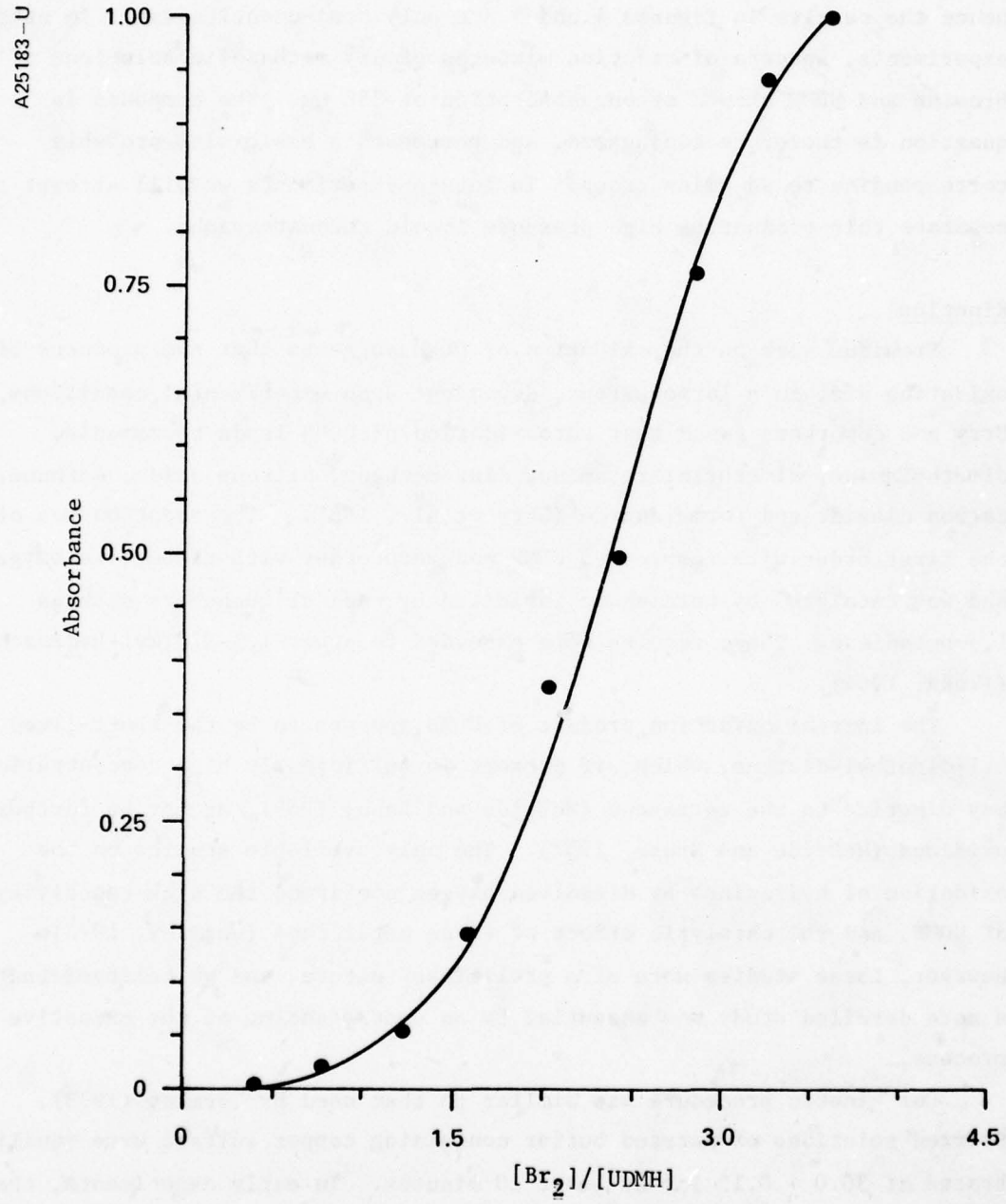


Figure 5. Variation of the absorbance at 356 nm. on bromination of [UDMH]. The values are derived from Fig. 4.

one mole equivalent of bromine. It must be noted, however, that the reaction solution evolved gas after addition of one mole equivalent of bromine, and hence the results in Figures 4 and 5 are only semi-quantitative. In other experiments, spectra of reaction mixtures of dry methanolic solutions of bromine and UDMH showed strong absorption at 356 nm. The compound in question is therefore conjugated, and possesses a basic site probably corresponding to an amine group. In future experiments we will attempt to separate this product by high pressure liquid chromatography.

Kinetics

Previous work on the oxidation of UDMH suggests that the products of oxidation are, to a large extent, dependent upon experimental conditions. Urry and coworkers found that autooxidation of UDMH leads to ammonia, dimethylamine, dimethylnitrosamine, diazomethane, nitrous oxide, methane, carbon dioxide and formaldehyde (Urry et al., 1965). The reaction was of the first order with respect to UDMH and zero order with respect to oxygen, and was catalyzed by metals and inhibited by radical quenchers such as 1,3-butadiene. These results were extended to other 1,1-dialkyl-hydrazines (Ikoku, 1964).

The initial oxidation product of UDMH appears to be the short-lived 1,1-dimethyl-diazene, which, if present in sufficiently high concentration, may dimerize to the tetrazene (McBride and Bens, 1959), or may be further oxidized (McBride and Kruse, 1957). The only available studies on the oxidation of hydrazines by dissolved oxygen confirmed the high reactivity of UDMH, and the catalytic effect of trace metal ions (Gormley, 1973). However, these studies were of a preliminary nature, and we believed that a more detailed study was essential to an understanding of the oxidative process.

Our kinetic procedure was similar to that used by Gormley (1973). Stirred solutions of aerated buffer containing copper sulfate were equilibrated at 30.0 $\pm$ 0.1° for at least 10 minutes. In early experiments, the reaction was initiated by introducing microliter quantities of a concentrated UDMH stock solution, such that [UDMH] >> [O_2]. The consumption of

oxygen was measured by a Dissolved Oxygen Monitor, and the observed pseudo zero-order rate constants were obtained from slopes of $[O_2]$-time traces which were linear except for some slight curvature towards the end of the reaction. Controls were run to ensure that loss of oxygen did not occur in the absence of UDMH. The kinetics under these conditions are irreproducible, possibly due to the formation of peroxides in the stock solution. This problem was overcome by weighing out solid UDMH.HCl into the tip of a disposable pipette, rinsing out the pipette several times with the reaction solution and then monitoring the decrease of oxygen concentration. First-order rate constants derived from a variety of copper concentrations and pH levels are listed in Table 1, and the variation of the rates with copper concentration is illustrated in Fig. 6.

The data in Table 1 indicate that the free base form of UDMH undergoes reaction, and that copper catalysis is not significant at concentrations less than 1×10^{-6}M. A disturbing feature of the data is the negative intercepts observed throughout. However, this could be a consequence of impurities in the substrate (UDMH.HCl is extremely hygroscopic) which would lead to apparently higher substrate concentrations. In any case, these errors will appear in the intercepts and leave the rate constants quoted in Table 1 essentially unaffected.

The curve in Fig. 6 suggests that the oxidation of UDMH contains a copper catalyzed as well as an uncatalyzed component. Hence, the observed rate may be expressed as $k_{obs} = k_1 + k_2\,[Cu^{++}]$, and the curve in Fig. 6 is constructed from $k_{obs} = 1.91 \times 10^{-3}$ min.$^{-1}$ + 596M^{-1} min.$^{-1}$ $[Cu^{++}]$ (linear regression analysis). A more satisfactory curve is obtained if the designated point in Fig. 6 is eliminated, and the dashed line is constructed from the equation $k_{obs} = 1.29 \times 10^{-3}$min^{-1} + 604M^{-1} min^{-1} $[Cu^{++}]$. In a future experiment, we will re-investigate the point in question.

The effect of Cu^{++} on the rate of oxidation suggests that the reaction proceeds via a radical mechanism of the following type.

$$Me_2N - \overset{+}{N}H_3 \underset{H^+}{\rightleftharpoons} Me_2N - NH_2 \xrightarrow{Cu^{++}} Me_2N - \overset{+\cdot}{N}H_2 \xrightarrow{O_2}$$

$$Me_2N - \overset{+\cdot}{N}OOH \xrightarrow{Cu^{+}} Me_2N - NHOOH \longrightarrow Me_2\overset{+}{N} = NH$$

Table 1

Summary of the Kinetics of Oxidation of UDMH.HCl

	pH	$[Cu^{++}] \times 10^6$ M	k (min^{-1}) x 10^4 [a]	Intercept (min^{-1}) x 10^7 [a]	CC[b]
1	9.13	0.0206	25.8	-88.6	0.996
2	"	0.0618	35.4	-146	0.997
3	"	0.206	25.2	-49.4	0.983
4	"	2.06	55.4	-130	0.941
5	"	7.73	208	-584	0.990
6	"	15.5	178	-984	0.997
7	"	20.6	294	-416	0.992
8	"	25.8	342	-388	-
9	8.40	0.0206	14.4	-32.4	0.989
10	8.88	2.18	21.0	-108	0.996
11	10.7	2.18	34.0	-17.0	0.987
12	6.90[c]		7.84	-11.1	0.9999
13	7.00[d]		12.6	-85	0.969

[a] Obtained from plots of k_{obs} vs. [UDMH.HCl]

[b] Linear regression correlation coefficient.

[c] Using water from Jamesville Reservoir.

[d] Using water from Oneida Lake.

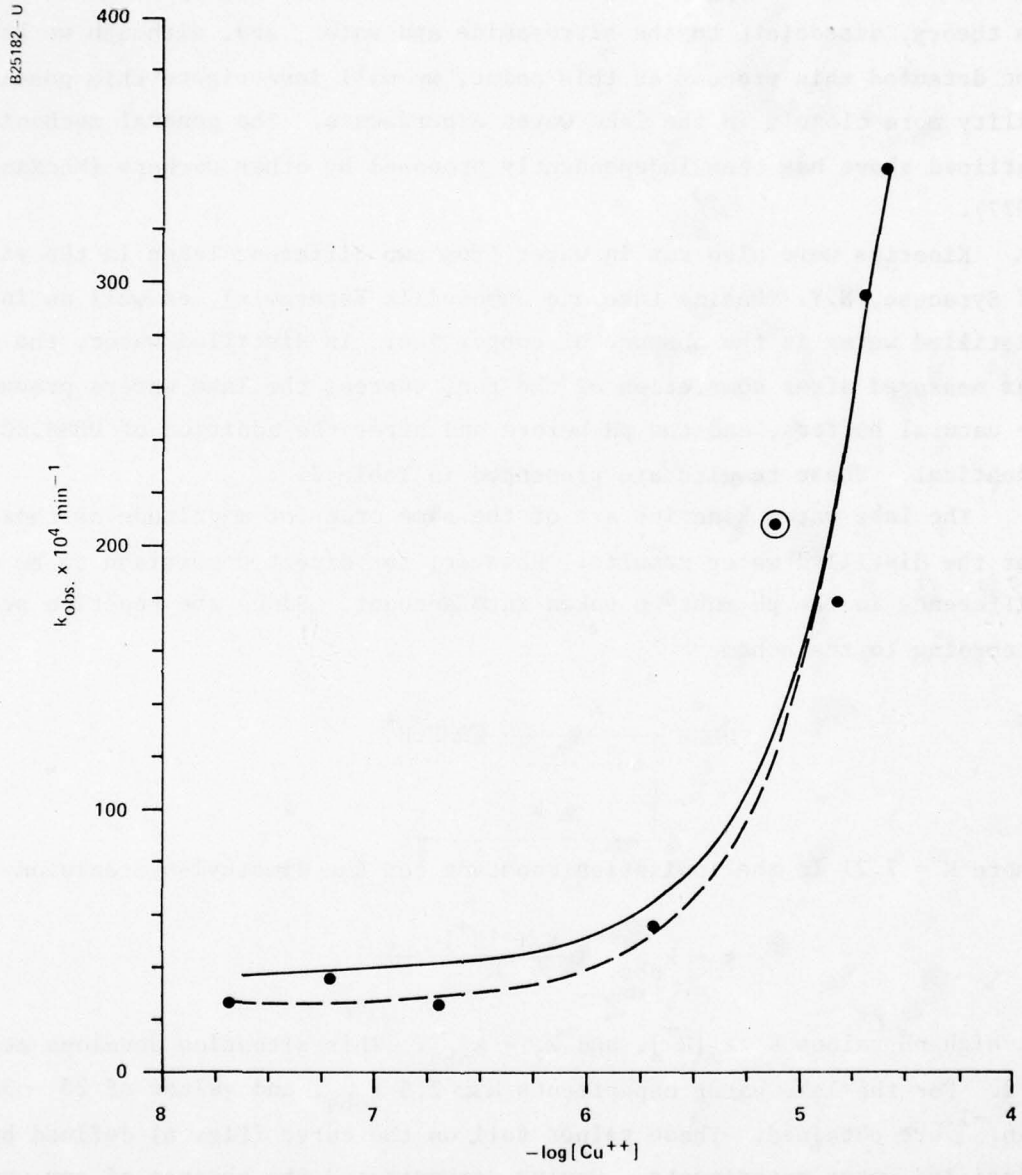


Figure 6. Variation of the rate of oxidation of [UDMH] with $[Cu^{++}]$

The uncatalyzed component could represent a wall reaction, or possibly a direct reaction of oxygen on UDMH. We note that the hydroperoxide could, in theory, dissociate to the nitrosamine and water, and, although we have not detected this process at this point, we will investigate this possibility more closely in the lake water experiments. The general mechanism outlined above has been independently proposed by other workers (MacNaughton, 1977).

Kinetics were also run in water from two different lakes in the vicinity of Syracuse, N.Y. (Oneida Lake and Jamesville Reservoir), as well as in distilled water in the absence of copper ion. In distilled water, the pH was measured after completion of the run, whereas the lake waters proved to be natural buffers, and the pH before and after the addition of UDMH.HCl was identical. These results are presented in Table 2.

The lake water kinetics are of the same order of magnitude as those for the distilled water results. However, for direct comparison to be made, difference in the pH must be taken into account. Since the reaction proceeds according to the scheme

$$\text{UDMH} \underset{\longleftarrow}{\xrightarrow{K}} \text{UDMH.H}^{+}$$

$$\text{UDMH} \xrightarrow{k}$$

where K = 7.21 is the ionization constant for the dimethyl-hydrazinium ion.

$$k = k_{obs.} \left(\frac{K + [H^{+}]}{K}\right)$$

At high pH values $K >> [H^{+}]$, and $k_1 = k_{obs}$. This situation develops at pH >> 7.2. For the lake water experiments $k \approx 2.5\ k_{obs}$, and values of $20 - 35 \times 10^{-4}$ $min.^{-1}$ are obtained. These values fall on the curve (Fig. 6) defined by the distilled water experiments. Having demonstrated the absence of any unusual catalysts or inhibitors in the lake waters used, half-life values for the disappearance of UDMH at environmentally realistic pH values may be generated with the use of the above equation and by utilizing a value of $k = 30 \times 10^{-4}$ min^{-1}. These are presented in Table 3, and are considered to be of predictive value.

Table 2

Kinetics of Oxidation of UDMH.HCl in Lake Waters

Source	pH	[UDMH.HCl] x 10^3M	k($M.min^{-1}$) x 10^6
Jamesville Reservoir	6.9	12.2	8.48
	6.9	24.2	17.8
	6.9	33.4	25.1
Oneida Lake	7.0	8.81	2.99
	7.0	10.2	6.22
	7.0	11.6	4.64
	7.0	13.4	5.05
	7.0	18.0	16.2
	7.0	20.2	19.7
	7.0	24.5	19.3
	7.0	28.7	28.3
Distilled Water	4.4*	11.1	0.54
	4.2*	12.6	2.53
	3.6*	15.1	2.89
	3.4*	21.1	4.38

* Measured after completion of the run.

Table 3

Half-lives for the Disappearance of UDMH as a Function of pH at 30°

pH	$t_{\frac{1}{2}}$ (hours)
5	630
6	66
7	10
8	4.5
9	3.9

DEGRADATION OF UDMH IN LAKE WATER

A preliminary experiment was carried out using water from the Jamesville Reservoir near Syracuse, N.Y. The water was filtered through coarse filter paper to remove solid particles, and divided into two portions, of which one was passed through a 0.45μ Millipore membrane filter for sterilization. The microbial population of the non-sterile water was 2.12×10^5 cells/ml. Ten ppm solutions of UDMH.HCl were prepared separately in the two solutions and u.v. spectra were obtained in 5 cm cells over a period of eight days. In the water samples filtered through the membrane filter, absorption at 326 nm. gradually developed, and was found to move to 356 nm. on acidification. It is, therefore, very likely that this product is identical to that observed on oxidation of UDMH in distilled water (wide supra). The non-sterile lake water showed only weak absorption at 230 nm. and 326 nm. After eight days, a 25 ml sample of the non-sterile lake water was added to a 500 ml aliquot of the sterile water, and spectra of the mixture were obtained and are illustrated in Fig. 7. After four days, the intensities of both peaks were greatly diminished, and the microbial count was up to 2.12×10^5 cells/ml.

It appears, therefore, that UDMH.HCl is oxidized in lake water in the absence of microbes to form a product with absorption at 326 nm. It is further evident that this latter product is degraded by microorganisms, and the failure to observe this product in non-sterile water is probably a consequence of microbial action. Our present work focuses on product identification using ^{14}C-radiolabelled UDMH.

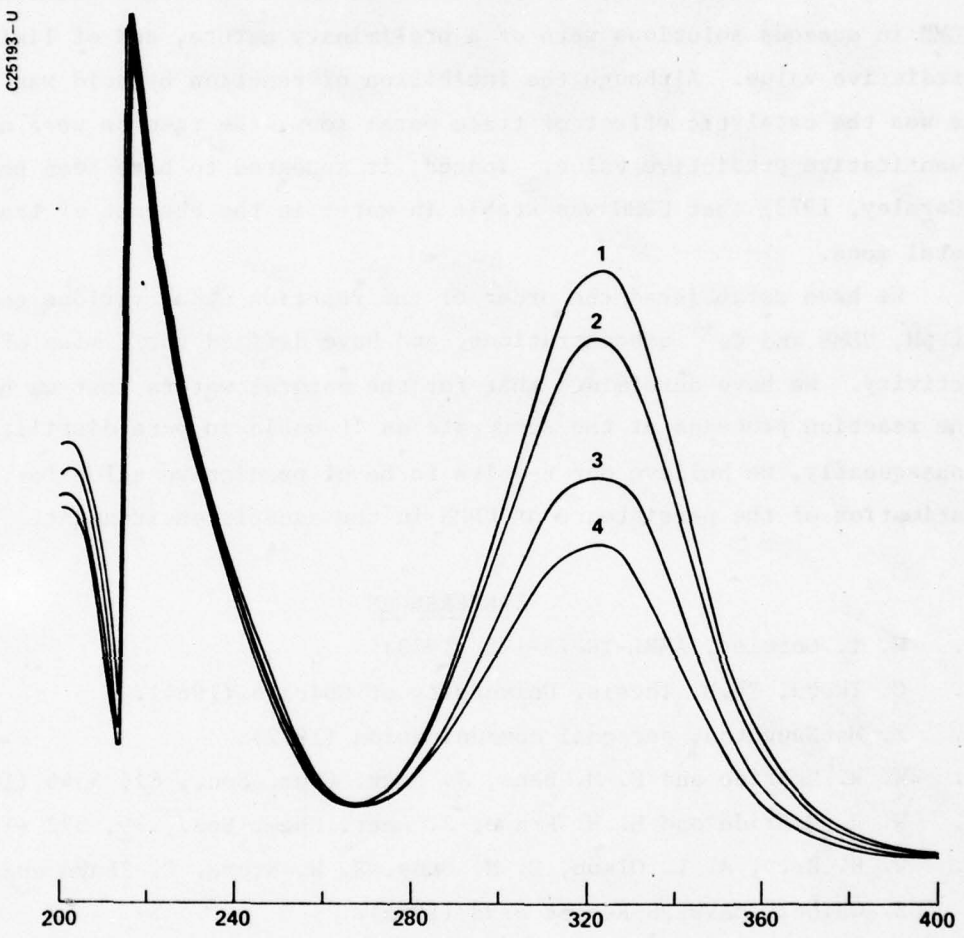


Figure 7. Spectra obtained on mixing the sterile water with the non-sterile water. The numbers represent time in hours.

CONCLUSIONS

Prior to the initiation of this study, existing data on stability of UDMH in aqueous solutions were of a preliminary nature, and of limited predictive value. Although the inhibition of reaction by acid was noted, as was the catalytic effect of trace metal ions, the results were not of quantitative predictive value. Indeed, it appeared to have been believed (Gormley, 1973) that UDMH was stable in water in the absence of trace metal ions.

We have established the order of the reaction under various conditions of pH, UDMH and Cu^{++} concentrations, and have defined the limits of catalytic activity. We have determined that for the natural waters that we have used, the reaction proceeds at the same rate as it would in pure distilled water. Consequently, we believe our results to be of predictive value for the estimation of the persistence of UDMH in the aquatic environment.

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Paper No. 12

GAS PHASE KINETIC STUDY AIR OXIDATION OF UDMH

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INTRODUCTION

Unsymmetrical dimethylhydrazine (UDMH) is a rocket fuel that is currently being used by the Air Force in its Titan missile system. It is also being proposed for use by NASA in its Space Shuttle Program.

Recent observations suggest that UDMH, upon exposure to air, may be converted to trace amounts of the potentially carcinogenic compound N-nitrosodimethylamine (NDMA). It has also been found some of the UDMH being stored and occasionally transported to various locations by the Air Force may contain small amounts of NDMA. During routine handling, a possibility exists that small amounts of UDMH could be inadvertently released into the atmosphere due to spillage, purging of transfer lines, etc.

For these reasons, and the possible resulting threat of NDMA to human populations in exposure areas, the Air Force's Space and Missile Systems Organization (SAMSO) Propellant Office has requested that a kinetic model be developed that could be used to estimate possible UDMH and NDMA concentration ranges as a function of distance and time from the point of accidental UDMH introduction into the environment.

This report summarizes the results obtained during an initial part of a program to obtain the information required for the development of such a kinetic model. Reported here are the important products formed and the rates of UDMH disappearance (as a function of initial UDMH concentration) in the nonphotolytic reaction of UDMH with dry air.

In the Background section that follows, the history of the UDMH/NDMA environmental problem is reviewed, and the experimental information needed to develop a kinetic model to predict UDMH and NDMA levels following a spill is outlined. Also outlined is the information available in the literature on the oxidation reactions of hydrazine and its methyl derivatives. In the Results section, the products formed and the rates of UDMH disappearance in the reaction of UDMH with dry air are described. These results are examined in the Discussion section in terms of a free radical mechanism proposed in an earlier study.

BACKGROUND

UDMH NDMA Environmental Problem. Over the past year and a half, an increasing number of public health scientists have become concerned about a possible correlation between the higher incidence of cancer and the higher levels of nitrosamines in industrial-urban areas. Nitrosamines are a well-established class of animal carcinogens. One way nitrosamines can be formed in the environment is through reactions of dialkylamines and nitrous acid, the nitrous acid being formed by atmospheric reactions of water and either NO or NO_2.

The presence of nitrosamines in the environment came to public attention when the Public Interest Research Group (a Ralph Nader organization) asked the Thermo Electron Corporation to make atmospheric nitrosamine measurements with one of Thermo Electron Corporation's newly developed nitrosamine detectors at several locations in the Eastern part of the United States.[1] Among the locations where measurements were first made was near an FMC Corporation plant in Baltimore, Maryland.

This plant was producing the rocket propellant unsymmetrical dimethylhydrazine (UDMH) for the Air Force by a process in which N-nitrosodimethylamine (NDMA) was used as a reaction intermediate. Thermo Electron Corporation found quantities of NDMA initially at the level of 0.3 micrograms per cubic meter of air near the plant[1], and then later (together with the Environmental Protection Agency) found levels up to 36 $\mu g/m^3$ of air on the property of the FMC plant.[2] As a result of these unexpectedly

high levels of NDMA, possibly due to the direct emission of NDMA from the plant into the environment, FMC eventually decided to shut down the UDMH production facility. This has led the Air Force to investigate methods to produce UDMH by which NDMA is not used as a reaction intermediate.

Information Needed for Kinetic Model. For the reasons outlined in the Introduction, information is needed to allow a kinetic model to be developed from which estimates can be made of: (1) the overall rate by which UDMH may be depleted from the point of a possible accidental introduction into the environment; (2) the rates by which NDMA is either directly or indirectly formed from environmental reactions of UDMH; and (3) the overall rate by which NDMA may be depleted in the environment if formed. The completed model would need to take into account such factors as environmental UDMH and NDMA transport rates, and the rates of photochemically induced, as well as nonphotochemically induced reactions.

Photochemically induced reactions of importance may include the effects of the reactive atmospheric pollutants, ozone, singlet molecular oxygen [$^1O_2(^1\Delta g)$], and NO_x (NO, NO_2, and HONO) on NDMA formation from UDMN and/or its oxidation products. Among other photochemically induced reactions of importance are the direct photolytic decomposition of NDMA by sunlight.[3]

Information required on nonphotochemically induced air oxidation reactions of UDMH includes:[4] (1) the identity of products formed (especially potential NDMA forming products), as well as the rates of UDMH disappearance and NDMA formation resulting from UDMH exposure to air (RX.1); (2) the rate of NDMA disappearance in air (RX.2); and (3) the rate of NDMA formation by reaction of dimethylamine with NO_x (NO, NO_2 or HONO) in air (RX.3), or (4) the rate of NDMA formation by the reaction of formaldehyde dimethylhydrazone with air (RX.4).

$(CH_3)_2 NNH_2$ + air ⟶ (RX.1)

UDMH

$(CH_3)_2 NNO$ + air ⟶ (RX.2)

NDMA

$(CH_3)_2 NH + NO_x$ ⟶ (RX.3)

Dimethylamine

$(CH_3)_2 NN = CH_2$ + air ⟶ (RX.4)

Formaldehyde dimethylhydrazone

As an initial phase of a program to obtain the information needed for the development of the kinetic model to estimate UDMH and NDMA levels following UDMH introduction into the environment, our effort has been limited to a study of the products formed and the rates of UDMH decay by RX.1 above. These studies were carried out at initial UDMH pressures between ~0.32 and 32 torr in close to an atmosphere of dry air.

We now outline the information available in the chemical literature on oxidation reactions of hydrazine and its methylated derivatives that may be relevant to the study of RX.1.

Information Relevant to RX.1 from Literature. Examination of the literature on the nonphotochemically induced gas phase oxidation reactions of hydrazine[5,6] and its methyl substituted derivatives[7,8] reveals that the kinetics of these reactions are generally not simple, and may involve radical processes.

Gas phase reactions[8] carried out (at the US Naval Ordnance Test Station in China Lake, California) with between ~40-100 torr of UDMH and generally close to an atmosphere of pure oxygen were observed to result in many products. Major products in these reactions were identified as formaldehyde dimethylhydrazone, nitrogen, and water; while minor products were

identified as ammonia, dimethylamine, N-nitrosodimethylamine (NDMA), diazomethane, nitrous oxide, methane, carbon dioxide, and formaldehyde.

These products were postulated to result from an autoxidation reaction of UDMH that also involved a free radical mechanism in the rate determining sequence. Although similar products might be expected to form in RX.1, the UDMH decay rates of the autoxidation reactions should not correspond to environmental loss rates of UDMH. This is because the autoxidation reactions were carried out with high initial UDMH pressures in close to an atmosphere of oxygen (rather than low UDMH pressures in air).

EXPERIMENTAL

The techniques of infrared (IR) and ultraviolet (UV) spectroscopy, and combined gas chromatography-mass spectroscopy (GC-MS) were used to identify the major products of RX.1. UDMH decay rates were determined by monitoring either IR or UV spectral changes as a function of reaction time.

Gas phase IR spectra were determined with Perkin-Elmer 467 grating infrared spectrophotometer. Gas phase UV spectra were determined with a Cary model 15 recording spectrophotometer equipped with a slidewire for the absorbance ranges 0-1.0, 1.0-2.0, and 0-0.1. The IR gas cells used were equipped with removable NaCl windows, as well as mixing loops to which the application of a temperature gradient allowed the rapid convection mixing of gases. The same cells were occasionally used as UV gas cells by replacing the NaCl windows with Suprasil windows. Generally Suprasil UV gas cells were used, which were not equipped with mixing loops.

A Finnigan model 3200-003E computerized GC-MS was also used for sample analysis. Either helium or methane was used as both the GC carrier gas and MS chemical ionization reagent gas. Separations were carried out with 1/8" o.d., 5' long glass columns packed with one of the following stationary phases: (1) Carbowax 20M TPA/2% KOH, (2) OV-227, or (3) Chromosorb-103.

A mercury- and grease-free vacuum system was fabricated and used to add known quantities of gases to reaction vessels and IR or UV gas cells. All liquid nitrogen-condensible chemicals were stored individually in evacuated storage tubes, and were thoroughly deareated at liquid nitrogen temperature under vacuum before use.

Pressures of gases below ~10 torr were measured into gas vessels of known volume using a Validyne Corp. DP7 differential pressure transducer (±0.1 psi diaphragm) in combination with a model CD15 carrier demodulator. An MKS Baratron type 170 series capacitance manometer was used to calibrate the Validyne pressure transducer. Pressures up to 760 torr were measured using a Matheson gauge (model 63-5601).

RESULTS

Identity of Products of RX.1

Infrared Spectral Changes with Reaction Extent. Attempts to identify the products formed in RX.1 were initiated by following the build up and loss of bands in the IR as a function of reaction extent. The IR spectra of 2.95 torr UDMH prior to and after 49 hours reaction time in 705 torr of dry air are compared in figs. 1a and 1b, respectively.

The vapor phase IR spectral assignments for UDMH have been made by Durig and Harris[9]. Prominent spectral features that were observed for UDMH are illustrated in fig 1a. They included: (a) a weak combination band (CH_3 stretch plus an unassigned ~250cm^{-1} torsional band) centered at approximately 3160 cm^{-1}, (b) strong CH_3 stretching bands with peaks at 2950, 2812, 2802, and 2760 cm^{-1}, (c) a NH_2 scissoring band centered at approximately 1580 cm^{-1}, (d) a CH_3 scissoring band with peaks at 1459 and 1447 cm^{-1}, (e) a NH_2 wagging band located at 1299 cm^{-1}, (f) a CH_3 rocking band centered at 1032 cm^{-1}, (g) a strong NH_2 rocking band originating at 908 cm^{-1}, and (h) a UDMH skeletal stretching band located at 808 cm^{-1}.

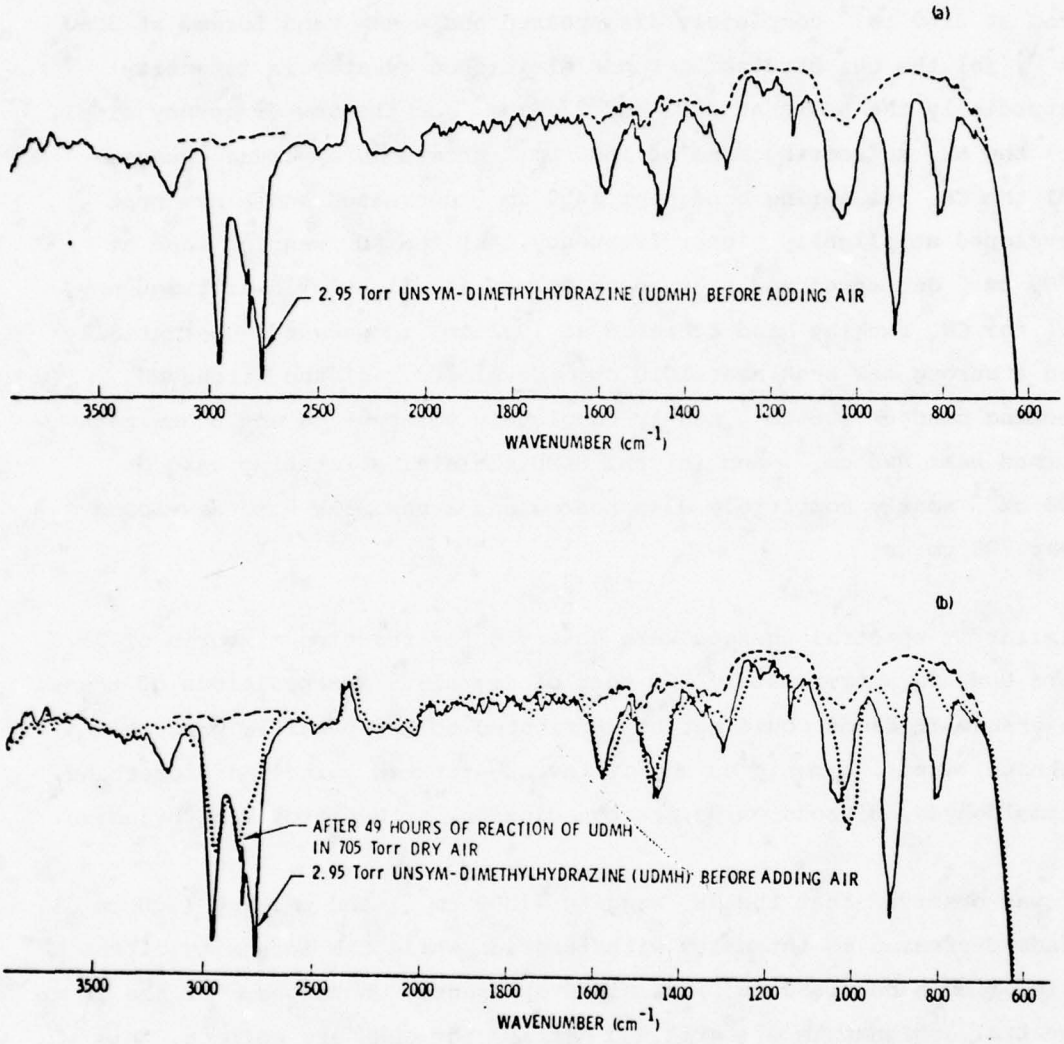


Fig. 1. (a) Infrared Absorption Spectrum 2.95 Torr UDMH before Adding Air,
(b) Infrared Absorption Spectra 2.95 Torr UDMH before and after 49 Hours of Reaction with 705 Torr Dry Air

Fig 1b illustrates the major changes observed in the UDMH vapor phase IR spectrum after 49 hours reaction time in dry air: (a) the weak combination band at 3160 cm^{-1} completely disappeared and a new band formed at 3060 cm^{-1}, (b) the CH_3 stretching bands diminished greatly in intensity (especially the peaks at 2802 and 2760 cm^{-1} on the low frequency side), (c) the NH_2 scissoring band at 1580 cm^{-1} showed no apparent change, (d) the CH_2 scissoring band near 1450 cm^{-1} decreased and a new peak developed at slightly higher frequency, (e) the NH_3 wagging band at 1299 cm^{-1} decreased and a new peak formed at slightly lower frequency, (f) the CH_3 rocking band centered at 1032 cm^{-1} decreased substantially and a strong new peak near 1010 cm^{-1} developed, (g) the strong NH_2 rocking band at 908 cm^{-1} nearly completely disappeared and a new peak formed near 885 cm^{-1}, and (h) the UDMH skeletal stretching band at 808 cm^{-1} nearly completely disappeared and a new weak band developed near 708 cm^{-1}.

Similar IR spectral changes were observed for reaction mixtures of 31.9 torr UDMH in approximately 760 torr of dry air. The positions of these major new IR bands could not be attributed to the possible products methane, water, ammonia or any of the substituted amines, diazomethane, formaldehyde, nitrous oxide, carbon dioxide, or N-nitrosodimethylamine.

It was observed that the NH_2 wagging (1299 cm^{-1}) and rocking (908 cm^{-1}) bands decreased in intensity with reaction while the intensity of the NH_2 scissoring band (1580 cm^{-1}) remained apparently unchanged. If the IR spectral assignments of Durig and Harris[9] for UDMH are correct, this can only be explained by the adventitious development of a new band at approximately 1580 cm^{-1} as the reaction progresses.

Ultraviolet Spectral Changes with Reaction Extent. To obtain further information on the identity of products in RX.1, UV spectral changes were also studied as a function of reaction extent. This is illustrated in fig 2. The solid line trace corresponds to the absorption spectrum of 0.694 torr UDMH obtained in the absence of air. A plateau for UDMH

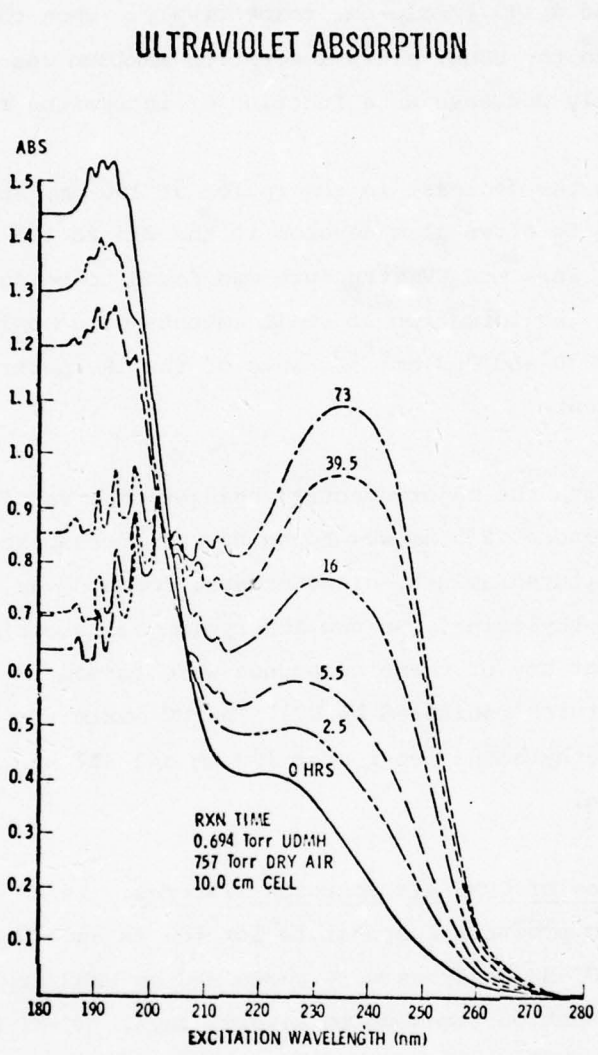


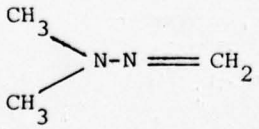
Fig. 2. Ultraviolet Absorption Spectra of 0.694 Torr UDMH/757 Torr Dry Air Mixture at Various Reaction Times

absorbance was observed near 220 nm while a maximum was observed near 190 nm. The UDMH molar extinction coefficients at these two wavelengths are 1,100 and 4,195 ℓ/mole-cm, respectively. Upon the addition of 757 torr of dry air to the UDMH, a new absorption maximum was observed to simultaneously decrease as a function of increasing reaction extent.

Accompanying the decrease in absorption at 190 nm, sharp UV structure was observed to often also develop in the 215 to 185 nm region as RX.1 progressed. This new UV structure was found to be due to the formation of ammonia. The formation of small amounts of ammonia could also be detected at 930 and 963 cm^{-1} in some of the IR spectra with increasing reaction extent.

Consistent with the major spectral changes observed in the IR studies, the new UV band at 235 nm was found not to correspond to the production of the substituted amines, diazomethane, formaldeyde, nitrous oxide, or N-nitrosodimethylamine. No new absorption bands could be detected that indicated that any of these compounds were formed in the UDMH/dry air reaction mixtures monitored by UV. The UV maxima for dimethylamine and N-nitrosodimethylamine occur near 190 nm and 227 nm, respectively, in the gas phase.

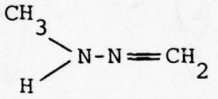
GC-MS Analyses of UDMH/Air Reaction Mixtures. In an attempt to identify the oxidation products responsible for the IR and UV absorbances, qualitative GC-MS analyses were performed on UDMH/dry air reaction mixtures at various reaction times up to several days. GC-MS analyses in which helium and methane were successively used as the mass spectrometric chemical ionization reagent gas suggested that formaldehyde dimethylhydrazone (FDH) was the predominant UDMH air oxidation product.



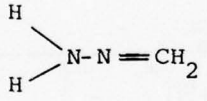
Formaldehyde dimethylhydrazone (FDH)

To determine if formaldehyde dimethylhydrazone (FDH) was responsible for the new IR bands and the UV band at 235 nm, an authentic sample of FDH was synthesized. The positions of the IR and UV absorption bands for FDH can be observed in figs 3 and 4 to be identical to those of UDMH/dry air reaction mixtures as RX.1 approaches completion. We thus attribute the IR and UV spectral changes observed in RX.1 with increasing reaction extent to be primarily due to FDH formation.

Minor oxidation products of RX.1 were identified by GC-MS as formaldehyde monomethylhydrazone (FMH), formaldehyde hydrazone, methylamine, dimethylamine, and N-nitrosodimethylamine (NDMA).



Formaldehyde monomethylhdrazone (FMH)



Formaldehyde hydrazone

Only limited attempts were made to identify low molecular weight reaction products in UDMH/dry air reaction mixtures by helium chemical ionization GC-MS analysis. Neither the presence of ammonia nor water could be detected in these attempts due to excessive interfering background peaks in the mass region of interest.

UDMH Decay Rates by RX.1

To model environmental UDMH decay rates by RX.1, decay curves for initial UDMH pressures from near its vapor pressure to as low as practical are of interest. UDMH decay rates, as a function of initial UDMH pressure, were determined by quantitatively monitoring IR or UV spectral changes as a function of reaction extent.

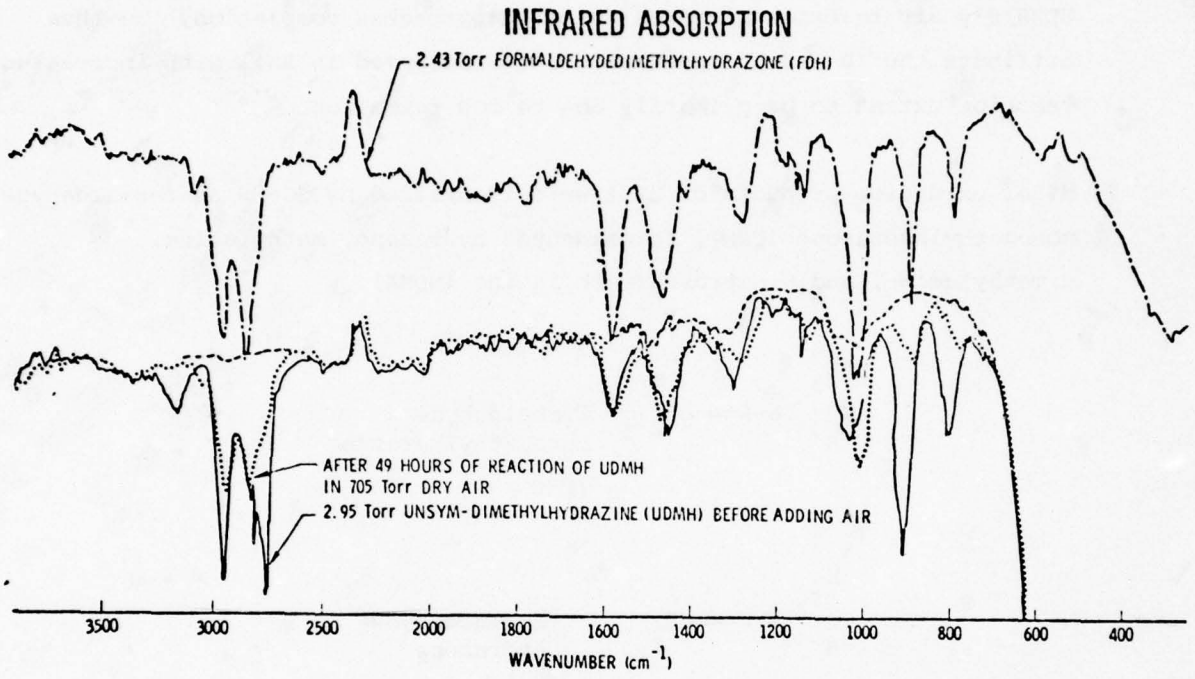


Fig. 3 Comparison of Infrared Absorption Spectra of 2.43 Torr FDH and UDMH Air Oxidation Products

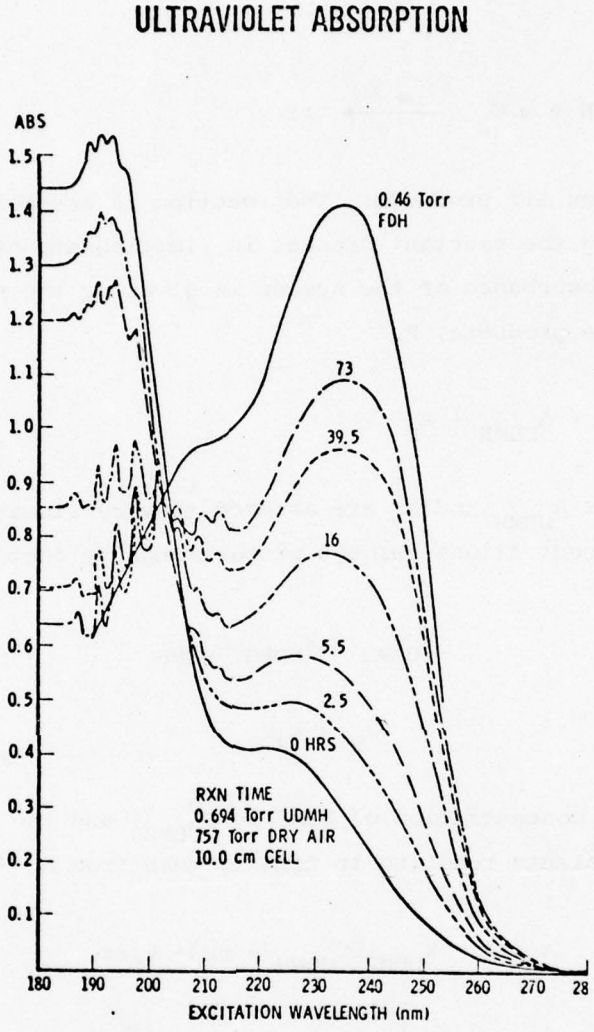


Fig. 4. Comparison of Ultraviolet Absorption Spectra of 0.46 Torr FDH and UDMH Air Oxidation Products

An equation relating IR or UV absorbances with UDMH concentrations can be derived by assuming the following general stoichiometry for UDMH decay by RX.1:

$$n\ \text{UDMH} + m\ O_2 \longrightarrow rP \qquad \text{eq(1)}$$

where P includes all products. The reaction is assumed to go to completion with UDMH being the reactant present in limiting amount. At any time, t, the total absorbance of the system is given by the sum of absorbances of UDMH and the products, P.

$$A\ (t) = A_{UDMH} + A_P \qquad \text{eq(2)}$$

The absorbances A_{UDMH} and A_P are assumed to vary linearly with their respective concentrations through proportionality factors k_{UDMH} and k_P:

$$A_{UDMH} = k_{UDMH}\ C_{UDMH}$$

$$A_P = k_P C_P$$

If the initial concentration of UDMH is C^o_{UDMH}, and the reaction variable x is the equivalents reacting in time t, then from eq (1):

$$A\ (t) = k_{UDMH}[C^o_{UDMH} - nx] + k_P rx \qquad \text{eq(3)}$$

and

$$A\ (0) = k_{UDMH} C^o_{UDMH} \qquad \text{eq(4)}$$

$$A\ (\infty) = k_P \frac{r}{n} C^o_{UDMH} \qquad \text{eq(5)}$$

where A(0) and A (∞) are the initial and final values of A(t), respectively. Subtracting eq (4) from eq (5) yields

$$A\ (\infty) - A(0) = (k_P \frac{r}{n} - k_{UDMH}) C^o_{UDMH} \qquad \text{eq(6)}$$

and subtracting eq (3) from eq (5) yields

$$A\ (\infty) - A(t) = (k_P \frac{r}{n} - k_{UDMH})\ [C^o_{UDMH} - nx] \qquad \text{eq(7)}$$

Thus, if the quantity $(k_P \frac{r}{n} - k_{UDMH})$ is appreciably different from zero (i.e. if difference in the molar absorptivities of products and reactants is large at a given wavelength), we can write using eqs (6) and (7):

$$\frac{A\ (\infty) - A(0)}{A\ (\infty) - A(t)} = \frac{C^o_{UDMH}}{[C^o_{UDMH} - nx]} \qquad \text{eq(8)}$$

Eq (8) is useful in expressing the first order loss rate of UDMH by eq (1) in terms of the reaction variable x, since the integrated form of

$$-\frac{ndx}{dt} = k\ (C^o_{UDMH} - nx) \qquad \text{eq(9)}$$

can be written as

$$\ln\left[\frac{C^o_{UDMH}}{C^o_{UDMH} - nx}\right] = \ln\left[\frac{A(\infty) - A(0)}{A(\infty) - A(t)}\right] = -kt \qquad \text{eq(10)}$$

Using IR or UV spectroscopic techniques, the disappearance of UDMH by RX.1 was followed in approximately an atmosphere of dry air at a series of different initial UDMH pressures between 32 and 0.32 torr. Analysis of these data suggests that (in this pressure regime) eq (10) is generally obeyed and first order loss of UDMH is observed.

With the short path length IR gas cells available, it was found inconvenient to follow the decay of UDMH at initial pressures below approximately 3 torr, even when operating the IR spectrophotometer in the expanded scale mode. Decay studies at initial pressures below 3 torr were most conveniently followed by monitoring UV spectral changes. To follow the disappearance of UDMH by IR, the UDMH skeletal stretching band at 808 cm^{-1} was monitored with time. To follow the disappearance of UDMH by UV, it was found most convenient to monitor with time either: (1) the increase in absorbance at 235 nm (due to formaldehyde dimethylhydrazone (FDH) production), or (2) the decrease in absorbance at 190 nm due to UDMH decay.

A typical UDMH decay plot obtained by plotting $\ln\left[\frac{A(\infty) - A(0)}{A(\infty) - A(t)}\right]$ versus t is illustrated in fig 5 for an initial UDMH pressure of 0.694 torr in nearly an atmosphere of dry air. For some of the kinetic runs these plots were either slightly curved or exhibited two distinct regions of linearity with time as illustrated in fig 6.

Summarized in Table I are the first order UDMH decay constants, k, (and UDMH half-lives, $t_{1/2}$) for various reaction conditions. Where the plots of $\ln\left[\frac{A(\infty) - A(0)}{A(\infty) - A(t)}\right]$ versus t are curved or have two regions of linearity both the initial (i) and final (f) slopes (rate constants) are tabulated.

Figure 7 displays graphically the data summarized in Table I. From this plot the rate constants for first order UDMH decay can be observed to decrease with decreasing initial UDMH pressure, P^{o}_{UDMH}.

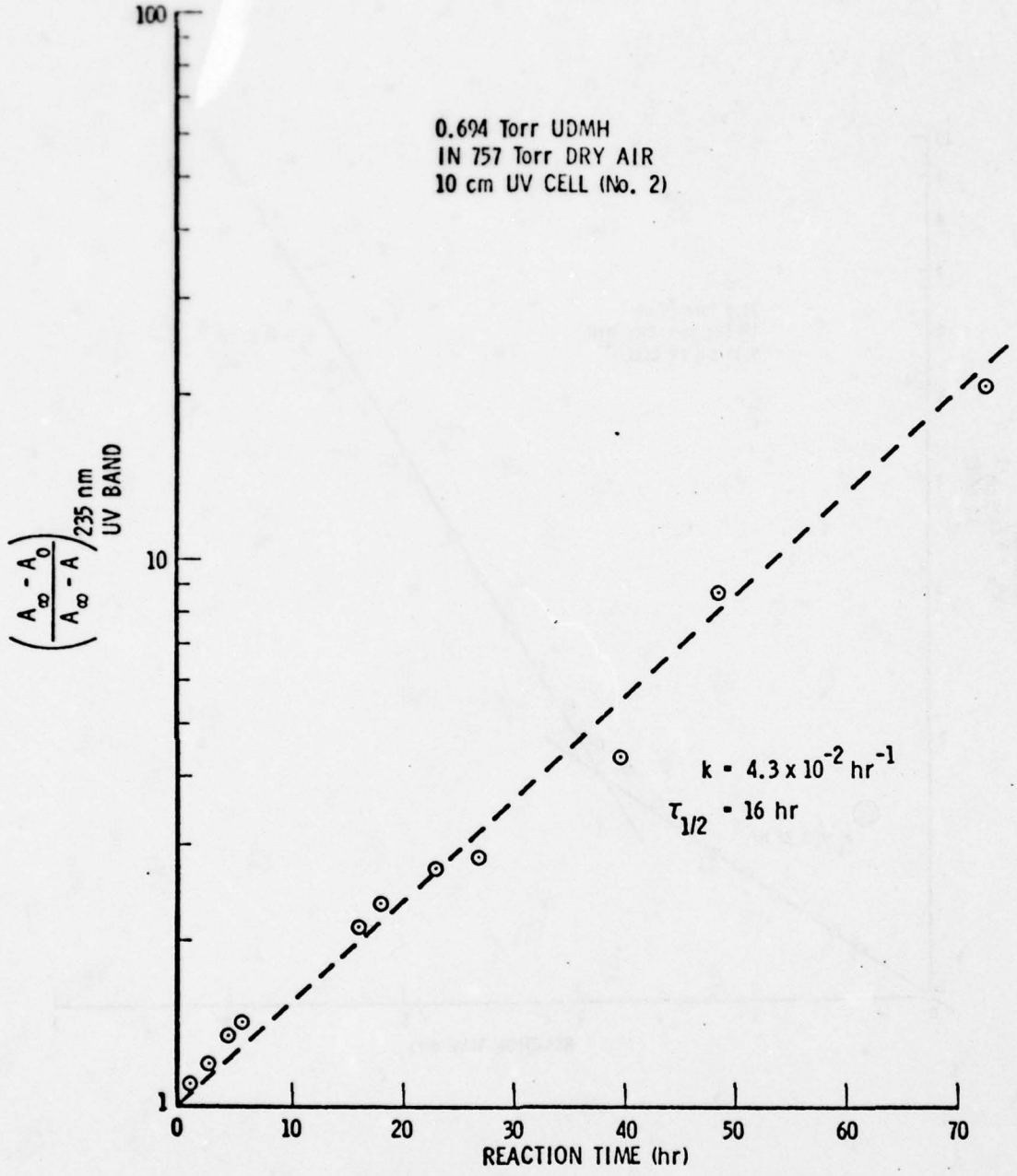


Fig. 5. Kinetic Data for 0.694 Torr UDMH/757 Torr Dry Air Reaction

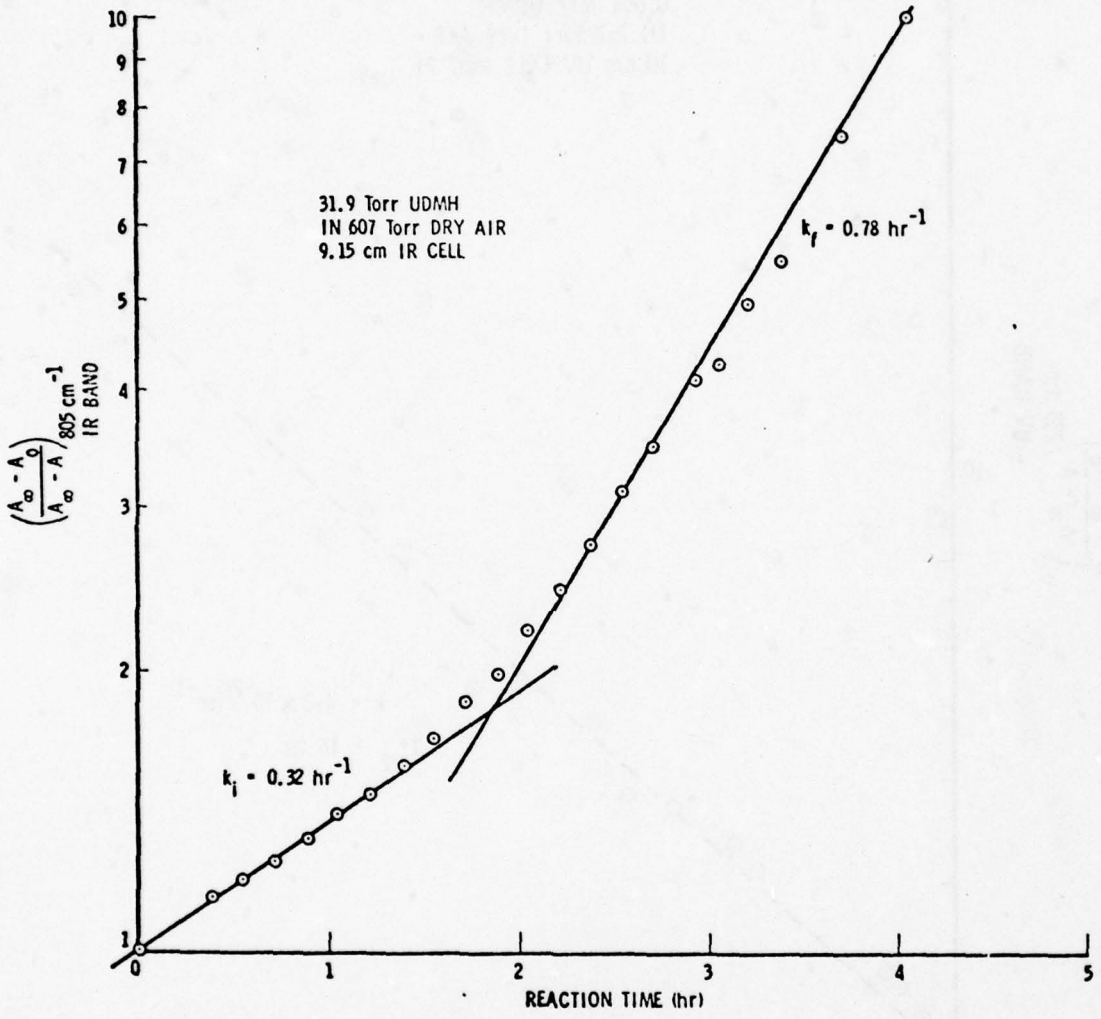


Fig. 6. Kinetic Data for 31.9 Torr UDMH/607 Torr Dry Air Reaction

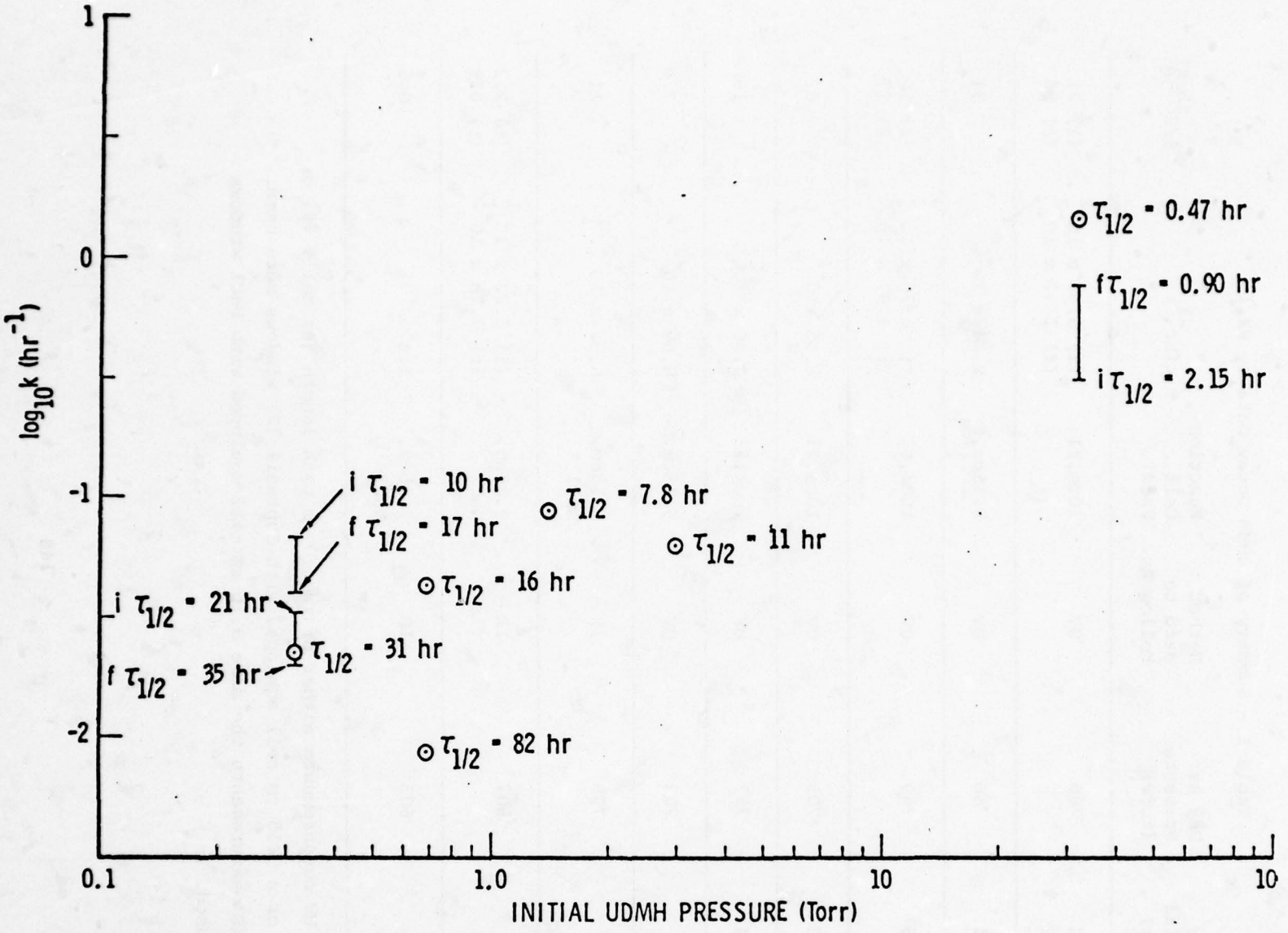


Fig. 7 Rate Constant Data for RX.1 as a Function of Initial UDMH Pressure

Table I - Summary of UDMH Decay Data by RX.1

UDMH Initial (torr)	Dry Air Pressure (torr)	Method used to Follow Rx.	Reaction Cell Used†	$k(hr^{-1})$	$t_{1/2}$(hrs)
0.314	760	UV	10cm,#1	(i) 3.30×10^{-2} (f) 1.97×10^{-2}	(1) 21 (f) 35
0.315	760	UV	9.15cm,S	2.24×10^{-2}	31
0.316	760	UV	10cm,#1	(i) 6.76×10^{-2} (f) 3.97×10^{-2}	(i) 10 (f) 17
0.690	703	UV	10cm,#1	8.45×10^{-3}	82
0.694	757	UV	10cm,#2	4.30×10^{-2}	16
1.40	703	UV	9.15cm,S	8.89×10^{-2}	7.8
2.95	705	IR	9.15cm, NaCl	6.32×10^{-2}	11
31.9	607	IR	9.15cm, NaCl	(i) 3.22×10^{-1} (f) 7.78×10^{-1}	(i) 2.2 (f) 0.9
31.9	603	IR	9.15cm, NaCl	1.47	0.5

†For UV measurements either of two 10 cm path length gas cells (#1 or #2), or a 9.15 cm cell equipped with Suprasil (S) windows were used. For IR measurements the same 9.15 cm cell equipped with NaCl windows was used.

The data presented in figure 7 cover two orders of magnitude in initial UDMH pressure. The study of UDMH decay rates for UDMH initial pressures up to a factor of 50 lower than studied here (i.e. down to approximately 0.015 torr) should be possible using the 0-0.1 absorbance range of the UV instrument used in this study. (The UDMH pressure regime examined here only required the use of the absorbance ranges 0-1.0 and 1.0-2.0). The study of UDMH decay rates at initial UDMH pressures several orders of magnitude below those possible by UV techniques should be possible by GC-MS.

Stoichiometry of RX.1. Information on the stoichiometry of the reaction n UDMH + m O_2 → rP was obtained by examining the quantities of each product formed from a given quantity of UDMH reactant as the reaction approached completion. As indicated previously, the predominant product of RX.1 was found to be FDH. The only other product of RX.1 that could be observed spectroscopically in the kinetic runs summarized in Table I was ammonia. The intensities of the sharp UV bands that develop in the 215 to 185 nm region can be conveniently used to estimate the amount of NH_3 formed by RX.1.

If only UDMH, FDH, and ammonia contribute significantly to the UV absorbance as RX.1 occurs, the absorbances at 190 and 235 nm (at anytime, t) are given by eqs. (11) and (12), respectively:

$$A_{190} = \varepsilon_{\substack{UDMH \\ 190}} C_{UDMH}\delta + \varepsilon_{\substack{FDH \\ 190}} C_{FDH}\delta + A_{\substack{NH_3 \\ 190}} \qquad \text{eq(11)}$$

$$A_{235} = \varepsilon_{\substack{UDMH \\ 235}} C_{UDMH}\delta + \varepsilon_{\substack{FDH \\ 235}} C_{FDH}\delta + A_{\substack{NH_3 \\ 235}} \qquad \text{eq(12)}$$

Here the contributions to the total absorbance at 190 and 235 nm are expressed in terms of the extinction coefficients, ε, and concentrations, C, of UDMH and FDH at each wavelength, the cell path length, δ, and the absorbance of NH_3, A_{NH_3}, at each wavelength. Eqs (11) and (12) may be solved simultaneously for the concentration of FDH, C_{FDH}, or UDMH, C_{UDMH}, at any time, t. Since $A_{\substack{NH_3 \\ 235}}$ is very small, and can be neglected, we obtained

$$A_{190} - A_{\substack{NH_3 \\ 190}} - \left(\frac{\varepsilon_{\substack{UDMH \\ 190}}}{\varepsilon_{\substack{UDMH \\ 235}}} \right) A_{235}$$

$$C_{UDMH} = \frac{}{\left[\varepsilon_{\substack{FDH \\ 190}} - \left(\frac{\varepsilon_{\substack{UDMH \\ 190}}}{\varepsilon_{\substack{UDMH \\ 235}}} \right) \varepsilon_{\substack{FDH \\ 235}} \right] \delta} \qquad \text{eq (13)}$$

and

$$C_{UDMH} = \frac{A_{190} - A_{NH_3}{}_{190} - \left(\frac{\varepsilon_{FDH}}{\varepsilon_{FDH}}{}_{190}{}_{235}\right) A_{235}}{\left[\varepsilon_{UDMH}{}_{190} - \left(\frac{\varepsilon_{FDH}}{\varepsilon_{FDH}}{}_{190}{}_{235}\right) \varepsilon_{UDMH}\right] \delta} \qquad \text{eq (14)}$$

The molar extinction coefficient values of UDMH at 190 and 235 nm are 4,195 and 749 ℓ/mole-cm, respectively. The corresponding values for FDH at 190 and 235 nm are 1,932 and 5,838 ℓ/mole-cm, respectively. For any particular kinetic run, the value of A_{NH_3} was obtained from the final UV spectrum of the reaction mixture through use of an empirical relationship† derived by reference to the vapor phase UV spectrum of NH_3.

Eq (13) can be used to calculate C^{∞}_{FDH}, the number of moles of FDH formed as RX.1 nears completion, while the number of moles of UDMH reacted, $C^{o}_{UDMH} - C^{\infty}_{UDMH}$, can be calculated using eq (14). The ratio $(C^{o}_{UDMH} - C^{\infty}_{UDMH})/C^{\infty}_{FDH}$ gives the ratio of coefficients, n/r, in the reaction $nUDMH + mO_2 \rightarrow rFDH$.

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†From the gas phase absorption spectrum of NH_3 it is observed that the value of $A_{NH_3}{}_{190}$ should be determined at the midpoint between the absorption peak at 191 nm and the NH_3 absorption valley at 189 nm. It can also be observed that the $A_{NH_3}{}_{190}$ value is nearly equal to the absorption difference between the NH_3 absorption peak at 191 nm and the NH_3 absorption valley at 189 nm. The value of $A_{NH_3}{}_{190}$ in eqs (13) and (14) was thus estimated by the empirical relationship: $A_{NH_3}{}_{190} \approx A_{NH_3}{}_{191} - A_{NH_3}{}_{189}$.

For kinetic runs summarized in Table I, it appears that a limiting value of 1.5 is approached for the ratio $(C^{o}_{UDMH} - C^{\infty}_{UDMH})/C^{\infty}_{FDH}$. For example, after the reaction between 0.316 torr UDMH and 760 torr dir air stopped, it was found that, of the original UDMH present, 7.5 percent remained unreacted and 8.2 percent formed NH_3. The ratio of $(C^{o}_{UDMH} - C^{\infty}_{UDMH})/C^{\infty}_{FDH}$ was 1.77. The reaction of 0.694 torr UDMH with 757 torr dry air stopped with 12.9 percent of the original UDMH remaining unreacted. The amount of NH_3 formed was 12.0 percent of the original UDMH, and the ratio $(C^{o}_{UDMH} - C^{\infty}_{UDMH})/C^{\infty}_{FDH}$ was 1.66. For the reaction of 0.690 torr of UDMH and 703 torr dry air, 3.0 percent of the original UDMH formed NH_3 and the ratio $(C^{o}_{UDMH} - C^{\infty}_{UDMH})/C^{\infty}_{FDH}$ was 1.53. No reaction was observed having a $(C^{o}_{UDMH} - C^{\infty}_{UDMH})/C^{\infty}_{FDH}$ ratio less than 1.5.

An n/r ratio of 1.5 for the reaction $nUDMH + mO_2 \rightarrow r\ FDH$ is consistent with the results obtained in the previously reported[8] higher pressure autoxidation study of UDMH in pure oxygen. The autoxidation of UDMH was reported to give FDH, water, and nitrogen as dominant products in a reaction in which the stoichiometry of eq (15) is approached.

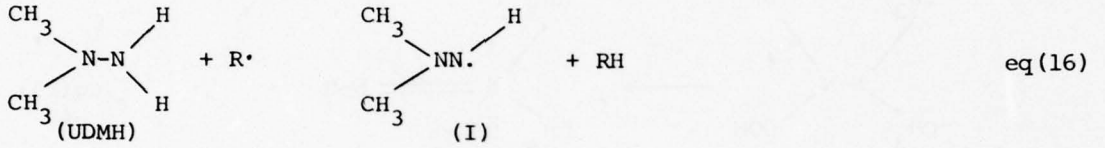
$$3\ UDMH + 2O_2 \rightarrow 2FDH + 4H_2O + N_2 \qquad \text{eq(15)}$$

As observed in the present study, the autoxidation reaction of UDMH was reported to exhibit first order decay in UDMH. Similar minor oxidation products were also observed in both studies.

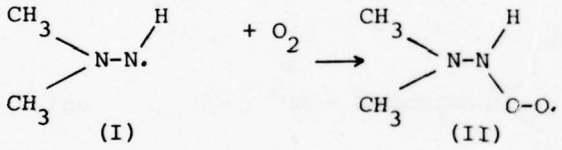
DISCUSSION

The similarities observed between the previously reported[8] vapor phase autoxidation reactions of ~ 40-100 torr UDMH in nearly an atmosphere of pure oxygen, and the vapor phase reactions of ~ 0.32-32 torr UDMH in nearly an atmosphere of air, suggest that these reactions may be taking place by the same mechanisms.

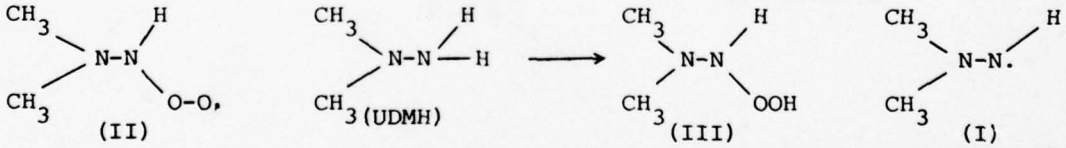
Urry, et al.[8] proposed a free-radical chain mechanism as the rate-determining reaction sequence in the vapor phase autoxidation of UDMH. Reaction initiation was thought to involve the free-radical decomposition of unsymmetrical dimethylhydrazine hydroperoxide, $(CH_3)_2 N - N\langle^{H}_{OOH}$, formed during an induction period. Eq (16) was proposed as the last step in an initiation sequence (where R = HO· or $(CH_3)_2$ N-NHO), while eqs (17) and (18) were believed to represent chain-propagating sequences. Chain termination was thought to involve the destruction of radicals such as II.



eq(16)

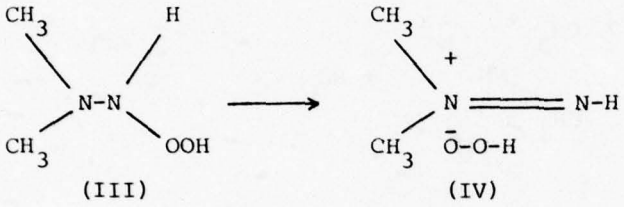


eq(17)

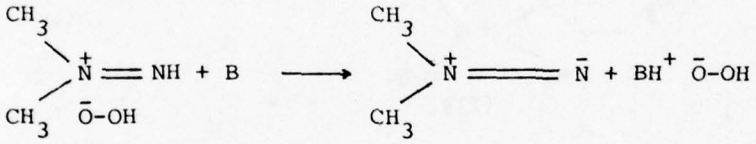


Support for the proposed attack of oxygen upon the hydrogen atoms of UDMH during the induction period to form III, and radical attack upon the hydrogen atoms of UDMH in eqs (16) and (18) was indicated by the observation [8] that substances without N-H groups (tetramethylhydrazine, tetramethyltetrazine, and FDH) were oxidized much more slowly than substances with N-H groups (hydrazine, methylhydrazine, and UDMH).

The unsymmetrical dimethylhydrazine hydroperoxide (II) was postulated to form the diazene (V) via the dimethyldiazenium hydroperoxide (IV):

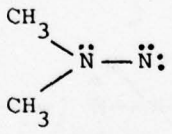


(III) (IV) eq(19)

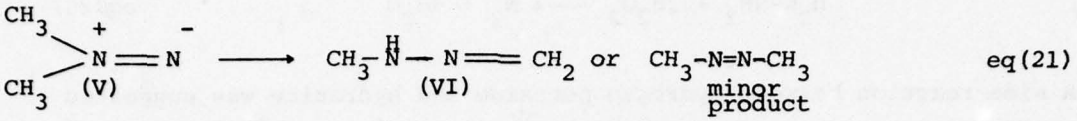


(IV) (V) eq(20)

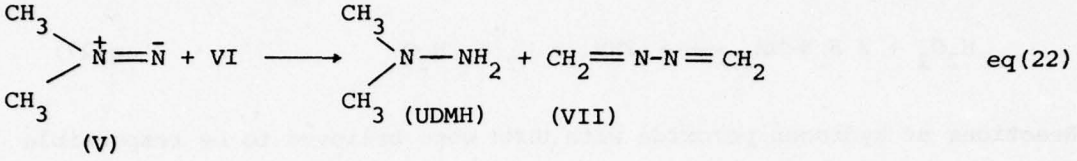
(where B: ≡ amines, or hydrazines)



Since ionic species are generally not formed in vapor phase reactions, it was suggested that the reactions given by eqs (19) and (20) took place instead on the walls of the reaction vessel. A reaction mechanism analogous to one that had been proposed earlier for the liquid-phase autoxidation of UDMH[10] was proposed by Urry et al.[8] to be operative (on the reaction vessel walls) in the vapor phase autoxidation of UDMH. By this mechanism, diazenes(V) were proposed to rearrange, eq (21), and to oxidize the rearrangement product formaldehyde monomethylhydrazone, (VI), eq (22).

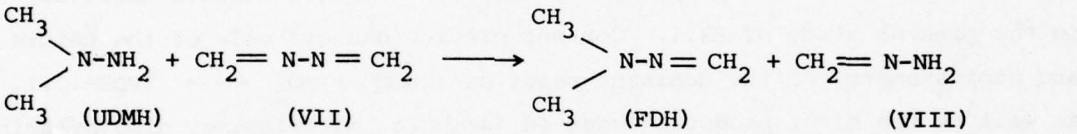


eq(21)

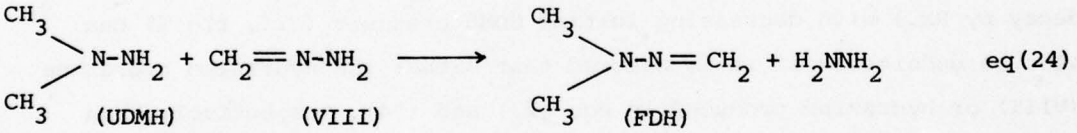


eq(22)

Reactions of UDMH with formaldazine (VII) or with formaldehyde hydrazone (VIII), eqs (23) and (24), were then postulated to give the major product, FDH.

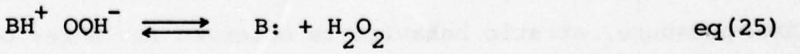


eq(23)



eq(24)

The overall stoichiometry of eq (15) is obtained by the above reactions, c.f. eqs (17)-(24), if it is assumed that the hydrazine formed in eq (24) is oxidized completely (to water and nitrogen) by the hydrogen peroxide produced on the reaction vessel walls during the reaction sequence.



eq(25)

$$H_2N\text{-}NH_2 + 2H_2O_2 \longrightarrow N_2 + 4H_2O \qquad \text{eq(26)}$$

A side reaction between hydrogen peroxide and hydrazine was suggested as being responsible for the formation of ammonia.

$$H_2O_2 + 2\ H_2N\text{-}NH_2 \longrightarrow 2NH_3 + N_2 + 2H_2O \qquad \text{eq(27)}$$

Reactions of hydrogen peroxide with UDMH were believed to be responsible for the formation of NDMA and FDH, while reactions of hydrogen peroxide with FDH were thought to be responsible for the formation of dimethylamine, methylamine, ammonia, and formaldehyde.

The sequence of free radical reactions represented by eqs (16)-(27) can be observed to also properly account for the major results observed in the present study of RX.1. Correct predictions are made of the nature and stoichiometry of the dominant reaction ($3UDMH + mO_2 \longrightarrow 2FDH+...$), as well as the minor products observed (ammonia, methylamine, dimethylamine, formaldehyde monomethylhydrazone, formaldehyde hydrazone, and NDMA). The gradual decrease observed in the rate constants for UDMH decay by RX.1 with decreasing initial UDMH pressure (c.f. fig 7) can also be understood if it is assumed that either the hydrazine hydrazone (VIII) or hydrazine produced in eqs (23) and (24), respectively, can form hydroperoxides much more efficiently than can UDMH. Thus at higher initial pressures of UDMH, higher concentrations of these peroxides could form, and their subsequent decomposition would be expected to result in more rapid initiation reactions.

Although the rate constant data presented in Table I and fig 7 show a gradual and generally self-consistent decrease with decreasing initial UDMH pressure, erratic behavior is observed for a few of the data points. This erratic behavior is illustrated by the nearly factor of five difference observed in the rate constants for the (0.690 torr UDMH/703 torr air) and the (0.694 torr UDMH/757 torr air) data points,

as well as the nonlinearity in some of the UDMH decay data. The lack of regularity observed for these data points may reflect the contribution of wall reactions to the free radical mechanism outlined above.

To model atmospheric UDMH decay rates by RX.1, it is important to experimentally minimize the occurrence of wall reactions. Free radicals may be produced on the walls of a reaction vessel by the adsorption and decomposition of stable molecules. Radical reactions may then occur on this surface, or (after desorption) in the gas phase. Conversely, gas phase free radicals can diffuse to the reaction vessel surface and combine to form stable molecules. The rates of these processes are sensitive to the nature of the reaction vessel surface and the reaction vessel surface/volume ratio.

The surface/volume ratios of the IR and UV glass gas cells used to determine the rate constant data presented in Table I and fig 7 were approximately $2.00 cm^{-1}$. The corresponding surface/volume ratios of the sperical 5ℓ and 12ℓ glass reaction vessels that were fabricated to study RX.1 by GC-MS analyses were $0.28\ cm^{-1}$ and $0.21\ cm^{-1}$, respectively. (A 22ℓ spherical glass flask is also available from which a reaction vessel could be fabricated that would have a surface/volume ratio of $0.17\ cm^{-1}$.) The use of GC-MS techniques to monitor the progress of RX.1 may thus allow a significant reduction in the contribution of wall reactions to the overall UDMH decay rate.

Other advantages that GC-MS techniques should offer over conventional UV or IR spectroscopic techniques to the study of RX.1 include: (1) the capability of simultaneously monitoring the concentrations of several (rather than just a few) components of the reaction mixture with time, and (2) the capability of achieving much lower detection limits for each of these components by GC-MS than by UV or IR spectroscopy.

For these reasons, it is suggested that reproducible GC-MS analysis procedures be established and used in any future studies of RXS. 1-4. A comparison of the rate constants obtained in the present study with those obtained at the same pressure but at substantially lower surface/volume ratios by GC-MS techniques should indicate whether wall reactions contribute significantly to the results reported here.

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Paper No 13

THE AUTOXIDATION OF HYDRAZINE AND UNSYMMETRICAL DIMETHYLHYDRAZINE

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INTRODUCTION

The oxidation of hydrazine fuels in the vapor phase at room temperature has been the subject of rather limited study.[1,2,3] The current investigation was undertaken to provide additional information about oxidation rates, oxidation products and chamber surface effects.

APPARATUS

Infrared spectroscopy was used to monitor the progress of the reactions. The spectrophotometer employed was a Digilab Model FTS-20 with a potassium bromide beamsplitter and a mercury cadmium telluride detector operated at 77°K. Hydrazine was monitored in the NH_2 asymmetric wagging region[4] at 910 cm^{-1}, while unsymmetrical dimethylhydrazine (UDMH) was monitored in the skeletal stretching region[5] at 808 cm^{-1}.

Over the course of this study a number of different reaction vessels have been employed in order to assess the role of concentration and the ratio of surface area to volume in the oxidation reaction(s).

MATERIALS

Hydrazine and unsymmetrical dimethylhydrazine were obtained from Rocky Mountain Arsenal and were fuel grade (>98% pure). Samples were drawn directly from the pint bottles received from the Arsenal and stored in pyrex sample containers with teflon valves. Before use, the material was degassed by several freeze-pump-thaw cycles using liquid nitrogen.

EXPERIMENTAL PROCEDURE

A number of different methods of observing the oxidation reaction were tried. Early work was carried out by vaporizing a few microliters of hydrazine via an input manifold into a 55 liter long-path cell. This cell was equipped with White[6]- type optics and had a path length of about 25 meters.

The next set of experiments was carried out in a 10 cm cell, where UDMH was expanded into the cell using a portable vacuum system. Pressures were measured with a Texas Instruments Model 145 precision pressure gauge. Later, UDMH oxidation runs were conducted in a 20 liter carboy. UDMH was introduced into a manifold through a septum and carried into the carboy in the fill gas stream. Samples were removed into an evacuated 10 cm cell and an infrared spectrum was recorded.

Hydrazine oxidation was carried out in the same manner except that the carboy was modified to include mechanical stirring with a teflon stirring paddle driven through an Ultra-Torr union with a variable speed motor. This system proved troublesome and was replaced by a system where circulation was accomplished via a teflon coated diaphram pump. Materials were circulated from the carboy through the pump and the 10 cm cell then returned to the carboy through 1/8 inch teflon tubing.

RESULTS

UDMH absorbance in the 10 cm cell decreased by about 75% in 120 hours when no oxygen was added. No product formation was observed. When placed in pure oxygen in the 10 cm cell, the UDMH absorbance decreased in a similar fashion with about a 15% yield of formaldehyde dimethylhydrazone (FDH). It was difficult to differentiate between oxidation and natural decay in the UDMH + O_2 system. The only unambiguous conclusion was that some oxidation did occur.

In the 20 liter carboy, the UDMH was much more stable. After 111 hours in nitrogen, UDMH absorbance had decreased by less than 5%. The same experiment conducted in one atmosphere of oxygen gave essentially the same result; there was slightly more removal of UDMH but very little, if any, FDH formed. The importance of the surface to volume ratio was shown by these experiments. For the 10 cm cell it is about 2 cm^{-1}, while the 20 liter carboy is about 0.17 cm^{-1}.

The results of the UDMH oxidation experiments are summarized in Table 1:

Table 1 UDMH Oxidation

Reaction Vessel	Initial Press UDMH (Torr)	O_2 Press (Torr)	Reaction Time (hrs)	Final Press UDMH (Torr)	FDH Press (Torr)
carboy	5	0	111	4.9	None
"	5	755	288	4.8	Trace
"	4.8	755	64	4.2	None
10 cm cell	11	0	24	7	None
			54	6	None
			120	4	None
"	4.9	755	23	3.5	0.2
"	7	753	23	5.5	-
			94	3	1.0
"	100	660	67.5	<1	15

Hydrazine oxidation in the 55 liter longpath cell was difficult to separate from natural decay processes. After being injected into the cell with 504 torr of nitrogen, the hydrazine was allowed to sit overnight in order to equilibrate. Then 126 torr of oxygen was added and decay was followed. There was rather large scatter in the data points and only general trends in half life could be ascertained.

In the 20 liter carboy system with the circulation pump and the flow through cell, the hydrazine oxidation rate was rapid, partly because of the need to work in the 25 torr pressure region in order to have adequate absorbance. Surface effects, however, seemed to dominate the rate.

The results of the hydrazine oxidation experiments to date are shown in Table 2.

Table 2. HYDRAZINE OXIDATION

Reaction Vessel	Initial Hydrazine Press (Torr)	Percent Oxygen	Ammonia Detected as a Product	Water Detected as a Product	Half life of Hydrazine
25 liter carboy	5	0	-	Yes	10 hrs
"	5	20	Yes	Yes	4-5 min
"	5	20	Yes	Yes	4-5 min
"	2.5	20	Yes	Yes	8-10 min
55 liter cell	0.5	0	-	-	40-60 hrs
"	0.5	20	Yes	Yes	15-20 hrs
"	0.5	40	Yes	Yes	8-10 hrs

A number of different combinations of cell surface to volume ratios were employed during the course of the hydrazine experiments. This ratio was varied from about 0.2 cm^{-1} to about 2 cm^{-1}. The hydrazine half life was definitely affected, decreasing by a factor of about two as the surface to volume ratio was increased by a factor of about 10.

Two different surface coatings were applied to one reaction vessel in an attempt to evaluate the effect of "deactivating" the glass surface. Triethanolamine gave unsatisfactory physical coating characteristics.

Paraffin wax, melted with a heat gun, gave a smooth coating in the vessel and increased the half life by about 15% over the uncoated surface.

CONCLUSIONS

The oxidation experiments conducted to this point seem to indicate that UDMH undergoes oxidation, which is mostly a heterogeneous surface reaction, to formaldehyde dimethylhydrazone. The very limited experiments to date favor the stoichiometry[2]

$$3(CH_3)_2NNH_2 + 2O_2 \longrightarrow 2(CH_3)_2NNCH_2 + 4H_2O + N_2.$$

Hydrazine oxidation experiments seem to indicate the following stoichiometry for the main reaction[7].

$$N_2H_4 + O_2 \longrightarrow 2H_2O + N_2.$$

Side reactions would then account for the ammonia observed in these experiments.

ADDED NOTE: Experiments conducted after the conference in a new reaction vessel made from a 5 liter flask with integral infrared optical parts have shown that the half life of the hydrazine was strongly influenced by the teflon lines and pump surfaces in the circulation system. Reaction products and side product(s) are unchanged in this new reaction vessel, however, half lives are now several hours.

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Paper No 14

BIOLOGICAL EFFECTS OF AQUEOUS HYDRAZINE SOLUTIONS

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INTRODUCTION

The biological impact of hydrazine fuels on the ecosystem in which it is used is of ultimate importance since this level of impact is directly coupled to the socioeconomic, medical, and legal constraints on the use of it as a fuel. The purpose of this paper is to summarize the recent work done by this laboratory in the area of biological effects. The hydrazine work was done under contract and by inhouse investigators. Only the contracted work is described in this presentation, and the reported information was extracted from the most recent annual progress reports.[1,2]

The contracted work was done at the University of California, Irvine Campus (UCI). This work considered algal systems as indicators of ecological stress. Both freshwater and seawater algal systems were studied. The Berkeley Campus (UCB) is performing bioassay work on fish and aufwuchs in an effort to define the effects of potential environmental contamination on fish.

ALGAL STUDIES

As just mentioned, the University of California, Irvine Campus studied both fresh and seawater algae. The same general procedure was followed in both cases, in that algal systems were systematically exposed to various concentrations of hydrazine in a batch type exposure of a closed algal system.

University of California, Irvine, research objectives for the past year were directed towards the establishment of dose/concentration responses of unicellular green algae to hydrazine, unsymmetrical dimethylhydrazine (UDMH), and monomethylhydrazine (MMH). Dose responses were determined for two algal species using the Standard Algal Bioassay procedure. Both freshwater and marine bioassays were conducted to simulate a range of aquatic ecosystems, such as oligotrophic lakes, eutrophic lakes, lakes of intermediate trophic status, estuaries and the open sea. The overall goals were to provide information for environmental impact statements and determine threshold limits under which the Air Force can operate within the National Environmental Policy Act. The specific objectives were:

1. Determining 'no effect' or safe concentration (SC) for the compounds under the various test conditions.
2. Determining EC_{50} for the compounds under various test conditions. The EC_{50} is defined as that concentration which causes a 50% decrease in growth at a specified time, relative to a control.

The 'no effect' or safe concentrations (SC) were determined by using a t-test to compare mean growth in the control flasks with mean growth for each concentration of test compound. The SC is the highest concentration

of test compound which causes no statistically significant difference in growth (at the 95% confidence level) when compared with the control flasks without test compound added.

Effective concentrations were determined graphically by plotting percent algal growth as a function of the initial concentration of test compound. The EC_{50} is that concentration which causes a 50% reduction in growth when compared with the controls without chemical added. Total cell number was used as the algal growth index.

Freshwater hydrazine bioassays were accomplished for 10% Standard Algal Assay Medium (SAAM), 33% SAAM, and 100% SAAM. The 10% SAAM medium is equivalent in nutrient status to freshwater of oligotrophic conditions.

Five replicate flasks were dosed with concentrations of 0.05, 0.50, 5.0, and 10.0µℓ of hydrazine per liter of 10% SAAM. These flasks and five controls without hydrazine were seeded with Selenastrum capricornutum to an initial concentration of 1×10^6 cells per liter. Algal growth and hydrazine concentrations were monitored daily for the first seven days and then once or twice per week until the 31st day.

Results of the growth data analysis are shown in Table I.

Table I. SC and EC_{50} for Hydrazine

	FRESHWATER					
	Percent SAAM					
	10%		33%		100%	
Day	SCμℓ/ℓ	EC_{50}μℓ/ℓ	SCμℓ/ℓ	EC_{50}μℓ/ℓ	SCμℓ/ℓ	EC_{50}μℓ/ℓ
3	0.001	0.02	0.001	0.013	0.001	0.006
4	0.002	0.02	———	———	———	———
6	———	———	———	———	0.005	0.041
7	0.002	0.02	———	———	———	———
8	———	———	0.01	0.037	———	———
14	0.003	0.07	———	———	———	———
	ARTIFICIAL SEAWATER, 35 PPT SALINITY					
6	0.0005	0.0008	0.001	0.0011	———	———
8	0.0005	0.0008	0.001	0.0037	———	———
11	0.0005	0.002	———	———	———	———

Also reflected in Table I are similar freshwater data for 33% and 100% SAAM medium and ASW data for 10% and 33% SAAM. The 33% SAAM medium is equivalent to conditions found in freshwaters of intermediate nutrient status, while the 100% SAAM medium is equivalent to eutrophic freshwater. With respect to Artificial Seawater (ASW) data shown in Table I the 10% SAAM medium is equivalent to seawater of full salinity (35 parts per thousand) with the nutrient level equivalent to that of inshore coastal water. The 33% SAAM medium is equivalent to seawater of full salinity but with additional nutrients, such as might occur naturally in estuarine waters. In the ASW experiments the flasks were seeded with Dunaliella

tertiolecta to an initial cell concentration of 1 x 10^6 cells per liter. Freshwater UDMH studies were conducted after the hydrazine experiments were completed. The 10% SAAM medium was used first. As stated previously, this medium is equivalent to oligotrophic freshwater conditions. The initial UDMH concentrations were 0.80, 2.0, 4.0, 6.0, 8.0, and 12μℓ per liter of 10% SAAM. Five replicate flasks for each concentration and ten replicate flasks without UDMH were seeded with Selenastrum capricornutum to an initial cell concentration of 1 x 10^6 cells/liter. Algal growth was monitored for ten days and results are presented in Table II.

TABLE II. SC AND EC_{50} FOR UDMH

	FRESHWATER					
	Percent SAAM					
	10%		33%		100%	
Day	SCμℓ/ℓ	EC_{50}μℓ/ℓ	SCμℓ/ℓ	EC_{50}μℓ/ℓ	SCμℓ/ℓ	EC_{50}μℓ/ℓ
6	5.0	0.80	0.5	4.7	0.5	5.3
8	5.0	2.0	3.0	6.6	0.5	8.0
10	5.0	2.0	0.5	10.5	0.5	8.0
	ARTIFICIAL SEAWATER, 35 PPT SALINITY					
6	-----	-----	0.01	0.92	-----	-----
8	-----	-----	0.5	0.96	-----	-----
10	-----	-----	0.01	0.98	-----	-----

Also shown in Table II are the results of the equivalent freshwater experiments conducted with 33% and 100% SAAM mediums. As in the case of hydrazine, UDMH experiments were conducted in ASW at 33 ppt salinity with

33% SAAM nutrients. The SC and EC_{50} for this experiment are also shown in Table II. It is interesting to note that in this latter case, low concentrations of UDMH generally caused an increase in agal growth as compared with the controls without UDMH added and that this increase was often highly significant statistically.

MMH bioassays were conducted using ASW at 35 ppt salinity with 33% SAAM nutrients. Initial MMH concentrations were 0, 0.20, 0.40, 0.80, 1.00, 2.00, and 4.00 µℓ/ℓ of growth medium. Five replicate flasks of each MMH concentration were seeded with Dunaliella teriolecta and algal growth was monitored for ten days. Based on cell number, the SC was 0.2, 0.4, and 0.4, µℓ/ℓ and the EC_{50} was 0.5, 0.5, and 1.1 µℓ/ℓ for days 6, 8, and 10, respectively.

With respect to the algal study conclusions, the concentration of hydrazine compounds decreases with time in growth media. Therefore, the initial concentration needed to cause a 50% reduction in growth increased with time. If the initial concentration is sufficiently high, growth is inhibited permanently even though with time the concentration will decrease to a point which would not have been growth-inhibiting initially. This suggests that algal cells are killed or rendered incapable of cell division by a sufficiently high concentration.

Data from bioassays completed indicate that of the three hydrazine compounds tested, UDMH is least harmful under the test conditions employed while hydrazine is by far the most toxic. The safe concentrations and EC_{50} concentrations for all are lower under marine conditions, even though the compounds are less stable in marine media. This difference between

freshwater and marine tests may reflect differential sensitivity of the test organisms used. It could also indicate that the by-products of decomposition under marine conditions are themselves toxic.

FISH STUDIES

The three studies to be summarized here include a range finding study, a jar test, and a simulated spill study. The preliminary range-finding study was conducted to determine the approximate concentration range for spill tests in the analog tanks and for acute static bioassays in 5-gallon jars.

A series of hydrazine concentrations of 0, 5, 15, and 30 mg/ℓ was studied for a 260-hour period using 1 gallon capacity jars, each containing three sticklebacks.

Results indicated that the 96 hour LC_{50} may be on the order of 5 mg/ℓ. Consequently, subsequent studies were conducted in the 10.0 mg/ℓ range.

Following the range-finding study, a static acute bioassay was conducted to determine the 96-hour LC_{50} of sticklebacks to hydrazine.

Nine to ten sticklebacks (Gasterosteus aculeatus) were added to each of 12 5-gallon jugs containing 16ℓ of bay water. Six duplicate hydrazine concentrations in the range of 0 to 10 mg/ℓ were investigated.

The jars, covered with aluminum foil, were gently aerated from house air supply and maintained at approximately 15°C. The hydrazine solutions were renewed daily, and routine measurements were taken of DO, pH, and temperature; pH was in the range 7.65 to 8.00, DO in the range 6.5 to 7.8, and temperature in the range of 14.0 to 15.5°C. The salinity of

the bay water was 18 mg/ℓ.

Stickleback survival followed the expected progression of increased mortality with increasing toxicant levels, and the replication was satisfactory. The LC_{50} at 24-hour was 8.5 mg/ℓ. The mean 96-hour LC_{50} of the duplicates was 3.4 mg/ℓ.

The loss of hydrazine after the initial 24-hour period was measured to ascertain whether the degradation rate was consistent with previous determinations. The loss indicated that in the critical range of 3.2 mg/ℓ the hydrazine degraded to approximately 2.2 mg/ℓ in 24 hours.

Therefore, the actual 96-hour LC_{50} was undoubtedly less than the 3.4 mg/ℓ specified. Because of significant degradation, the need for continuous flow bioassays for hydrazine becomes evident.

The effects of a hydrazine spill were simulated by adding a single dose of hydrazine to an analog tank operated as a static (non-flow through) unit. A rack containing 30 aufwuchs substrates was suspended 50 cm beneath the water surface of each of seven tanks. The tanks were operated on a continuous flow of bay water at a rate of 4.8 ℓ/min for two weeks to establish aufwuchs growth.

The nominal hydraulic residence time at this flow rate was 14.58 hours. Bay water flow was then terminated and eight of the aufwuchs growth units were removed from each tank and examined for metabolic response, chlorophyll a content and biomass. At this time also fish

cages each containing ten fish (stickleback) were placed in each analog tank. Two tanks were dosed with hydrazine to produce nominal hydrazine concentrations of 10 mg/ℓ; two tanks were dosed to produce hydrazine concentrations of 5.6 mg/ℓ; one tank was dosed to produce a hydrazine concentration of 3.2 mg/ℓ; two control tanks received no hydrazine. Hydrazine concentrations were measured 2 hours after hydrazine introduction and periodically thereafter for the 240 hour duration of the experiment. Air was slowly bubbled into the tanks throughout the assay period, and DO measurements were taken daily. The fish were observed daily for mortality and signs of stress. Eight aufwuchs growth units were removed from each tank 48 hours and 96 hours after hydrazine introduction and on each occasion analyzed for metabolic response, chlorophyll *a* content and biomass. Essentially, it was found in this analog tank study of the effect of a hydrazine "spill" (i.e., static bioassay with no hydrazine renewal) the 96-hour LC_{50} to sticklebacks was 6.6 mg/ℓ (95% confidence limits of 5.0 to 8.8 mg/ℓ) based on the initial hydrazine concentrations dosed to the tanks. In this concentration range the loss of hydrazine over 96 hours was approximately 50% of initial values as assessed by actual measurements. It was also determined that aufwuchs are more sensitive to hydrazine than are sticklebacks. In a "spill" situation an initial hydrazine concentration of 3.2 mg/ℓ (degrading to approximately 1 mg/ℓ in 96 hours) causes complete cessation of metabolic function after 96 hours.

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