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HYDRAZINE DISPOSAL BY BURNING.(U)

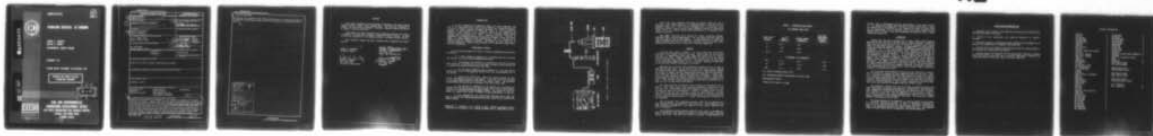
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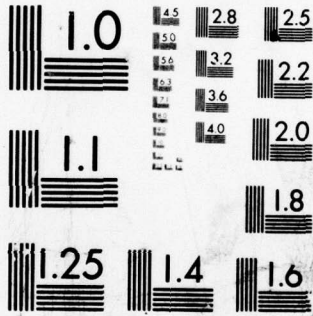
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HYDRAZINE DISPOSAL BY BURNING

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ENVIRONMENTAL SCIENCE DIVISION

DECEMBER 1978

INTERIM REPORT SEPTEMBER 1978-OCTOBER 1978

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destruction, and potential cost savings make burning an attractive alternative to chemical neutralization under controlled conditions as discussed in this report.

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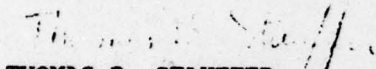
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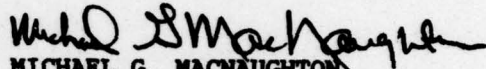
PREFACE


This report documents work performed in September 1978 under Program Element 62601F, Project 1900, Subtask 4C01. The work was conducted at Tyndall Air Force Base by Thomas B. Stauffer, research chemist and Melvin D. Fannon, research assistant.

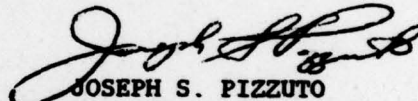
This report has been reviewed by the Information Officer (OI) and is releaseable to the National Technical Information Service (NTIS). At NTIS it will be available to the general public, including foreign nations.

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


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INTRODUCTION

It is well documented that hydrazine (N_2H_4) is a toxic substance, and due to its high volatility, small spills should be cleaned up and neutralized to protect exposed personnel (Reference 1). Several different methods of neutralization are available based on the oxidation of hydrazine which require large amounts of the oxidizing agents making cleanup and neutralization a slow, laborious process. Burning is suggested as an alternate method for hydrazine disposal, offers two advantages (1) rapid removal of the spilled N_2H_4 , and (2) elimination of monetary cost for chemical treatment. The object of this study was to evaluate burning as a means of N_2H_4 disposal and to quantitate N_2H_4 vaporized during burning.

EXPERIMENTAL METHODS

The following procedure was used to evaluate hydrazine neutralization by burning:

a. A 25/ml aliquot of hydrazine or an aqueous hydrazine solution was placed in an 18 cm x 28 cm enameled steel pan.

b. A stainless steel shroud was situated over the top of the pan (See Figure 1) to provide a path for any fumes released during burning and to contain the flames produced during the burn.

c. An all-glass sampling probe attached to a gas wash bottle filled with 75 ml of 2N H_2SO_4 was centered over the round exhaust port of the shroud.

d. During the entire burn, sample was pulled through the wash bottle, absorbing any N_2H_4 in the sample. A wet-test meter was attached to the pump exhaust port for measuring the sample volume. The gas phase concentration calculated was an average of the entire burn time.

e. To analyze for hydrazine in the exhaust air an aliquot was removed from the gas wash bottle and reacted with a four percent aqueous solution of p-dimethylaminobenzaldehyde (PDAB). The yellow azo dye produced was quantitated using a Coleman 55 Spectrophotometer at 460 nm.

f. The enameled pan was rinsed with distilled water after the burn to recover any remaining hydrazine and this solution was treated with PDAB as above.

Reference 1. Stauffer, T. B., and A. E. Eyl, "Studies on Evaporation of Hydrazine and Procedures for Cleaning of Small Spill," CEEDO-TR-12, 1978.

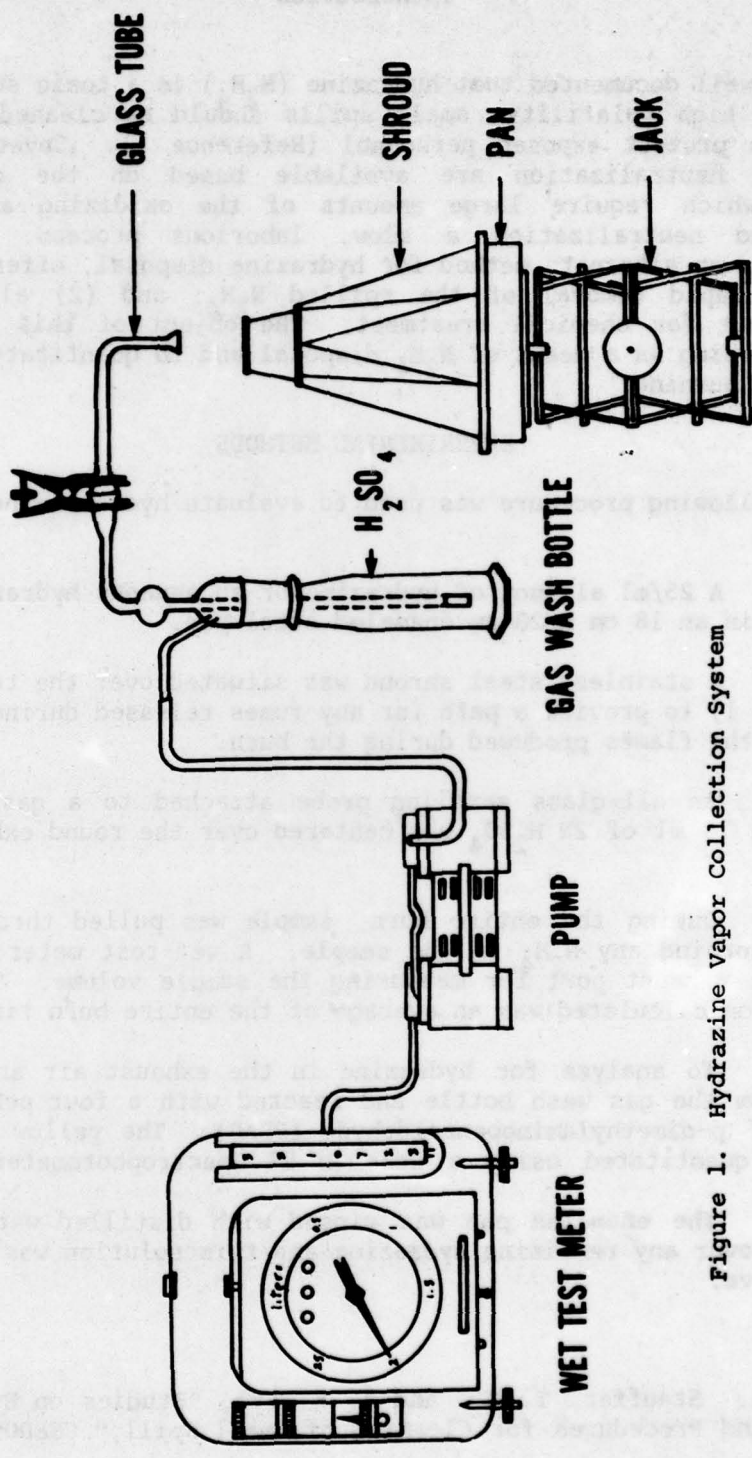


Figure 1. Hydrazine Vapor Collection System

Three runs were conducted with both 100 percent hydrazine, and a 70-percent (V/V) aqueous mixture of hydrazine which is used in the F-16 emergency power unit. One run was attempted with a 50-percent (V/V) hydrazine solution, and a test was also conducted outside to simulate an actual spill on concrete using fifty milliliters of 70-percent (V/V) hydrazine solution.

The sample solutions were ignited by several different methods. Commercial HTH, calcium hypochlorite, (lg) was thrown directly into the pool and ignited some of the samples. If the HTH failed to ignite the sample, matches were used to ignite the solution; and in one case, paper was placed in the pool to act as a wick to initiate combustion.

RESULTS

From the data given in Table 1, it can be seen that the burning progressed quite rapidly with the neat fuel. When 1g HTH, was thrown into the fuel it immediately burst into flame and burned with an intense yellowish-red flame. Flames extended about two feet up into the shroud with no apparent smoke being given off. The concentration of N_2H_4 found in the air sample ranged from < 0.1 to 11.5 mg/m^3 . Oxidation of the fuel was practically complete averaging 99.3 percent.

Igniting the 70 percent (V/V) hydrazine solution was not as easy as igniting the neat fuel. On the first run the 70 percent solution ignited but burned rather slowly compared to the neat fuel. Flames barely reached six inches in height, and the reddish glow seen with the fuel was absent. The second run failed to ignite when HTH was introduced. A dense white cloud of fumes emanated from the solution for 72 seconds. These fumes were₃ sampled and gave the highest observed concentration of hydrazine, 75 mg/m^3 . This run was finally ignited with a match and 93.6 percent of the N_2H_4 was lost through burning and fuming.

The third run with 70 percent (V/V) solution was extremely hard to ignite. Since mixed results were obtained using HTH, matches were tried for this run. The matches would burn momentarily when thrown into the solution but then were extinguished. Finally, a crumpled piece of paper was thrown into the pan, allowed to soak up some solution, and then ignited. The hydrazine solution then burned slowly for 330 seconds giving an air hydrazine concentration of 2.1 mg/m^3 and consuming 96.9 percent of the hydrazine.

The 50 percent (V/V) hydrazine solution could not be ignited even when a bunsen burner was applied to ignite the pool. There appeared to be some hydrazine consumption at the junction of the burner flame and the pool of hydrazine.

Since hydrazine would normally evaporate from a spill, an attempt was made to quantitate this amount and subtract it from measurements obtained during the burns. The neat fuel burned so rapidly, in approximately 20

TABLE 1. HYDRAZINE BURN RESULTS

100 PERCENT (NEAT FUEL)

<u>BURN TIME (1)</u> <u>(secs)</u>	<u>N₂H₄ (2)</u> <u>(mg/m³)</u>	<u>PERCENT BURNED</u> <u>(PERCENT)</u>	<u>N₂H₄ CONC</u> <u>BACKGROUND</u> <u>CORRECTED</u> <u>(mg/m³)</u>
17	11.5	99.7	-
17	0.4*	98.8	-
16.3	< 0.1*	99.3	-

70 PERCENT (V/V HYDRAZINE)

88	0.1	92.0	- 0.6
72	75.0**	93.6	74.3
330	2.1	96.9	1.4

(1) Time to consume entire 25 ml

(2) Average gas phase concentration over burn time

*Extrapolated values.

**Dense white fumes, no flame.

seconds, that no background could be quantitated in this short period, i.e. an insufficient volume was collected to permit quantitation. Since the sensitivity is approximately 1 mg, samples less than 0.8 mg/m³ could not be quantitated. The 70 percent (V/V) runs burned longer and the figures given in Table 1 have been background corrected for the 0.7 mg/m³ background evaporation.

DISCUSSION

Pooled neat fuel burns readily with a bright reddish flame probably produced by the calcium in the HTH used to ignite the pool. Levels of N₂H₄ measured during the burn are in excess of threshold limit values (TLV) for personnel exposure, however, no measurement of total effluent volume were made and therefore the mass of hydrazine released could not be calculated. It is not anticipated that significant quantities of hydrazine would be released due to the short intense burn time and low concentration in the gas effluent. It is probable that the majority of any hydrazines released occurs at initial ignition when the pool is heated, but insufficient combustion temperatures have been achieved. Higher volumes would be expected to burn with a higher overall measured efficiency. The impact of high evaporation without combustion shown by the high concentration measured in the second 70% run. The current method of chemical neutralization also exposes personnel to hydrazine concentrations exceeding the TLV and therefore, both methods require protective equipment for handling the fuels.

The 70 percent (V/V) hydrazine solution was more difficult to ignite, and it burned less rapidly and less completely than the neat fuel. Again in a controlled environment burning could possibly be used as an alternative to chemical neutralization. Care would have to be taken to avoid the situation that produced the dense white fumes, since this gave the highest levels of airborne hydrazine. This could be achieved by a positive ignition source and insuring an adequate quantity of HTH is used.

The analytical results were not as precise as desired because such small quantities of material were analyzed. Unfortunately, the laboratory scale experiments necessitated working near the detection limit of hydrazine; however, it is felt that the importance of the results is that in all cases of burning very little hydrazine was measured in the escaping gases, indicating a high combustion efficiency. The analytical results should be interpreted in this light.

The actual burning of the hydrazine on concrete showed little promise as a possible destruction method. A pool is apparently required for burning to be self-sustaining and the concrete interferes by absorbing some of the hydrazine and may also absorb combustion heat. The combined effect of these interferences extinguishes the burning hydrazine.

CONCLUSIONS/RECOMMENDATIONS

1. Hydrazine and 70 percent (V/V) hydrazine solutions can be burned with good (92-99 percent) efficiency.
2. Burning is not appropriate for unpooled hydrazine on concrete pavement.
3. Personnel exposure to hydrazine during handling would probably be no greater for burning than for chemical neutralization.
4. Burning would save chemical neutralization costs but could present a fire hazard in a uncontrolled environment.
5. Burning should be evaluated from an operational viewpoint to assess potential benefits and risks as an alternate destruction technique for large quantities of hydrazine under controlled conditions.

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