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THE CHEMICAL AND BIOCHEMICAL DEGRADATION OF HYDRAZINE

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The properties and methods of analysis for hydrazine are reviewed and evaluated relative to the study of hydrazine degradations. Previous work on the environmental degradation of hydrazine is reviewed. Experimental studies are described for the degradation of hydrazine by diazoluminomelanin, transition metals, hydrogen peroxide, and clay. Ion chromatography was used as the analysis method.

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INTRODUCTION

Hydrazine is a weak base that is slightly weaker than ammonia (pKa = 7.96). The U.S. Air Force and the National Aeronautics and Space Administration use hydrazine (N_2H_4), monomethyl hydrazine (MMH), 1,1-dimethyl hydrazine (unsymmetrical dimethyl hydrazine (UDMH)), and Aerozine-50 (AE-50, a 50-50 mixture by weight of hydrazine and UDMH) in auxiliary power units, small thrusters, Titan II and Minuteman III missiles, and space vehicles. Uses for hydrazine are also numerous in the pharmaceutical and catalyst industries.

The routine handling of these fuels occasionally results in the accidental spillage of small quantities, which must be collected and properly disposed. Large volumes of hydrazine are also shipped, ranging from 55-gallon drums all the way up to rail cars capable of holding 110,000 to 155,000 kilograms of the fuel. Since hydrazine fuels are carcinogenic and a host of toxic effects are known to result from exposure to these substances, the Air Force needs a rapid method to safely degrade hydrazine and hydrazine containing compounds. The present method used by the Air Force for hydrazine spill neutralization is the addition of large quantities of oxidizers such as household bleach (5.25% NaOCl) or calcium hypochlorite ($Ca(ClO)_2$. This method of hydrazine neutralization is very dangerous for several reasons. First, it has been shown that hypochlorites can cause the hydrazine to ignite, resulting in an explosion. Second, the breakdown products including formaldehyde monomethylhydrazone, formaldehyde demethylhydrazone, N-nitrosodimethylamine, dimethylamine, and trimethylamine, which are more toxic than the hydrazine itself. In fact, the nitrosoamine breakdown products are considered to be among the most potent carcinogens known.[1]

In this study, hydrazine and monomethylhydrazine degradation in aqueous samples was catalyzed through the use of transition metals such as copper, nickel, iron, and manganese in conjunction with a new biopolymer, diazoluminomelanin (DALM), developed at the Occupational and Environmental Health Directorate at Brooks AFB, TX.

Toxicology of Hydrazine

The acute toxicity of hydrazine exposure to some representative animal species is shown in Table 1. Death from acute exposure results from convulsions, respiratory arrest and cardiovascular collapse.[2] Anorexia and vomiting are common symptoms associated with ingestion of hydrazines. Cardiac depression and hypotension may occur. Exposure to vapors can produce eye irritation, conjunctivas, facial edema, and salivation. Acute exposure to low concentrations of hydrazine may cause delayed death (days) and produce bronchial mucous

destruction and pulmonary edema. Liver and kidney damage has also been reported. Hydrazine may cause strong skin irritation. Hydrazine is considered a potential carcinogen by the EPA.[3]

Table 1. Acute Toxicity Values for Hydrazine[4]

Species	Determination	Value
Mouse	Oral LD_{50}	59 mg kg^{-1}
Rat	Oral LD_{50}	60 mg kg^{-1}
Mouse	Inhalation LC_{50} (4 h)	252 ppm
Rat	Inhalation LC_{50} (4 h)	570 ppm
Rabbit	Inhalation LC_{50} (7 months)	0.7 ppm

History/Physical Properties of Hydrazines

Hydrazine, including substituted derivatives, MMH and UDMH, were first isolated and characterized by Fisher as early as 1875.[5] Mass production of hydrazine and hydrazine related compounds started during World War II in support of Germany's rocket research program. Since World War II, the use of hydrazine in the aircraft and space industries has increased dramatically. Hydrazine compounds have also realized extraordinary growth in the pharmaceutical and chemical industry.

A large amount of research has been done on the physical properties of hydrazine and hydrazine compounds. A short list of the properties of the three major hydrazine compounds is shown in Table 2.

Table 2. Physical Properties of Hydrazine and Hydrazine Compounds

Property	Hydrazine (N_2H_4)	Monomethylhydrazine ($CH_3N_2H_3$)	Unsymmetrical Dimethylhydrazine ($(CH_3)_2N_2H_2$)
Molecular Weight	32.04	46.08	60.08
Boiling Point (°C)	113.5	87.5	63
Freezing Point (°C)	2.0	-52.37	-57.2
Flash Point (°C)	52.0	17.2	-15
Flammability Range in Air (Vol. %)	4.7 - 100	2.5 - 98	2 - 95

Industrial Uses of Hydrazine

Several pharmaceuticals including anti-depressant phenelzine and the anti-hypertensive agent hydralazine are derivatives of hydrazine. Hydrazine sulphate itself is undergoing evaluation as a treatment for cancer cachexia.[6] Hydrazines are impurities of a number of agrochemicals, among them the plant growth retardant maleic hydrazide, which is widely used in tobacco and potato cultivation[7], and diaminozide, which is used to delay apple and peanut ripening. Hydrazine compounds have numerous other applications including rocket propellant, reactants in military fuel cells, reducing agent in nickel plating, chain extender in the polymerization of urethanes, water treatment for the removal of halogens, photographic developers, corrosion inhibitor in boiler feedwater, soldering fluxes, and in the manufacture of other drugs and agricultural chemicals. It has also been used as an experimental drug for the treatment of tuberculosis and sickle cell anemia.[8]

METHODS OF ANALYSIS

Several methods have been reported for the determination of trace amounts of hydrazine including spectrophotometric (or colorimetric), titrimetric, potentiometric, conductimetric, coulometric, potentiometric, conductimetric, spectrofluorimetric, and gas and liquid chromatography methods.

Analysis of Hydrazine

Analysis by Colorimetric Methods

Since hydrazine does not absorb in the ultraviolet or visible spectrum, it is

complexed with a variety of different organic compounds. Amlathe and Gupta[9] used a one-step condensation reaction with vanillin forming a yellow color in acidic medium. The absorbance was then measured at 400 nm. The method had a linear range of 0.065 - 0.5 μg mL^{-1}. The effects of different interferents on the determination of hydrazine using their are summarized in Table 3. Later work by Gupta's group used vertraldehyde[10] (3,4-dimethyoxybenzaldehyde) as the complexation reagent. The resulting yellow solution has a maximum absorbance at 410 nm and obeys Beer's law in the range of 0.065 to 0.3 μg mL^{-1} of hydrazine. It has the advantage that it is less susceptible to interferents than vanillin.

Table 3.
Effects of Interferents on the Determination of Hydrazine by condensation with Vanillin

Interferant	Tolerance Limit (ppm) Vanillin	Tolerance Limit (ppm) Veratraldehyde
PO_4^{3-}	3000	30000
Br^-, Cl^-, SO_4^{2-}	1000	10000
Ca^{2+}, Ba^{2+}, Sr^{2+}	1000	10000
Cu^{2+}, Cd^{2+}	200	2000
Fe^{2+}	100	1000

Manes *et. al.*[11] described an extraction-spectrophotometric method for the determination of hydrazine based on its reaction with 2-hydroxy-1-naphthaldehyde to form a water-insoluble yellow aldazine, 2,2'-dihydroxy-1-naphthaldazine. The procedure was very time consuming, including twenty minutes of heating and an organic extraction in chloroform prior to measuring the complex's absorbance at 412 nm. It, like most of the colorometric methods, had interferences from ions such as Cu (200 μg/mL), NH_4^+ (100 μg/mL), and Fe/Mn (10 μg/mL). Pal *et. al.*[12] developed a method of determining hydrazine using a silver-gelatin complex through a one-step reduction process as the reduction of silver(I) by hydrazine proceeds to produce a silver sol stabilized by gelatin. The process required a 30 minute reaction time and had limited linear response (0.65 - 2.62 μg/mL). A summary of the different methods utilizing visible spectroscopy are summarized in Table 4.

We tested several of the colorimetric methods of determining hydrazine a found them to be inadequate both in detection limit and in linear range. A calibration curve (Figure 1) for the

veratraldehyde complex is a perfect example of why we did not choose a colorimetric analysis for this work.

Table 4.
Comparison of Different Spectrophotometric Methods

Complexation Reagent	Linear Range (ppm)	Molar Absorptivity ($l\ mol^{-1}\ cm^{-1}$)	Time for Development (min)	Remarks
p-Dimethylamino-benzaldehyde[13]	0.06 - 0.77	-	-	Semicarbazide/urea interfere, reagent unstable
Salicyladlehyde[14]	0.29 - 1.25	2.38×10^4	15	-
Silver-gelatin[15]	0.65 - 2.62	4.2×10^4	30	Reagent unstable
2-Hydroxy-1-naphthaldehye[16]	0.035 - 0.7	2.7×10^4	20	Reaction at 100°C
Picryl Chloride[17]	1 - 30	-	-	Many Interferents
Vanillin[18]	0.065 - 0.50	5.25×10^4	10	Stable Reagent
Veratraldehyde[19]	0.065 - 0.30	6.72×10^4	10	Stable Reagent
Copper(III)-neoalproline[20]	0.2 - 1.6	-	10	Less Sensitive

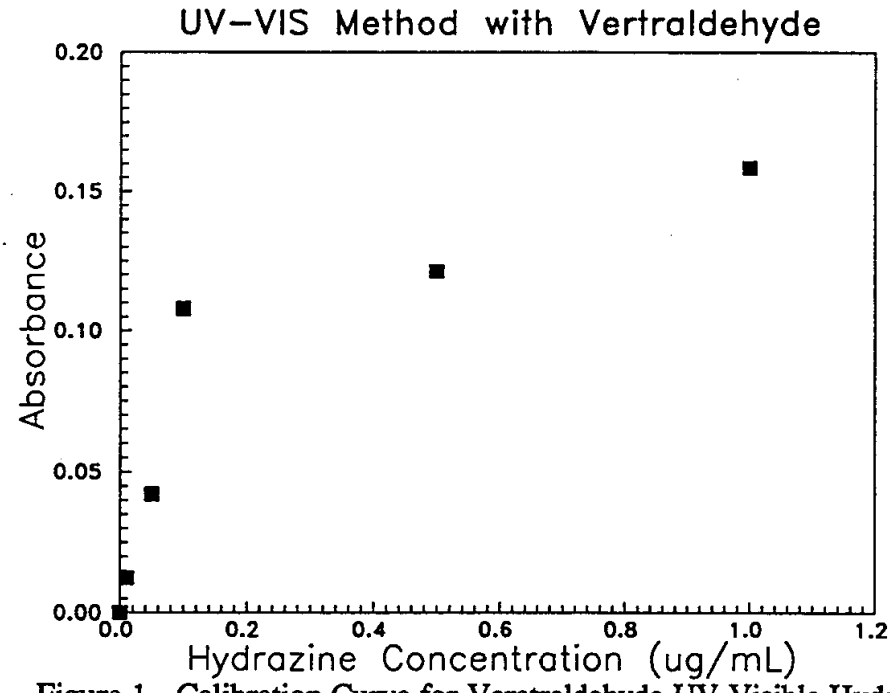

Figure 1. Calibration Curve for Veratraldehyde UV-Visible Hydrazine Determination

Analysis by Gas Chromatography with Nitrogen Sensitive, Electron Capture, and Mass Spectrometric Detection

Matsui *et. al.*[21] derivatized hydrazine with benzaldehyde to form benzalazine which was detected using a nitrogen-phosphorus alkali thermionic detector and a coiled-glass column packed with 2% OV-101 on Chromsorb. The instrument temperatures were: injector port, 275°; column, 250°; and detector, 300°. The hydrazine was reacted with the benzaldehyde and extracted with n-heptane, which was free of interfering impurities and was a good solvent for the internal standard (5-chloro-2-methylaminobenzophenone). Contaminant with the formation of benzalazine in the derivatization step is the formation of a hydrazone from the condensation of hydralazine with benzaldehyde. This compound is not separated from benzalazine by extraction and appears at 4.3 and 8.1 min, well after the appearance if benzalazine and the internal standard at 1.2 and 1.6 min, respectively.

Gyllenhaal *et. al.*[22] also used benzaldehyde derivatization for the determination of hydrazine in a drug matrix of hydralazine. After extraction into an organic phase containing a homologue as an internal standard (4-fluorobenzalazine), the sample is subjected to capillary column gas chromatography with nitrogen-selective detection. The fused-silica column (25m X 0.32 mm ID) was coated with SE-54 (0.25 μm). The instrument temperatures were 280°C, detector 300°C, and oven 100°C (1 min), increased at 15°C min^{-1} to 285°C.

Preece *et. al.*[23] used gas chromatography with electron capture, nitrogen phosphorus, and mass spectrometric detection following derivatization of the hydrazine with pentafluorobenzaldehyde. Typical conditions for GC-NPD were 12 m X 0.22 mm ID OV-1 bonded phase of 0.25 μm, isothermal (140°C) with injection temperature of 300°C, detector temperature, 350°C, and helium (1 mL min^{-1}) as the carrier gas. Similar conditions were used for the GC-ECD. GC-MS-SIM was performed using an identical column but the temperature program was 35°C for 3 min, then ramped to 180°C at 20°C min^{-1}. Detection limits for the different detectors were as follows: NPD - 100 ng nitrogen atoms s^{-1}, ECD - 1 ng of fluorine atoms s^{-1}, and the quadrupole mass spectrometer with undetermined but superior detectivity. Schaller and Lewalter[24] also complexed hydrazine and other hydrazine containing compounds using pentafluorobenzaldehyde with ECD detection. Their detection limit for hydrazine using this method was 2 μg L^{-1}. No interferences from other primary amines, ammonia, urea, and other urinary compounds could be detected.

Analysis by High Performance Liquid Chromatography

Shustina and Lesser[25] complexed hydrazine with benzaldehyde by reacting it for 30 min in a 70°C constant temperature bath. The mobile phase was an acetonitrile-buffer (45:55) flowed at 2.0 mL min^{-1}. The buffer was prepared by adding 13.6 g of potassium dihydrogen phosphate that was adjusted to pH 7.0 with a few drops of potassium hydroxide. Detection was at 310 nm but the hydrazine derivative's maximum absorbance was at 301 nm. The detection limit under these conditions was 17 ppb at a signal-to-noise ratio of 3. Kester and Danielson[26] determined hydrazine and 1,1-dimethylhydrazine after derivatization with salicylaldehyde was done using HPLC with electrochemical detection. A mixture of 55% CH_3CN/45% H_2O gave the optimum separation between both hydrazine derivatives and salicylaldehyde. The detection limits for hydrazine and 1,1-dimethylhydrazine solutions were estimated to be 0.025 and 0.20 ppm, respectively.

George and Stewart[27] developed a method that complexed hydrazine with salicylaldehyde with subsequent UV detection at 209 nm. The lower wavelength was chosen due to its increased absorptivity by a factor of five than that at 254 nm. The procedure required no extraction and concentration steps nor an internal standard. The detection limit was 10 ppm based upon 100 mg of phenelzine sulphate. Absorbance and hydrazine concentrations are linear over the range of 10-1000 ppm. A 60/40 mixture of CH_3CN/phosphate buffered water was used as the mobile phase with a 15 cm C-18 column.

Jackson and Kahler[28] determined low concentrations of hydrazine in sulfuric acid by the precolumn formation of benzalanin from hydrazine using benzaldehyde, followed by reversed phase separation and UV absorption detection at 313 nm. The detection limit was 2 ppb at a 2X signal-to-noise.

More recently, the use of electrochemical detection techniques have begun to be examined for hydrazine determinations without preliminary derivatization. Such approaches employing the direct oxidation of the hydrazine functionality have been limited by the fact that most simple hydrazines undergo oxidation at conventional electrode surfaces only at a substantial overpotential. Fiala and Kulakis[29] employed a glassy carbon electrode maintained at +1.0 V vs. Ag/AgCl were able to achieve sensitivities only slightly improved over those obtained via salicylaldehyde derivatization/UV detection and significantly poorer than the sensitivity usually characteristic of the amperometric detection approach. Ravichandran and Baldwin[30] used a pretreated glassy carbon electrode for the direct determination of hydrazine. Electrochemical

pretreatment of the electrode by initial application of brief anodic and cathodic potentials shifted the oxidation waves observed for hydrazine and its monomethyl and dimethyl derivatives to potentials 0.2-0.8 V lower than those required at untreated glassy carbon surfaces. When employed as amperometric sensors following liquid chromatographic separation of the hydrazines, detection limits from 2 to 50 pmol injected were obtained with an applied potential of + 0.50 V vs. Ag/AgCl. At higher hydrazine concentrations, sufficiently selective response was obtained at detector potentials as low as + 0.10 V that no sample treatment was required for quantitation of 1,1-dimethylhydrazine in urine at the 125-pmol level.

Analysis by Titrimetric Methods

Burns and Lawler[31] used potentiometric and photometric end point determination of mixtures of hydrazine and 1,1-dimethylhydrazine after complexation with salicylaldehyde. The two-step equilibria of crystal violet indicator in glacial acidic acid produced a sharp endpoint.

Budkuley[32] used differential titration for the determination of hydrazine. For compounds containing hydrazine, the Andrews titration with iodate is generally used, but fails for compounds such as $(N_2H_5)_2SO_3$. During an investigation of the reaction between hydrazine hydrate and gaseous sulphur dioxide and of the $N_2H_4 \cdot H_2O$-SO_2-metal ion system, it was found that this apparent source of error could be turned to an advantage, since the sulphur species can be determined by oxidative titration with iodine under appropriate conditions, and the hydrazine content by difference from the sum of hydrazine and sulphur species determined by Andrews titration. The relationship of 1 mL of 0.025 M KIO_3 being equal to 0.801 mg of N_2H_4 was determined. This method, although simple, is not very sensitive, only allowing determinations in the mg range.

Verma *et. al.*[33] used a bromine chloride titration for the determination of hydrazine and its organic derivatives. On treatment of the sample with an excess of the reagent, the reaction is complete within a minute; the residual reagent is back titrated to determine the hydrazine concentration. The hydrazine reacts as follows:

$$NH_2NH_2 + 2BrCl \rightarrow N_2 + 2HBr + 2HCl$$

The detection of hydrazine and its derivatives using this method is 0.1 - 0.3 mmole.

Nair *et. al.*[34] used bromamine-T, the sodium salt of N-bromo-*p*-toluene sulfonamide. Again the hydrazine was reacted with excess reagent and back titrated to determine the amount of hydrazine in the solution.

Analysis by Ion Chromatography

Hydrazine was determined by Gilbert *et. al.*[35] using ion chromatography with an electrochemical detector, similar to the method used in this work. The mobile phase used was 0.003M HCL + 0.0025 M L-lysine at a flow rate of 0.77 mL/min. The detection limit was 1 ppb using a 100 μL injection. The solution they were examining contained Na, NH_3, K, C_4H_9NO, and $C_6H_{11}NH_2$, none of which were detected using the electrochemical detector.

Ion chromatography was used in this study for several reasons. First, the linear range for hydrazine was five orders of magnitude--much better than any of the colorimetric methods. Second, the detection limit was much lower than any of the colorometric methods, about 1 ppb with a 10 μL sample loop. Third, it required no derevitization like the colorometric, gas chromatographic, or high performance liquid chromatography methods. We used an Dionex 500 series ion chromatography with a CG-12 column and a ED40 electrochemical detector, measuring with a platinum electrode amperometrically. Fourth, little if any interferences were found using ion chromatography, unlike many of the other methods described previously. A example of a typical calibration curve is shown in Figure 2. Comparing this to Figure 1 the detection limit is two orders of magnitude better and the calibration is linear over five orders of magnitude.

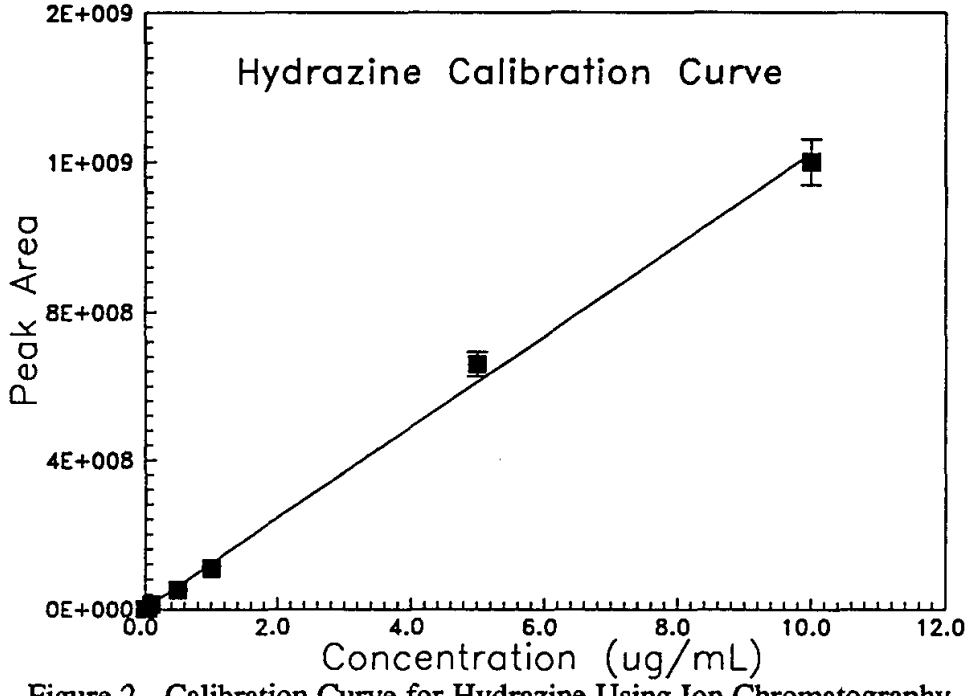

Figure 2. Calibration Curve for Hydrazine Using Ion Chromatography

Analysis of Monomethyl- and Unsymmetrical Dimethylhydrazines

There is much less literature on the detection of monomethyl and unsymmetrical dimethylhydrazine compounds than on hydrazine compounds. Bailey and Medwick's[36] spectrophotometric method could be used for both hydrazine and 1,1-dimethylhydrazine, but attempts to adapt the method of analysis to other methylated hydrazine derivatives such as methyl hydrazine were unsuccessful. Later work by the same group[37] was able to detect both hydrazine and unsymmetrical dimethylhydrazine in mixtures using high performance liquid chromatography using the same derivative formation.

Mach and Baumgartner[38] explored the degradation of unsymmetrical dimethylhydrazine (UDMH) using gas chromatography with a thermal conductivity detector. They found that by using a molar excess of $Ca(OCl)_2$ led mainly to the formation of formaldehyde dimethylhydrazone and tetramethyl tetrazene but not to N-nitrosodimethylamine (NDMA). Using the copper sulfate/hydrogen peroxide method led to the formation of approximately 25% NDMA. It was also shown that the order of addition of the H_2O_2 and $CuSO_4$ significantly affected the amount of UDMH that was destroyed in the reaction. When copper was added first, only 65% of the UDMH was destroyed, but if the peroxide was added first, 100% of the UDMH

was destroyed.

Environmental Fate of Hydrazine

Aqueous Systems

A variety of environmental, chemical, and biological factors are involved in determining the rate and extent of degradation of hydrazine and hydrazine-containing compounds. Environmental and chemical factors include air temperature, humidity, moisture, availability of oxygen and nutrients, soil or water pH, and the chemical composition of the surrounding environment. Although the interaction of hydrazine with the environment depends on many factors, the absence of catalysts enables the fuel to remain remarkably stable. In aquatic as well as in soils and clays environments, the organic content is a major contributing factor in degradation.

Research into the degradation effects of different compounds on hydrazine has been extensive. Moliner and Street[39] studied the effect of ionic strength, copper concentration, and phosphate concentration on hydrazine degradation in aquatic systems. Their results show that the rate of hydrazine degradation increased proportionally to the concentration of copper II and phosphate added to the solution. They determined the primary pathway of hydrazine in their aqueous solutions as:

$$N_2H_4 + O_2 \rightarrow N_2 + 2H_2O$$

and that this reaction is catalyzed by the addition of copper or phosphate ions, apparently through the abstraction of an H^+ from the hydrazine molecule:

$$Cu^{2+} + N_2H_4 \rightarrow Cu^+ + N_2H_3 + H^+$$

Small amounts of ammonia were also detected, probably as a result of a side reaction:

$$2N_2H_4 + \tfrac{1}{2}O_2 \rightarrow N_2 + 2NH_3 + H_2O$$

Similar work was completed by Braun and Zirrolli[40] showed that the rate of aqueous degradation depended upon metal ion catalysts, aeration, the organic matter, ion concentration, and the temperature of the water. They concluded that despite their energetic properties, hydrazines are remarkably stable in uncatalyzed aqueous solutions with a half-life ranging from 10 to 14 days. Dissolved oxygen extensively degrades hydrazines at high pH values.[41] At 1.8 mM in pond water, hydrazine was degraded by 20% after one hour, 74% after one day and 80% after two days. Under similar conditions, river water with a higher organic content showed 100% degradation after two days.[42]

Street and Moliner[43] studied the effect of copper concentration on hydrazine degradation. They found that during the preparation of their solutions of copper and hydrazine that a greenish precipitate formed at copper concentrations as low as 0.015 mmol/L of Cu, presumably from the formation of the Cu^{+} from Cu^{2+}. As long as an adequate supply of oxygen was available, the copper caused rapid degradation of the hydrazine. Temperature was also found to play a major role in the degradation with warmer temperatures increasing the degradation rate. Copper/clay solutions were found to degrade slower than the copper alone, possibly due to the reduced activity of Cu in the presence of clay.

Soils and Clays

Hayes *et. al.*[44] reported that at pH 4 hydrazine sorption was greatest for Na-clays because the process involved simple ion exchange of Na^{+} for the hydrazinium ($N_2H_5^{+}$) ions. In a study with humic acid preparations at pH 4, Isaacson and Hayes[45] found that hydrated hydrazine was more extensively held by H^{+}-saturated humic substances than by Ca^{2+}- or Al^{3+}-saturated humic substances. The polarity of the N-H bond also allows the hydrazine to form hydrogen bonds with electronegative groups on the surfaces of the clays and organic matter. Davis *et al.*[46], using diffuse-reflectance spectroscopy, found the primary surface-hydrazine interaction with silica, silica-alumina, and alumina surfaces was via hydrogen bonding. Ion exchange and hydrogen bonding are not the only processes occurring in soil samples. In addition, unprotonated hydrazine is a strong nucleophile that can take part in condensation reactions with carbonyl groups in humic substances, to form hydrazone.[47] Hydrazine can also be oxidized (metals reduced) by metals such as Fe^{3+}, Cu^{2+}, and Mn^{3+}, which are widely found in soils.

Moliner and Street[48] studied the absorption of hydrazine into various soil and clay samples. They calculated the amount of hydrazine absorbed as the difference between the amount of hydrazine added and the amount left in the supernatant after equilibrium with the suspension based on their assumption that the disappearance was due solely to absorption and not to any catalytic breakdown of hydrazine by other components of the clays and soils. To support this absorption only hypothesis, they plotted the Na released as the hydrazine was added and absorbed. At pH 4.0 in kaolinite clay up to 4 mmol L^{-1} the hydrazine absorbed and the Na released were almost identical.

When released onto the soil, hydrazine is expected to undergo rapid degradation owing to its high reactivity, especially in soils with a high organic content. In sandy soils or soils with a low organic content, hydrazine may leach to the groundwater. In clay soils, hydrazine is

expected to absorb strongly. Owing to its inherent bacterial toxicity, biodegradation from spills is not expected to be significant but may become important at the lower concentration levelsOther researchers demonstrated that the degradation of hydrazine is proportional to the pH of the system, and enhanced in the presence of heterogeneous surfaces of K^+, Na^+, Mg^{2+}, and Ca^{2+} through homoionic exchange.[49]

Transition metals, whether in aqueous solution or contained within the soil, have been shown to catalyze the degradation of hydrazines. These catalysts can function in the absence of oxygen when the metals act as one or two electron acceptors. Experimental work by Lurker[50] showed that except for Cu^{2+}, the concentrations of transition metals occurring in natural waters was not high enough to catalyze the degradation of hydrazine. Clays containing Cu^{2+}, Mn^{2+}, and Fe^{3+} catalyze the degradation of hydrazine in redox reactions, but the degradation is most rapid with Cu^{2+}. Hayes believed that the soil sorption of hydrazine was largely dependent on humic acids, and that once bound, most of the hydrazine could not be removed.

Hydrazine complexation with different clays is also a pathway of disappearance in the environment. Griffith *et al.*[51] using Mossbauer spectroscopy, showed that hydrazine not only reduced Fe^{3+} in montmorillonitic clay and humic acids but it also complexed with it. Cation exchange at lower pH values in soils and clays was studied by Moliner and Street.[52] At the lower pH values, hydrazine exists as $N_2H_5^+$ and is able to exchange with Na^+ or H^+ at different sites in the different clays and soils examined.

Bioremediation of Hydrazine

Bioremediation of high concentrations of hydrazine is highly unlikely due to its toxicity. Lower concentrations have been degraded using the bacterium *Nitrosomonas*. In the presence of *Nitrosomonas*, the rate at which hydrazine was oxidized was doubled.[53] Organisms which can tolerate hydrazine usually develop mechanisms to endure, but the process results in an extended lag period of growth.[54] Kane and Williamson[55] state that hydrazine concentrations typically associated with hydrazine wastewater would require a dilution of at least 100 to 1 in order to achieve biological degradation.

Spill Degradation

Degradation of hydrazine spills has been attempted using several different methods. The chemical oxidation of hydrazine has been studied for well over 80 years, and more recently, the

oxidation of the methylated hydrazines has also been studied experimentally in both the liquid and the gas phase. Hydrazine and methylated hydrazines have been reacted with hypochlorite, a strong oxidizer, to degrade large quantities of pure hydrazine. Drawbacks to this method include the production of nitrosamines as methyl hydrazine by-products which are known carcinogens. The chemical oxidation of hydrazine itself is often quantitative but studies of the oxidation of methylated hydrazine fuels have shown that these reactions are rarely, if ever, quantitative and that a wide variety of partial oxidation products are usually formed. Because oxidation of methylated hydrazines is often incomplete, there is some reason for concern regarding the use of chemical neutralization procedures before the disposal of these fuels. Brubaker *et al.* studied the nitrosamine products formed from the hypochlorite reaction of mono-methyl and unsymmetrical dimethyl hydrazine.[56] Normal degradation of hydrazine can be achieved through interaction with its environment, including with oxygen and water as shown in equations (1) and (2):

$$N_2H_4 + O_2 \rightarrow N_2 + 2H_2O \quad (1)$$

$$N_2H_4 + H_2O \rightarrow NH_4OH + N_2 + H_2 \text{ (pH dependent)} \quad (2)$$

The Background of Diazoluminomelanin (DALM)

Diazoluminomelanin (DALM) is a polyanionic polymer produced from the diazotization of 3-amino-L-tyrosine and luminol. Bacteria that contain nitrate reductase can form the polymer on their plasma membranes (presumably at the site of the nitrate reductase) in medium containing nutrients, 3-amino-L-tyrosine, luminol, and nitrate. The bacteria experience accelerated growth followed by death from the production of the polymer. Certain *Bacillus* species, *E. coli* strain K-12, and a nitric oxide reductase negative strain of *Pseudomonas stutzeri* produce copious amounts of the polymer in large mass culture. The bacteria containing the polymer can be heat killed (including autoclaving) and dried (air or lyophilization) to yield a partially oxidized stabilized product. This material can be activated with a small amount of hydrogen peroxide (about 0.003%) and sodium carbonate or bicarbonate solution (mM range) and/or exposure to sunlight or long wavelength UV (360 nm). The DALM produces self-sustaining redox cycling based upon the endogenous content of reductant, oxygen, and carbon dioxide. The carbon dioxide reversibly binds to the DALM and cycles through the formate radical (a redox potential of -0.420 V at pH 7.0). Photochemical reactions can drive this redox chemistry. Copper ions and other transition metal ions are bound to the DALM. Copper ions are especially active in facilitating the free radical reaction of DALM. DALM itself is a very resistant polymer, being resistant to

strong acids and bases and being fragmented only by aqua regia. DALM is very much more photochemically and oxidatively active than melanin and other humic acids and may be the only one of the group capable of cycling carbon dioxide. DALM also binds nearly irreversibly to silica and can be immobilized on fluidized magnetite for magnetic manipulation (dispersal and recovery).[57]

RESULTS AND DISCUSSION

The Degradation of Hydrazine using DALM + Transition Metals in Aqueous Solutions

The goal of this project was to evaluate different compounds and combinations of compounds, especially DALM, as to their ability to degrade hydrazine in an aqueous environment. The experiment consisted of spiking known quantities of hydrazine (usually 10 μg/mL) into 100 mL of deionized water. Known quantities of different compounds including DALM, copper, iron, manganese, nickel, $KMnO_4$, H_2O_2, and clay were added to the solution. Samples were immediately taken and analyzed by the previously described ion chromatography method. Samples containing soluble species, such as the copper sulfate, were loaded into the ion chromatograph's autosampler. Samples were taken every 7 minutes for the first 4 hours and then every 30 minutes thereafter until 24 hours. Samples from the remaining solution were injected every 24 to 48 hours thereafter until the sample solution was exhausted or the hydrazine was undetectable on three successive measurements.

DALM Alone

DALM itself was shown to degrade the hydrazine, even at levels as low as 10 μL in 100 mL as shown in Figure 3. The initial concentration of this solution was 10 μg/mL but even before the first sample could be analyzed (approximately 10 minutes), the concentration had already dropped to approximately 1 μg/mL. The sample spiked with 10 μL of DALM immediately showed a degradation of 90% of the hydrazine but in the hours following the solution's hydrazine concentration showed no additional degradation remaining at a constant 1 μg/mL. The 50 and 100 μL DALM spikes showed similar rapid degradation but unlike the 10 μL spike of DALM, continued to degrade the hydrazine until after approximately 330 hours where there was no detectable levels of hydrazine in the either the 50 or 100 μL spikes. An additional analysis after this time found hydrazine levels very near the detection limit of 10 ppb.

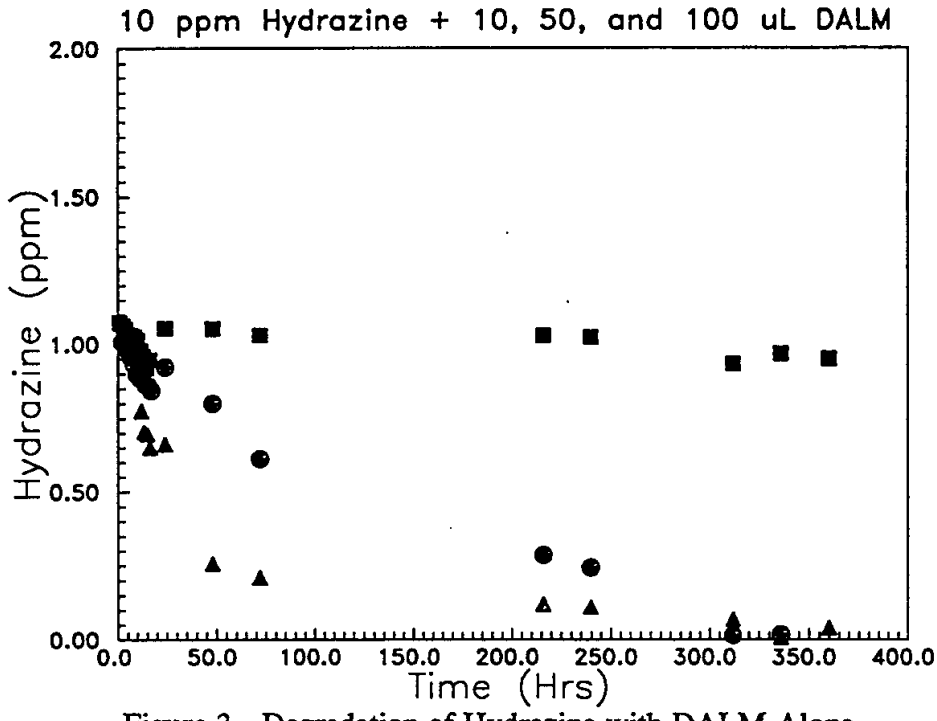

Figure 3. Degradation of Hydrazine with DALM Alone
■ 10 μL DALM, ● 50 μL DALM, ▲ 100 μL DALM

H_2O_2 Alone

Hydrogen peroxide is known to degrade hydrazine through the following pathway:

$$H_2O_2 + N_2H_4 + \frac{1}{2}O_2 \longrightarrow N_2 + 3H_2O$$

In this study hydrogen peroxide was spiked in at three times the level of the hydrazine in an attempt to push the equilibrium towards the degradation of the hydrazine. As shown in Figure 4 and further in Figure 5 the degradation rate was actually slower than that of the DALM-spiked solutions. The initial degradation of hydrazine was rapid from 10 to 4 μg/mL in just over one hour. Subsequent degradation was much slower, and hydrazine could be detected even after 500 hours of exposure to the peroxide-containing solution.

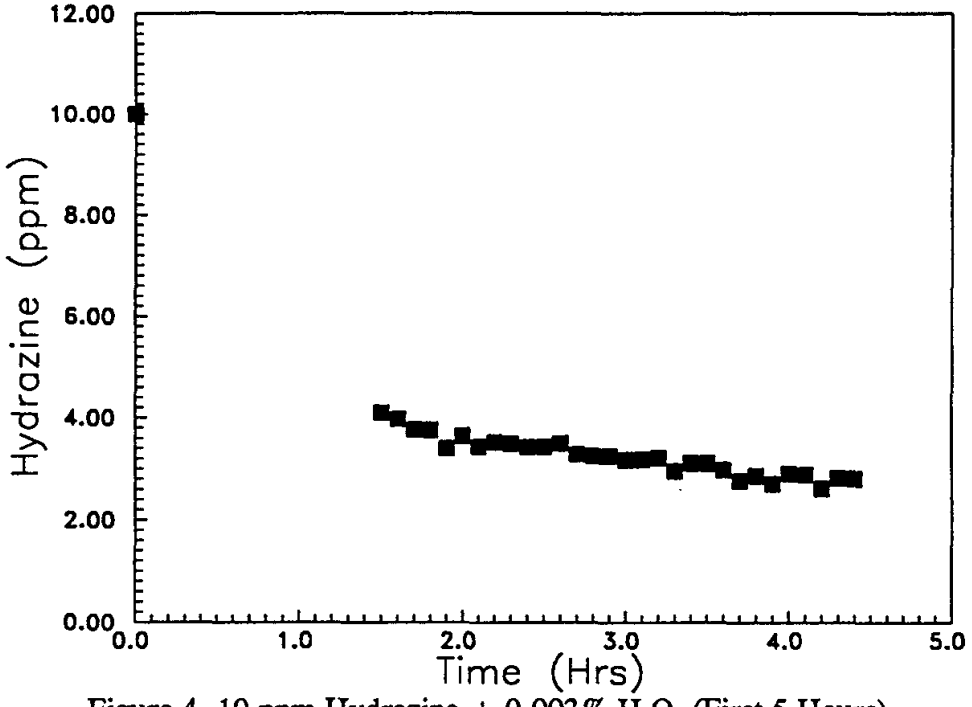

Figure 4. 10 ppm Hydrazine + 0.003% H_2O_2 (First 5 Hours)

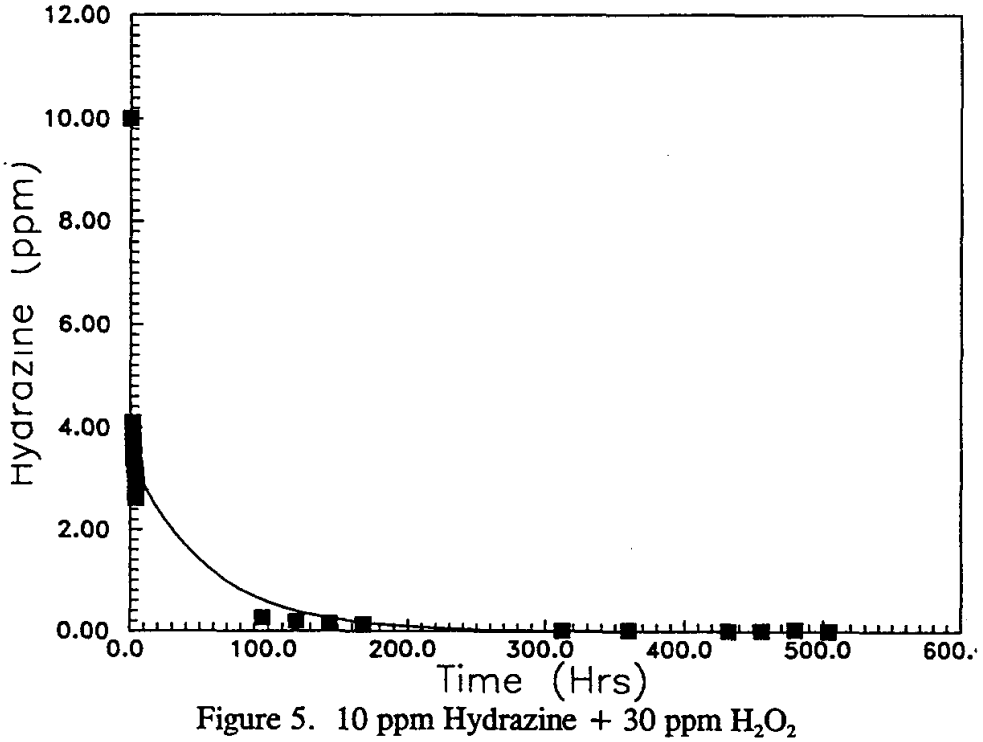

Figure 5. 10 ppm Hydrazine + 30 ppm H_2O_2

Clay Alone

Clay has been shown to trap the hydrazine through ion exchange. Clay was studied as a possible medium for trapping the hydrazine, thereby reducing the risk of the contamination spreading and allowing the use of the DALM to degrade the hydrazine. The clay used, a commercial kitty litter, bound the hydrazine but did little to degrade the hydrazine. One, five, and ten grams of clay were added to 100 mL of a 10 ppm hydrazine solution. Aliquots were taken from each and analyzed a specific time intervals as shown in Figure 6. The more clay in solution, the lower the measured hydrazine level was, remaining between 1 and 2 ppm/mL. At this point it appears an equilibrium was set up, since the hydrazine level remained constant for over 150 hours. Additional water was added to the clay when all but 20 mL of solution had been used for analysis. This is shown as the drop from 1-2 ppm to one-fifth that value as the solution was once again diluted to 100 mL. Hydrazine could still be detected after almost 700 hours (28 days) when the study of the clay itself was stopped. Clay's ability to trap the hydrazine could be used to absorb liquid hydrazine spills and subsequent basic washes could be used to remove the hydrazine from the clay for subsequent degradation in an aqueous medium.

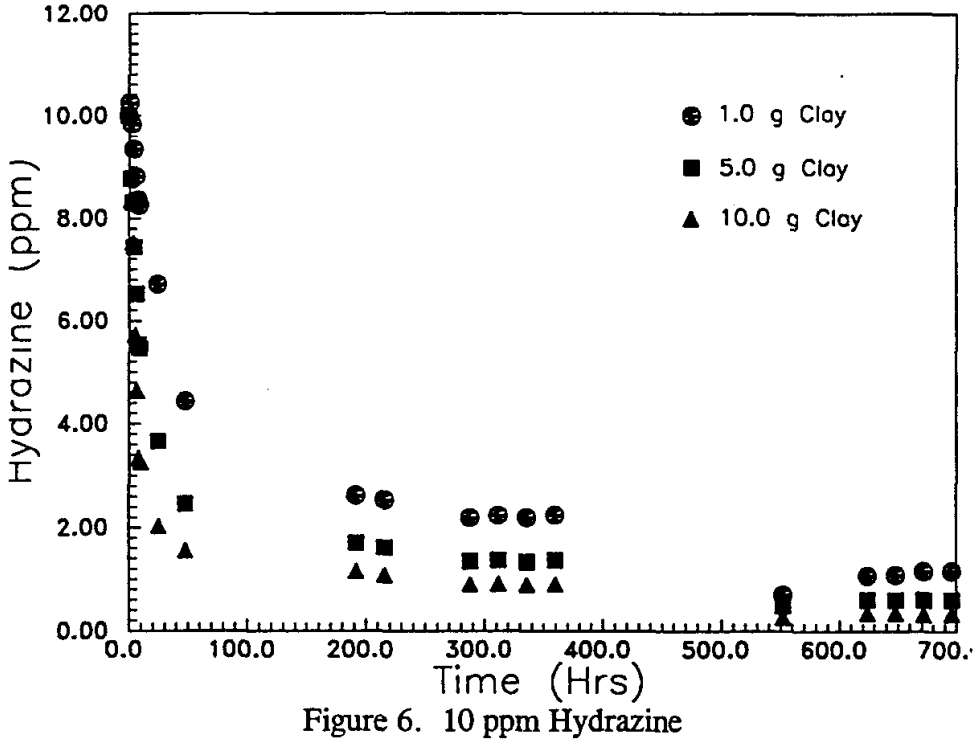

Figure 6. 10 ppm Hydrazine
+
Various Amounts of Clay in 100 mL H_2O

Transition Metals Alone

Transition metals, especially copper compounds, catalyze the degradation of hydrazine. In this study, several transition metals including copper, iron, manganese (both as manganese sulfate and potassium permanganate), and nickel were studied at various concentrations to determine their effects on catalyzing the degradation of the hydrazine. Copper was the first to be tested. As shown in Figure 7, the copper (as copper sulfate) reduced the concentration of the hydrazine to zero in less than four hours. The level of copper used was a concern (0.001M), because replacement of the hydrazine contamination with heavy metal contamination is undesirable. A second experiment using even higher concentrations of copper showed a different trend in hydrazine degradation--the increased concentrations actually slowed the rate of degradation and pointed to the possibility of an optimum copper concentration at lower levels, not higher. The results of this study are shown in Figure 8.

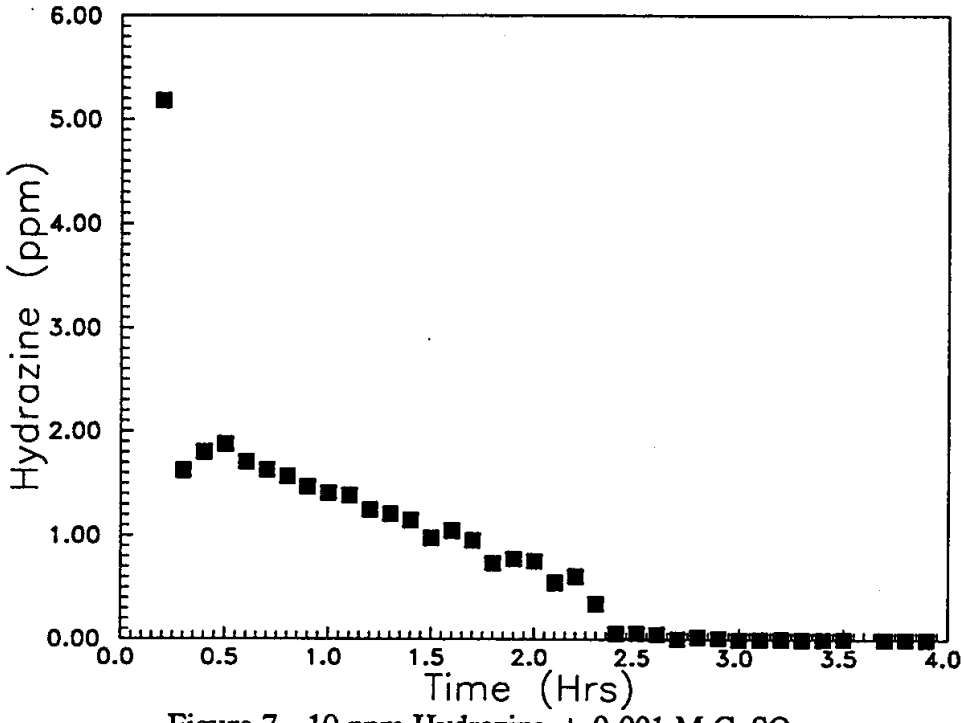

Figure 7. 10 ppm Hydrazine + 0.001 M $CuSO_4$

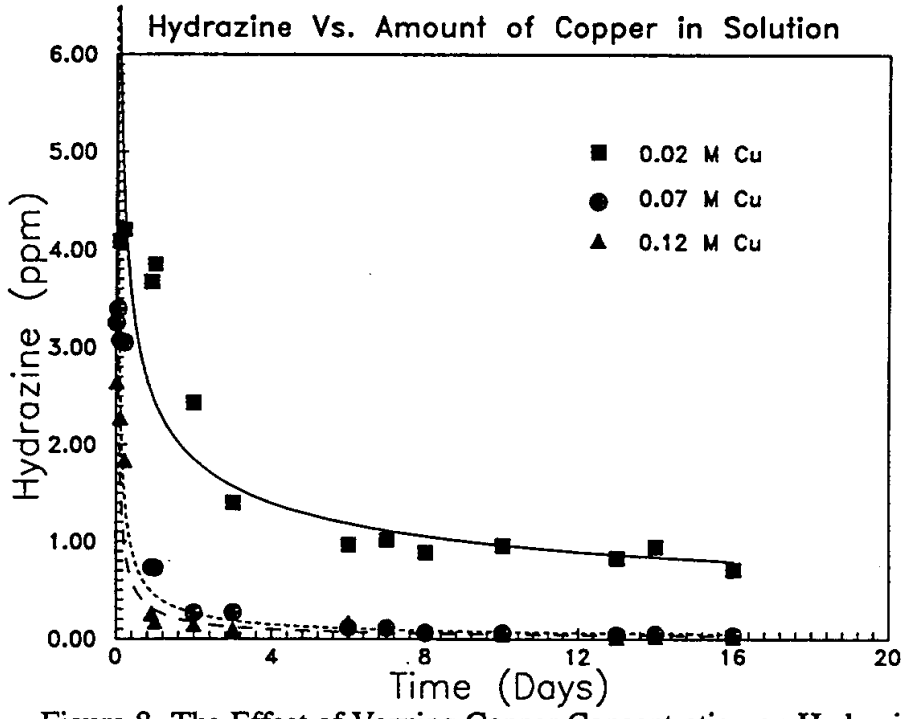

Figure 8. The Effect of Varying Copper Concentration on Hydrazine Degradation

Iron(III) was the next transition metal tested and had a much slower rate of degradation than the copper at the same relative concentration. Even after 300 hours, over 40% of the original hydrazine was left in solution as shown in Figure 9.

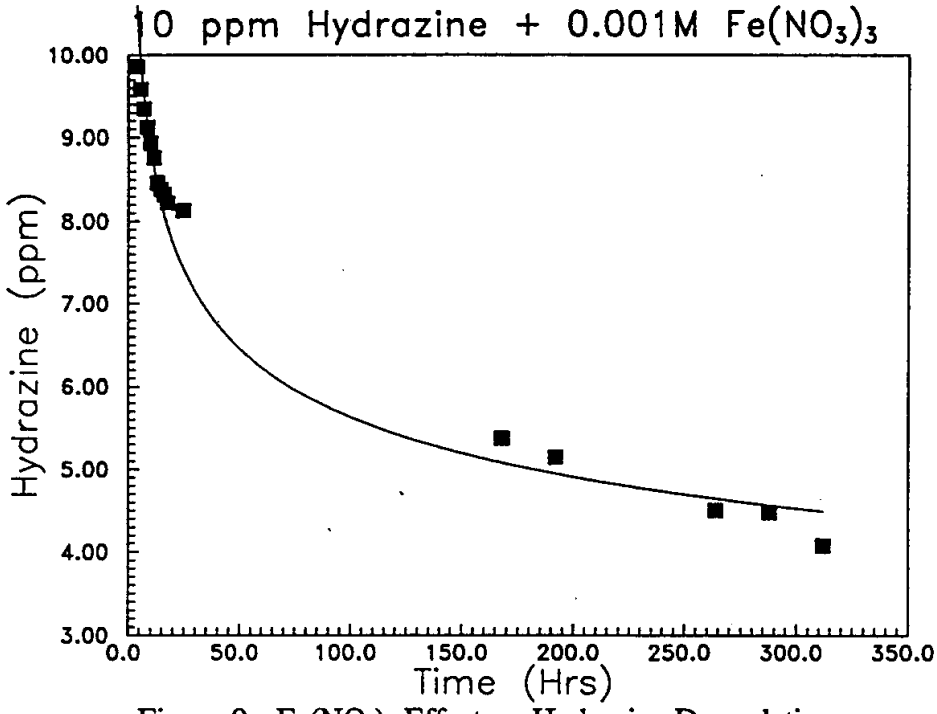

Figure 9. $Fe(NO_3)_3$ Effect on Hydrazine Degradation

Manganese compounds were tested with interesting results. $KMnO_4$ in which manganese is in the +7 oxidation state, degraded the hydrazine very quickly with the loss of the traditional purple color. Figure 10 shows that the hydrazine was completely degraded in under five hours. $MnSO_4$, in which Mn is in the +2 oxidation state, was somewhat slower, but still the hydrazine was completely gone within 24 hours (Figure 11). This difference in degradation rate with the higher the oxidation state causing the more rapid degradation was also seen in iron where Fe(III) degraded hydrazine much quicker than Fe(II).

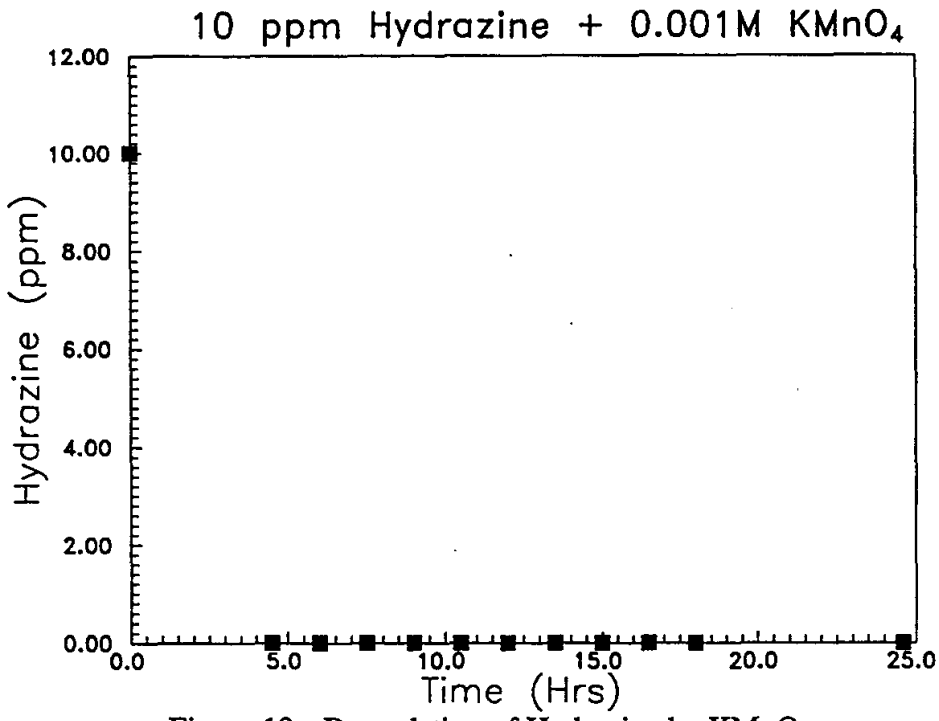

Figure 10. Degradation of Hydrazine by $KMnO_4$

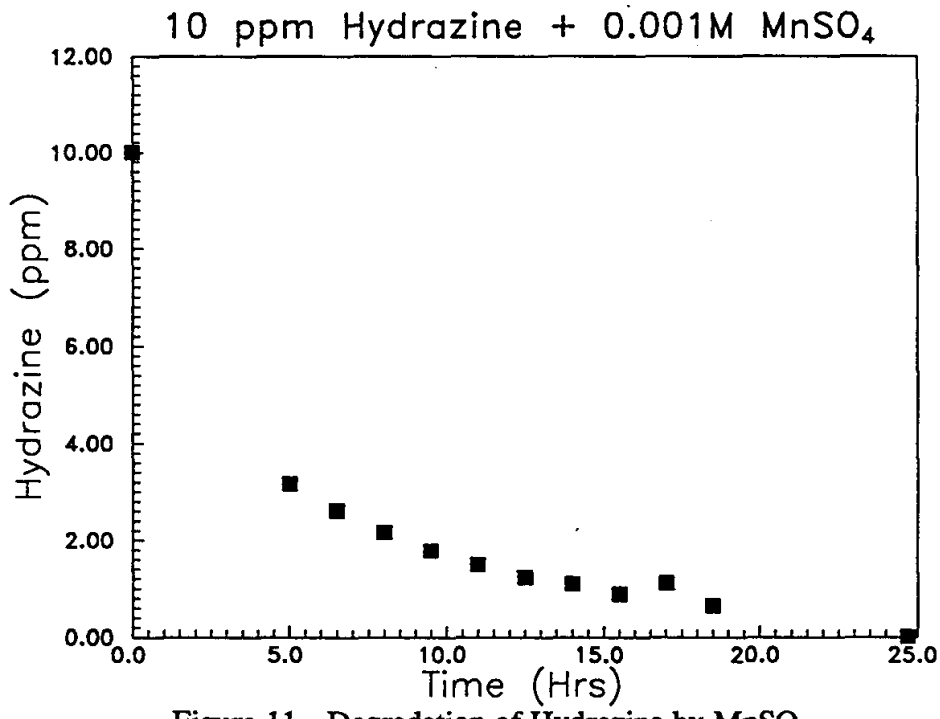

Figure 11. Degradation of Hydrazine by $MnSO_4$

Nickel was also tested to determine its ability to catalyze to oxidation of hydrazine and is shown in Figure 12. Nickel's results were very similar to that of copper, reducing the concentration of

hydrazine to zero in just over three hours. Again, the concentration of nickel used, 0.001M, was a major concern. Lower levels of nickel were not explored, due to time constraints.

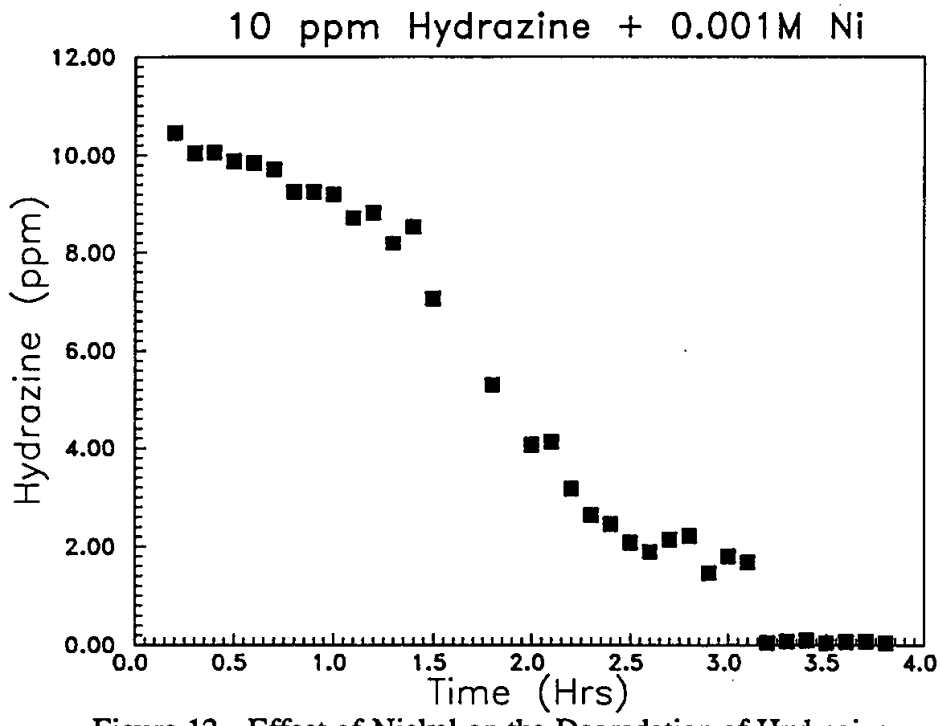

Figure 12. Effect of Nickel on the Degradation of Hydrazine

Use of Chemical Mixtures in Hydrazine Degradation

Once individual compounds were shown to degrade hydrazine in solution, mixtures were attempted to see if an even better degradation medium could be found using the effects of two or more compounds. Since DALM was the focus of this study, it and other compounds were tested first. Figure 13 shows the degradation rate a hydrazine with $NaHCO_3$ and $NaHCO_3/H_2O_2$ added to the DALM. The addition of either $NaHCO_3$ or $NaHCO_3/H_2O_2$ reduced the rate of hydrazine disappearance as compared with Figure 3.

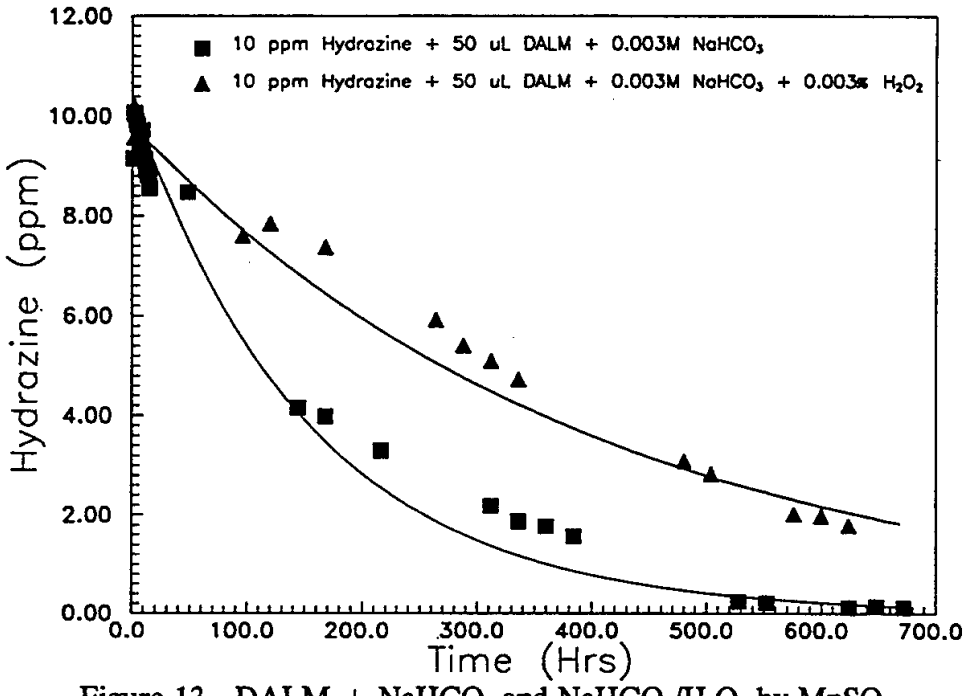

Figure 13. DALM + $NaHCO_3$ and $NaHCO_3/H_2O_2$ by $MnSO_4$

DALM was next tested with copper since that metal ion had shown excellent degradation results. Figure 14 shows the effect of clay as a trap for the hydrazine in aqueous solutions. The 10 ppm hydrazine solution had 100 ppm copper sulfate and 50 μL DALM added. It is interesting to note that the optimum concentration of clay in this case is 2.0 grams/100 mL of solution and that more clay did not help in reducing the level of hydrazine found in the solution.

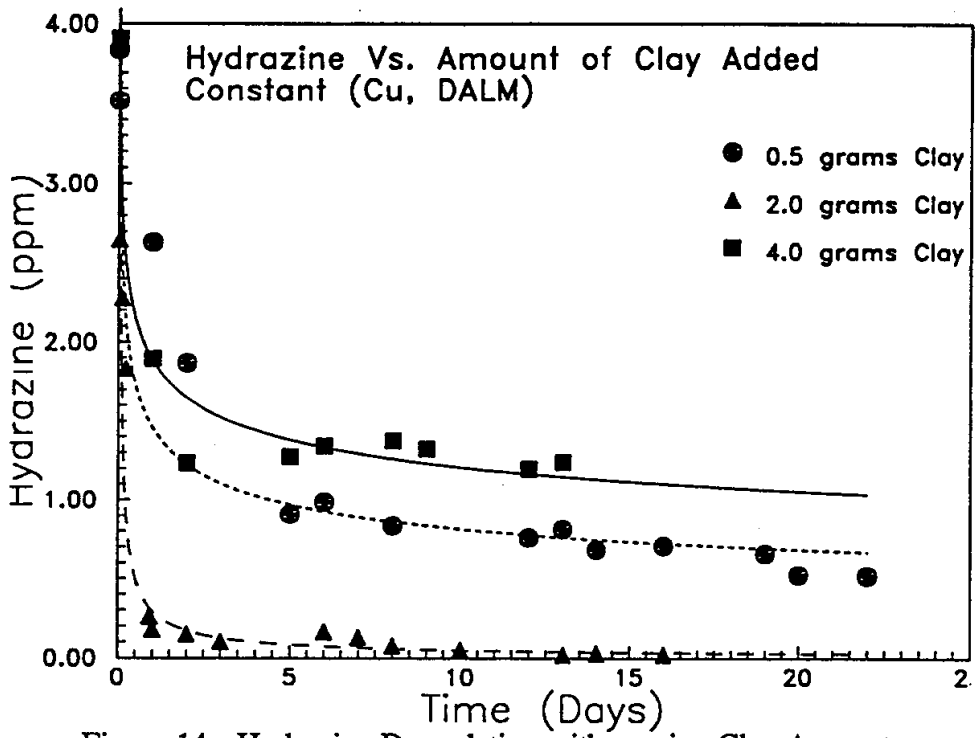

Figure 14. Hydrazine Degradation with varying Clay Amounts (Copper/DALM Constant)

Another combination tested was varying the amount of H_2O_2 added while keeping the amount of clay constant. Again there was no increase in the degradation of hydrazine, even when significantly higher levels of peroxide were used. This can be seen by comparing Figure 15 and Figure 5.

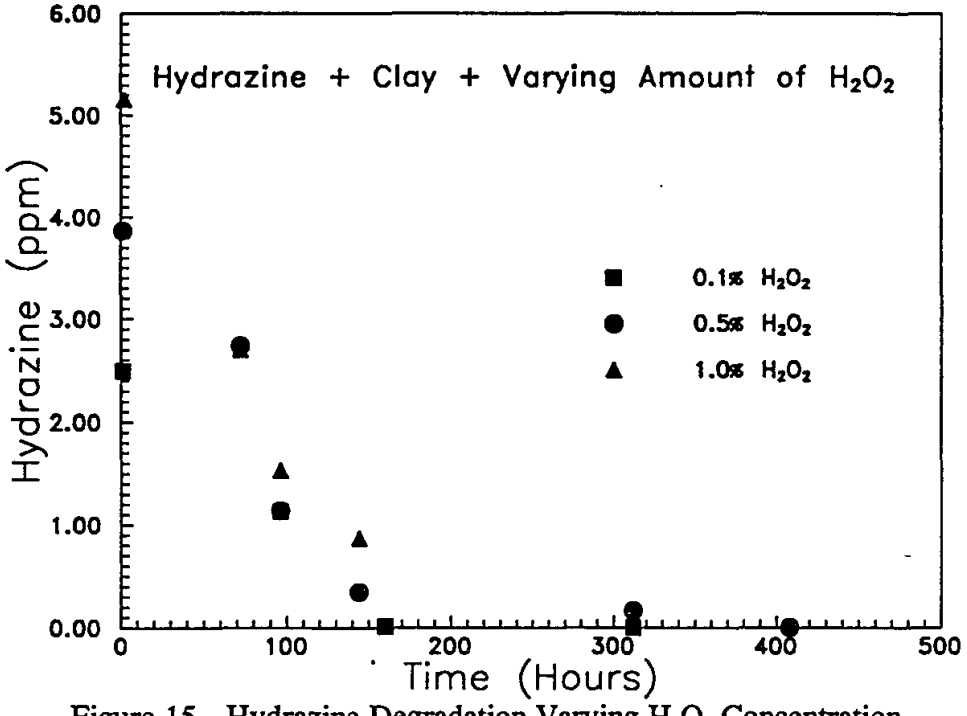

Figure 15. Hydrazine Degradation Varying H_2O_2 Concentration (Clay - 2.0 grams, Hydrazine - 10 ppm)

The optimum mixture of compounds was DALM, 100 ppm copper sulfate, 100 ppm $NaHCO_3$, and 2.0 grams of clay. All analyses of this mixture showed no presence of hydrazine after only fifteen minutes.

CONCLUSION/FUTURE RESEARCH

Hydrazine in aqueous environments was studied extensively, but the monomethyl and unsymmetrical dimethylhydrazine need additional research to determine optimum DALM and supporting transition metal catalyst concentrations. DALM, the primary focus for this research, was shown to facilitate the rapid degradation of hydrazine from aqueous systems. Ion chromatography has been shown to be a superior method to colorometric and chromatographic techniques with little or no interferences or sample preparation required. A major concern in the degradation of hydrazine and hydrazine-containing compounds is the formation of compounds more harmful than the original spill contents, such as nitroso-compounds, known carcinogens. Solid phase microextraction was used as a quick screening method with gas chromatography/mass spectroscopy, and there was no evidence of any nitroso-compounds in the aqueous hydrazine samples during degradation. Further studies are needed to test the detection

limit of some of the possible nitroso-compounds seen in other studies of the degradation of monomethyl or unsymmetrical dimethylhydrazine. Methyl amines should also be included in the analysis of by-products of the degradation process, because they are known breakdown products of higher molecular weight amine compounds.

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