Hydrazine Degradation in Aquatic Systems

A. R. Slonim[1] and J. Brennan Gisclard*[2]

[1]*Aerospace Medical Research Laboratory*
Wright-Patterson Air Force Base, Ohio 45433

[2]*Air Force Flight Dynamics Laboratory*
Wright-Patterson Air Force Base

As hydrazine, which is a strong reducing or anti-oxidant agent and quite toxic, becomes more and more widely used in industry and (as a propellant) in aerospace operations, interest continues to mount concerning its potential pollution of the environment and hazards to living organisms. One of the many potential problem areas receiving attention in the Air Force is hydrazine interaction with water and effects on aquatic organisms. Two approaches were undertaken almost simultaneously in the early stage of this program. One was to determine the effect of hydrazine on various properties of water (pH, dissolved oxygen, alkalinity, hardness, etc.) prior to studying its toxicity to fish; the behavior of hydrazine compounds in water was investigated (SLONIM 1975), and the results on acute toxicity will be reported elsewhere. The other approach was to first develop a rapid and sensitive method for analyzing hydrazine in solution and second to apply it in studies to determine if hydrazine is stable or degrades in various types of aquatic systems. To meet the first requirement, a polarographic technique was developed recently that is highly specific for hydrazine, impervious to interfering substances, and relatively simple to perform (GISCLARD 1975). Second, this method was applied in this study to analyzing various water samples in which hydrazine was added and its concentration followed for four days. The results of five experiments are reported in this paper. Three experiments consisted of analyzing hydrazine in water taken from various outdoor sources and on-base facilities, the same samples equalized in terms of temperature and dissolved oxygen (DO), and water of varying hardness. The last two experiments involved the effect of fish excretions on hydrazine and some preliminary data on hydrazine uptake by fish.

Experimental

Polarographic method. Since hydrazine is not electroreducible and thus not amenable to direct polarographic analysis, an indirect method was developed based on the ability of hydrazine to react with salicylaldehyde in a weakly alkaline, neutral or weakly acidic medium to form an insoluble aldazine (FEIGL 1956). The addition of a nitro group to the reacting compound forms a product that is more reducible in the electrolysis cell of the polarograph with resulting well defined waves on the polarogram (GISCLARD 1975). Therefore, hydrazine was made to react with

*Deceased.

Bulletin of Environmental Contamination & Toxicology,
Vol. 16, No. 3 © 1976 by Springer-Verlag New York Inc.

5-nitrosalicylaldehyde in slightly acid solution to form 5-nitrosalicylaldehyde azine, or 5-nitrosalicylaldazine, as follows:

$$H_2NNH_2 + 2\ C_6H_3OH(NO_2)CHO \longrightarrow C_6H_3OH(NO_2)CH{:}NN{:}CH(NO_2)OHC_6H_3 + 2H_2O$$

Due to their stoichiometric relationship, the amount of nitroaldazine formed is directly related to the amount of hydrazine consumed in the reaction. Moreover, nitroaldazine, even in low concentrations where only cloudiness appears, is easily separated in solution by filtration and dissolved in alkali prior to rapid electroreduction in the polarograph, thus permitting a very sensitive indirect measurement of hydrazine.

A Sargent Polarograph Model XXI was used in this study. The reagents consisted of an acetate buffer (0.5M sodium acetate in 2.5M acetic acid, pH 4), 5-nitrosalicylaldehyde (obtained from G. Frederick Smith Co.) - 0.5% in ethanol, and 0.1N NaOH. The hydrazine liquid (obtained from Matheson Coleman & Bell) was in anhydrous form and over 97% pure, the remainder being water.

The procedure consists of placing 20 ml of sample in a 25 ml graduated test tube followed by the addition of 2 ml of acetate buffer and 0.5 ml of 0.5% 5-nitrosalicylaldehyde. The mixed contents are placed in a 90° water bath for 15 minutes, cooled and filtered (while still warm) through a glass fiber filter. The precipitate is washed and redissolved in 0.1N NaOH, diluted to 25 ml with more NaOH, and read on the polarograph. The total procedure requires 30 minutes and can measure down to 0.05 mg/l hydrazine, although it is much more reproducible (within a 5% error) above 0.2 mg/l (GISCLARD 1975). Recoveries were 96-100% for analyzing hydrazine in the 8.0 to 0.27 mg/l range in solutions from hard water (> 400 mg/l) to distilled water. However, newer polarographs developed recently should improve the sensitivity of the method even further.

As used in this study, in contrast to more laborious polarographic procedures (e.g., WHITNACK et al. 1956), this method was not sensitive to monomethylhydrazine or dimethylhydrazine, but was quite specific for hydrazine, being able to measure hydrazine in an admixture of hydrazine and 1,1-dimethylhydrazine (Aerozine-50). Although a variety of wet chemical and instrumental methods exist for analyzing hydrazine quantitatively (reviewed in part by AUDRIETH and OGG 1951, FEINSILVER et al. 1959, DAMBRAUSKAS and CORNISH 1962, and DEE 1971), with some reportedly highly sensitive (DAMBRAUSKAS and CORNISH 1962) or capable of analyzing more than one type of hydrazine compound simultaneously (DEE 1971), none combines altogether the speed, simplicity, specificity and sensitivity inherent in the present method.

Water sources. The major sources of water collected on the same October day and tested with hydrazine were (A) river immediately after a long rainstorm, (B) small pond on-base fed by an underground spring, (C) Dayton city water, which is chlorinated, filtered and softened, (D) county water, which is treated like city water but not softened, and (E) hard water (HW) stored in the laboratory. In addition, two other samples were collected four days later; these were (F) river water collected from the same

site as A above but in good weather, and (G) large lake with very active flow and located near Mad River (the source of A and F). Aliquots of water from these sources were submitted immediately upon arrival in the laboratory for routine analysis (temperature, pH, DO, etc.); the major portion of each water sample was used as diluent for making the hydrazine solution.

Hydrazine experiments. Throughout this study, the hydrazine solutions were prepared in 2-liter volumetric flasks in duplicate at a concentration of 5.0 mg/l unless otherwise noted. They were then transferred to coded bioassay jars (3.8 l), from which aliquots were submitted for polarographic analysis usually within one hour after preparation; the data were recorded under Day 0. The standing samples were then analyzed at 24 hour intervals after the initial polarographic analysis began, and these data were tabulated under Days 1 through 4, respectively. Evaporative losses of water on the fourth day were relatively small and inconsequential.

In view of the large differences noted in temperature and DO among the various water samples (see Table 1), the original samples next were all left standing uncovered for 8 days and then vigorously aerated for 1-1/2 hours; this equalized the samples in terms of temperature and DO. The water from each was then used to make new hydrazine solutions, which were again coded and submitted for daily polarographic analysis.

Since the hardness of the various samples differed markedly from each other also, hydrazine was tested further in water of varying hardness. Four solutions were used starting with hard water (440 mg/l as $CaCO_3$) and diluting the hard water 1:2, 1:4 and 1:20 with glass distilled water to make water at 440, 220, 110 and 22 mg/l of hardness, respectively. Thus, the solutions, which were qualitatively alike, differed only in one variable, a quantitative difference in content. Preparation of the hard water used here and hard and soft water used later in this study was described previously (SLONIM 1973). Duplicate hydrazine solutions were then coded and analyzed daily as before.

The next experiment was conducted to determine if chemicals excreted by aquatic organisms have an effect on hydrazine. Eight guppies were placed in 2.8 liters of hard water (HW) and 8 in soft water (SW); two other HW and SW bioassay jars without fish served as controls. After six days, the fish were removed and 2-liter solutions of hydrazine (5 mg/l) were prepared from each of the four jars, respectively, coded, and analyzed daily as before.

The last experiment was designed to determine hydrazine uptake in guppies by measuring the difference in hydrazine content between solutions with fish and those without fish. Ten one-gallon (3.8 l) bioassay jars were set up with hard water and soft water hydrazine solutions. Four jars were made up at 0.5 mg/l hydrazine in HW and four at 0.25 mg/l hydrazine in SW; both hydrazine concentrations are tolerable to a majority of guppies, i.e., below the LC25 level (SLONIM, to be published). Two jars were made up at 5 mg/l hydrazine in HW to compare with previous tests as a check on the accuracy of the analysis. In each of two of the four 0.5 mg/l hydrazine HW jars, 5 guppies of the same size were placed; similarly, 5 fish were placed in each of two 0.25

mg/l hydrazine SW jars. Very small aliquots were removed from each 2-liter solution and analyzed daily by polarography as before.

Results and Discussion

The characteristics of the different types of aquatic systems tested on hydrazine are shown in Table 1. Physically, the water sources varied considerably, ranging from very dirty water filled with much organic debris (dead insects, leaves, wood, etc) following a rainstorm to clear, softened municipal water; in the case of the river sample, the picture was just the opposite under good weather conditions. In general, the water sources showed a large variation in temperature (14.5 to 27.3°), DO (5.3 to 12.3 mg/l) and hardness (120 to 468 mg/l) and a small variation in conductance (328 to 900 μmhos/cm) and pH (7.5 to 8.3).

The results of adding hydrazine to the different waters are shown in Table 2. Within the first couple of hours, the most polluted water (A) caused the greatest breakdown of hydrazine, to below one-third of its original level. Hydrazine degradation at the start was also appreciable in pond and county water (B&D), both of which were very hard, but differed from each other in appearance, temperature and DO levels. The rate of degradation was highest within the first 24 hours in those samples showing immediate change in hydrazine content, and the hydrazine concentration approached its lowest level on the second day (A,B&D) and was not measurable by the third day (A&D). Stored laboratory water (E), which was clear, with no organic matter, and less hard than A and D, did not degrade hydrazine significantly until the second day and only about 35% by the fourth day. The second river sample collected in good weather (F) showed no hydrazine breakdown initially as did the first river sample (A); however, like A, there was no detectable hydrazine in F on the fourth day. Lake water (G) affected hydrazine the same way as clear river water (F) and, surprisingly, showed no initial breakdown of hydrazine in the presence of a high DO level. Only treated city water (C) contained near the original amount of hydrazine at 96 hours.

In view of the large differences in temperature and oxygen (DO) levels observed on fresh samples from these sources, the unused portions of sufficient quantity (A-E) were subsequently equalized in terms of these two variables without changing their chemistry and then tested with hydrazine (5.0 mg/l). The results are presented in Table 3. The temperature in all samples was from 26.3 to 26.7°, and the DO from 7.30 to 7.58 mg/l. There was at the start no marked reduction in hydrazine concentration, especially in those three types of water that showed a reduced hydrazine concentration previously; this included river water originally with the lowest temperature (A), county water with the lowest DO level but warmest temperature (D), and pond water with the hardest water and a low temperature (B). This initial effect of equating temperature and oxygen in all samples was short-lived,

TABLE 1

Characteristics of different water sources tested.

	Water	Appearance	Temp. (°C)	DO (mg/1)	pH	EDTA Hard. (mg/1)	Specific Conduct. (μmho/cm)
A.	River (after rain)	cldy, v. dirty	14.5	7.05	8.3	372	630
B.	Pond	sl. cloudy	16.0	7.60	8.2	468	850
C.	City (Cl,f,-Ca)*	clear	24.0	7.45	8.2	120	328
D.	County (Cl,f)	clear	27.3	5.30	7.5	456	900
E.	Stored HW	clear	22.5	7.50	7.5	328	780
F.	River† (good weather)	clear	16.2	6.11	7.9	372	650
G.	Lake†	sl. cloudy	15.8	12.3	8.3	252	490

*Cl=chlorinated, f=filtered, -Ca=softened.

†Samples F&G collected 4 days after A-E; samples A&F collected from same site in river but under different weather conditions.

TABLE 2

Fate of hydrazine in different water sources.*

Water	Hydrazine, mg/l				
	Day 0	1	2	3	4
A. River	1.5	0.8	0.05	<0.05†	<0.05
B. Pond	2.75	0.47	0.42	0.42	0.27
C. City	4.7	4.7	4.7	4.7	4.5
D. County	2.75	0.15	0.083	<0.05	<0.05
E. Stored HW	4.5	4.25	3.80	3.87	3.2
F. River	4.5	----	-----	------	<0.05
G. Lake	4.3	----	-----	------	<0.05

*Original hydrazine concentration in all samples = 5.0 mg/l.

†Limit of detection = 0.05 mg/l.

TABLE 3

Hydrazine in water equalized in terms of temperature and oxygen.

Water	Temp. (°C)	DO (mg/l)	Hydrazine, mg/l				
			Day 0	1	2	3	4
A. River	26.7	7.58	3.87	0.2	<0.05	<0.05	<0.05
B. Pond	26.7	7.33	4.00	1.3	1.0	0.92	0.92
C. City	26.4	7.33	5.00	4.25	4.5	4.5	4.5
D. County	26.3	7.45	3.63	<0.05	<0.05	<0.05	<0.05
E. Stored HW	26.3	7.30	4.75	4.25	3.2	3.2	3.0

See legend under Table 2.

because hydrazine degradation followed the same pattern as exhibited previously; this was essentially a first order kinetic degradation of hydrazine as evidenced by the concentration-time data.

Water hardness was another characteristic that varied greatly among the different water systems tested. Hydrazine (5 mg/l) was tested in water of four different hardnesses. By using hard water from undiluted to 1:20 dilution, the water samples were qualitatively alike but quantitatively different. The effect of water hardness on hydrazine was easily discernible as shown in Table 4. Hydrazine started to degrade in the beginning only in hard water (HW) but not in waters of lower hardness. With time, hydrazine in soft water remained unchanged except for a small decrease at 96 hours; whereas, it was reduced only 21% in water of 110 mg/l hardness (LW) and about 50% in moderately hard (MW) to hard water (HW) on the fourth day. (In one extended analysis, hydrazine in HW was reduced 82% on the 13th day.) The hydrazine level in LW may not be significantly different from that in city water (C) of nearly the same hardness, but was consistently lower than that in soft water (SW). In general, although hardness contributes to hydrazine degradation, other factors appear to be more important than hardness *per se*, since 50% degradation in the hard waters was much less than that seen previously in the other waters (Table 2: A,B, D,F&G). Degradation of hydrazine may not depend on any single parameter present in these systems but the sum total of many ingredients. Indications are from the rapid hydrazine breakdown in stormy river water that polluting material rich in organic matter is a leading contributor to hydrazine degradation. Hydrazine can also be affected the same way by inorganic oxidants (SLONIM, unpublished data). That other factors must be involved also was evidenced by the eventual breakdown of hydrazine in the *clear* river water sample (F).

TABLE 4

Hydrazine in water of varying hardness.

	Hardness, mg/l		Hydrazine, mg/l				
Water*	Prepared	Measured	Day 0	1	2	3	4
HW	440	420	4.75	3.87	3.40	2.40	2.40
MW	220	216	4.94	4.69	3.83	2.89	2.60
LW	110	108	4.94	4.85	4.62	4.37	3.93
SW	22	24	5.00	5.10	5.06	5.00	4.63

*HW=hard water, MW=moderately hard water, LW=lightly hard water, SW=soft water.

The next question raised was whether or not chemicals excreted by living organisms affect hydrazine in water. The results of comparing hydrazine in hard or soft water versus HW or SW containing 6-day excretions from guppies are shown in Table 5. There was a significant effect of fish waste products on the amount of hydrazine in solution. Even in soft water, there was a slight reduction of hydrazine at the beginning. In three days, the fish excretions reduced hydrazine to one-half of the amount present in plain soft water, and on the fourth day to one-third of the control level. The greatest decrease in hydrazine in soft water caused by the excretions occurred in two days. In hard water, the effect of fish wastes on hydrazine was significant immediately, and the degradation rate was highest within the first day (as in other HW solutions). The effect of the wastes became severe in time, reducing hydrazine to a concentration of 0.05 mg/l versus a control value of 2.25 mg/l on the third day and to a negligible level on the fourth day. The magnitude of hydrazine degradation to such low levels was indicative of an additive effect of the excretions and water hardness.

TABLE 5

Effect of fish excretions on hydrazine in hard and soft water.

Water	Fish Excretions	Hydrazine, mg/l				
		Day 0	1	2	3	4
Hard	No	3.84	2.80	2.50	2.25	2.25
Hard	Yes	2.40	0.87	0.20	0.05	<0.05
Soft	No	4.75	4.75	4.50	4.50	4.50
Soft	Yes	4.45	3.87	2.87	2.25	1.50

In the last experiment using this polarographic method, hydrazine concentration was compared between water samples with and without guppies to gain some insight as to if and to what extent hydrazine is taken up by fish. The results are presented in Table 6. For this experiment, the concentrations of hydrazine at the start were 0.5 mg/l in HW and 0.25 mg/l in SW (both below the LC25 level). In hard water, differences between the jars with and without guppies increased with time. In 96 hours, an average of 0.072 mg/l or 0.144 mg of hydrazine was absorbed by five fish of equal size. This was approximately 28.8 micrograms per fish (or about 144 micrograms/gram of guppy). In soft water, there was no detectable difference between the fish and no fish jars, due in part to the method as used here having a high sensitivity error at or below 0.2 mg/l hydrazine as stated earlier. Radioisotope studies, such as was reported previously (SLONIM 1973), are suggested to obtain direct uptake measurements in fish.

TABLE 6

Hydrazine uptake in guppies.

Water	Hydrazine Prepared (mg/l)	Fish Present	Hydrazine, mg/l Day 0	1	2	3	4	Δ
Hard	0.5	No	0.49	0.49	0.45	0.46	0.44	0.072*
Hard	0.5	Yes	0.50	0.48	0.43	0.40	0.37	
Soft	0.25	No	0.24	0.22	0.22	0.24	0.22	0*
Soft	0.25	Yes	0.24	0.22	0.22	0.24	0.22	
Hard	5.0	No	4.93	4.59	4.20	3.88	3.81	

*See text for explanation.

Acknowledgments

The assistance of Sgt. Edwin E. Ray in preparing the hydrazine solutions and Mr. Richard G. Allison, Jr., in collecting the outdoor water samples is gratefully acknowledged. This paper was presented in part before the American Fisheries Society, Las Vegas, September 1975, and is catalogued as AMRL-TR-75-108.

References

AUDRIETH, L. F., and B. A. OGG: The Chemistry of Hydrazine. New York: John Wiley & Sons, Inc. 1951.

DAMBRAUSKAS, T., and H. H. CORNISH: Am. Ind. Hyg. Assn. J. 23, 151 (1962).

DEE, L. A.: Anal. Chem. 43, 1416 (1971).

FEIGL, F.: Spot Tests in Organic Analysis. 5th ed. New York: Elsevier Publishing Co. 1956.

FEINSILVER, L., J. A. PERREGRINO, and C. J. SMITH, JR.: Am. Ind. Hyg. Assn. J. 20, 26 (1959).

GISCLARD, J. B.: Technical Report AFFDL-TR-75-116, Air Force Flight Dynamics Laboratory, Wright-Patterson AFB, Ohio. 1975.

SLONIM, A. R.: J. Water Pollution Control Fed. 45, 2110 (1973).

SLONIM, A. R.: Technical Report AMRL-TR-75-72, Aerospace Medical Research Laboratory, Wright-Patterson AFB, Ohio. 1975.

WHITNACK, G. C., J. E. YOUNG, H. H. SISLER, and E. S. C. GANTZ: Anal. Chem. 28, 833 (1956).