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October 14, 1983

MEMORANDUM

TO: H. D. HARMON

FROM: D. G. KARRAKER

*Del Karaker*

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THE OXIDATION OF HYDRAZINE BY NITRIC ACID

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 R.L. COLLINS  
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INTRODUCTION

Hydrazine nitrate-nitric acid solutions are used in the ion exchange process for separating Pu-238 and Np-237, and have been found<sup>1</sup> to dissolve plutonium metal in a manner advantageous to SRP metal recovery operations. However, overheating of a Pu<sup>3+</sup>-nitric acid-hydrazine nitrate solution at SRL led to the auto-catalytic oxidation of Pu<sup>3+</sup> to Pu<sup>4+</sup>, presumably because hydrazine had been oxidized by nitric acid at high temperatures.<sup>2</sup> Laboratory tests on the stability of hydrazine in nitric acid solutions were performed to obtain accurate data, and the results of these tests are reported here. These tests provide sufficient information to specify temperature control for hydrazine-nitric acid solutions in plant processes.

SUMMARY

Hydrazine is oxidized by 5M HNO<sub>3</sub> at 70°C in a pseudo-first-order reaction with a half-time of 23 hours. At 100°C, the reaction

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proceeds through an intermediate step and reaches a pseudo-first-order rate with a half-time of 34 minutes. The reaction is catalyzed by  $\text{Fe}(\text{NO}_3)_3$ ; at  $100^\circ\text{C}$ ,  $10^{-3}\text{M}$   $\text{Fe}(\text{NO}_3)_3$  decreased the half-time to 24 minutes. Further study of this reaction is necessary to define hydrazine stability for specific process systems other than the JB-Line metal dissolver.

## EXPERIMENTAL

### Reagents

Nitric acid and ferric nitrate were CP grade, and diluted with distilled water. Hydrazine nitrate was obtained from SRP in a 3.1M solution.

### Analyses

Nitric acid was determined by titration with standard NaOH solution with methyl red (pH 4.5-6.0) indicator. The  $\text{N}_2\text{H}_5^+$  ion (pK 6.07) does not interfere.<sup>3</sup>

Hydrazine was determined by the iodate method. The sample was added to a measured volume of standard  $\text{KIO}_3$  solution, which is in excess. The excess  $\text{KIO}_3$  is determined by reduction to  $\text{I}_2$  with KI solution and titration of the released iodine with standard  $\text{Na}_2\text{S}_2\text{O}_3$  solution.

Hydrazoic acid was determined by nitrogen-sparging the sample and passing the effluent gas through a measured volume of standard NaOH solution. A few drops of  $\text{Fe}(\text{NO}_3)_3$  solution were added to the sample before sparging; the disappearance of the red-brown color of the ferric azide complex ion indicates the complete removal of  $\text{HN}_3$  from the sample. The excess of NaOH solution was determined by titration with standard HCl solution with phenolphthalein as an indicator.

Ammonium ion was determined by adding the sample to excess 6M NaOH, and nitrogen-sparging the ammonia released into excess standard HCl solution. The excess HCl was determined by titration with standard NaOH solution, with a methyl red indicator.

### Experimental Procedures

Experiments on the rate of the reaction between hydrazine and nitric acid were limited to solutions in 5M  $\text{HNO}_3$ . For kinetic measurements, solutions were maintained at constant temperature in a thermostat and samples withdrawn for hydrazine analysis at timed intervals.

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Experiments to determine the reaction products were performed in a closed system. The solution was contained in a flask fitted with a reflux condenser. Gases from the reflux condenser passed through a gas-sampling tube and their volume was measured by displacement of water. The effluent gases were analyzed qualitatively on a Hewlett-Packard Model 5830A gas chromatograph.

### Results

Representative kinetic data are shown in Figures 1 through 3. Figure 1 shows the oxidation of hydrazine by 5M HNO<sub>3</sub> at 70°; over a 36-hour period the reaction was pseudo-first-order with a half-life for hydrazine oxidation of 23 hours.

Figure 2 shows data for the oxidation of hydrazine at 97°C, and Figure 3 shows data for the reaction at 100°C with 10<sup>-3</sup>M Fe(NO<sub>3</sub>)<sub>3</sub> present. Both reactions have an apparent initiation period of 1/2 to 1 hour. The half-life of N<sub>2</sub>H<sub>4</sub>·HNO<sub>3</sub> in 5M HNO<sub>3</sub> at 97°C was 34 minutes after the initiation period. The reaction is catalyzed by Fe<sup>2+</sup> and/or Fe<sup>3+</sup> ions. Figure 3 shows a 25-minute half-time for the reaction with 10<sup>-3</sup>M Fe(NO<sub>3</sub>)<sub>3</sub> added. The initiation period also appeared to be shorter with Fe(NO<sub>3</sub>)<sub>3</sub> present.

The reaction stoichiometry was partially measured in experiments at 100°C; the data are shown in Table 1. An attempt to measure the reaction rate by the gas evolution was unsuccessful because of the small volume of gas evolved and problems in maintaining a constant temperature. Gas evolution began for the uncatalyzed reaction about one hour after initiation of the reaction and proceeded at a relatively constant rate of about 0.54 mL/min for the duration of the experiment, 150 minutes. The iron-catalyzed experiment began gas evolution after about 30 minutes, and evolved gas at an average rate of 0.92 mL/min for 125 minutes, the duration of the experiment.

Gas samples from both experiments showed only N<sub>2</sub> on gas chromatography through a column packed with molecular sieve. (Polar compounds are retained by the molecular sieve.) Gas chromatography through a chromasorb column showed HN<sub>3</sub> and an unidentified additional polar compound in the gas from the uncatalyzed experiment. HN<sub>3</sub> was the only polar compound in the gas from the iron-catalyzed reaction.

No apparent change in the acid concentration was observed between the initial and final solutions. It should be noted that each mole of hydrazine consumed releases one mole of acid.

## DISCUSSION

The reaction at 70°C shows adequate stability for hydrazine in 5M HNO<sub>3</sub> for plant operations that involve only a few hours at elevated temperatures. However, no measurements have been made for the iron-catalyzed oxidation, so unnecessary exposure of hydrazine-nitric acid solutions to elevated temperatures should be avoided.

Rate data and gas evolution experiments indicate that the reaction at 100°C is a two-step process involving some intermediate species. After a buildup of this intermediate, the reaction then becomes pseudo-first-order and relatively rapid for the reaction. Catalysis of the reaction might be expected for other transition metal ions, such as Mn<sup>2+</sup> or Cu<sup>2+</sup>, and these preliminary experiments did not test the effect of increasing the concentration of iron.

The stoichiometry of the reaction is incomplete; as shown in Table 2, more equivalents of nitrogen compounds were consumed in the reaction than were found in the products. The discrepancy is large for the uncatalyzed reaction, where the products account for only 60% of the nitrogen in the reactants. The products of Fe-catalyzed reaction were 88% of the reactants.

It is tempting to propose that the discrepancy between the nitrogen in the reactants and the nitrogen in the products is the nitrogen contained in an intermediate product and that the effect of iron catalysis is to accelerate the decomposition of the intermediate to the final products. Possible intermediates are hyponitrous acid, H<sub>2</sub>N<sub>2</sub>O<sub>2</sub> or its isomer, nitramide, NH<sub>2</sub>NO<sub>2</sub>,<sup>4</sup> although neither appears to have the stability in strong acid that the intermediate probably has. The unidentified polar compound found by gas chromatography may be the intermediate (or its decomposition product). A gc/ms gas chromatograph/mass spectrometer could resolve this question, but identification by gas chromatography alone is not possible.

In conclusion, these results show that the hydrazine-nitric acid system is sufficiently stable at 70°C for most process requirements, but that hydrazine destruction at 100°C is too rapid for process operations.

~~CONFIDENTIAL~~

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1. D. G. Karraker. Dissolution of Plutonium Metal in  $\text{HNO}_3 \cdot \text{N}_2\text{H}_4$ -KF. DP-166, E. I. du Pont de Nemours & Co., Savannah River Laboratory, Aiken, SC (1983).
2. J. H. Gray to H. D. Harmon, Memorandum: Process Incident Report No. PI-ATD-83-1. DPST-83-907 (October 1983).
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4. Ibid, p 52-106.

TABLE 1

Oxidation of Hydrazine by 5M HNO<sub>3</sub> at 100°C

Initial Conc, M		Final Concentration, M			Gas		
HNO <sub>3</sub>	N <sub>2</sub> H <sub>5</sub> <sup>+</sup>	N <sub>2</sub> H <sub>5</sub> <sup>+</sup>	HN <sub>3</sub>	NH <sub>4</sub> <sup>+</sup>	Vol	m·moles	mL/min
5	0.72	0.064	0.20	0.081	-	-	-
4.86	0.59	0.155	0.128	0.065	81	3.6	0.54
4.93 [8 x 10 <sup>-4</sup> M Fe(NO <sub>3</sub> ) <sub>3</sub> ]	0.55	0.15	0.155	0.068	115	5.2	0.92

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TABLE 2

 $\text{N}_2\text{H}_4 \cdot \text{HNO}_3$  - 5M  $\text{HNO}_3$  Reaction Stiochiometry at 100°C

<u>Initial Conc, M</u>		<u>Consumed, m·moles</u>		<u>Produced, m·moles</u>			<u>Sum of N Equivalent</u>
<u><math>\text{HNO}_3</math></u>	<u><math>\text{N}_2\text{H}_4 \cdot \text{HNO}_3</math></u>	<u><math>\text{N}_2\text{H}_4 \cdot \text{HNO}_3</math></u>	<u>N* Equivalent</u>	<u><math>\text{HN}_3</math></u>	<u><math>\text{NH}_3</math></u>	<u><math>\text{N}_2</math></u>	
4.86	0.59	8.70	26.1	2.56	1.30	3.6	16.2
4.93	0.55	8.00	24.0	3.10	1.36	5.2	21.0

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\* N from  $\text{N}_2\text{H}_4 \cdot \text{HNO}_3$  consumed.

Figure 1  
Oxidation of Hydrazine  
in 5M HNO<sub>3</sub> at 70°C

N<sub>2</sub>H<sub>4</sub>  
Conc.  
M

0.3  
0.2  
0.1  
.08  
.06  
.05

10

30

50

TIME, HRS

T 1/2 = 23 hrs

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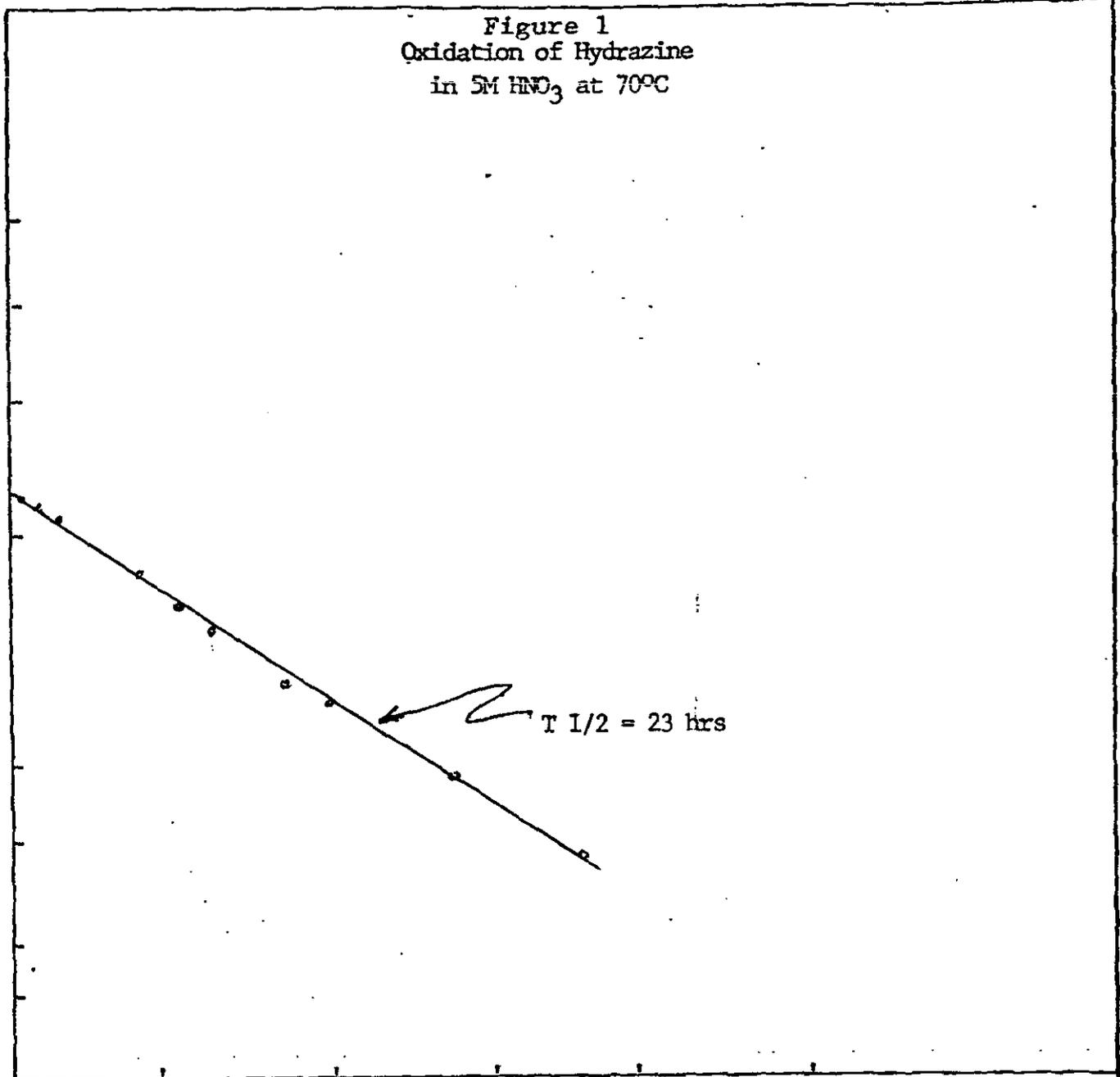
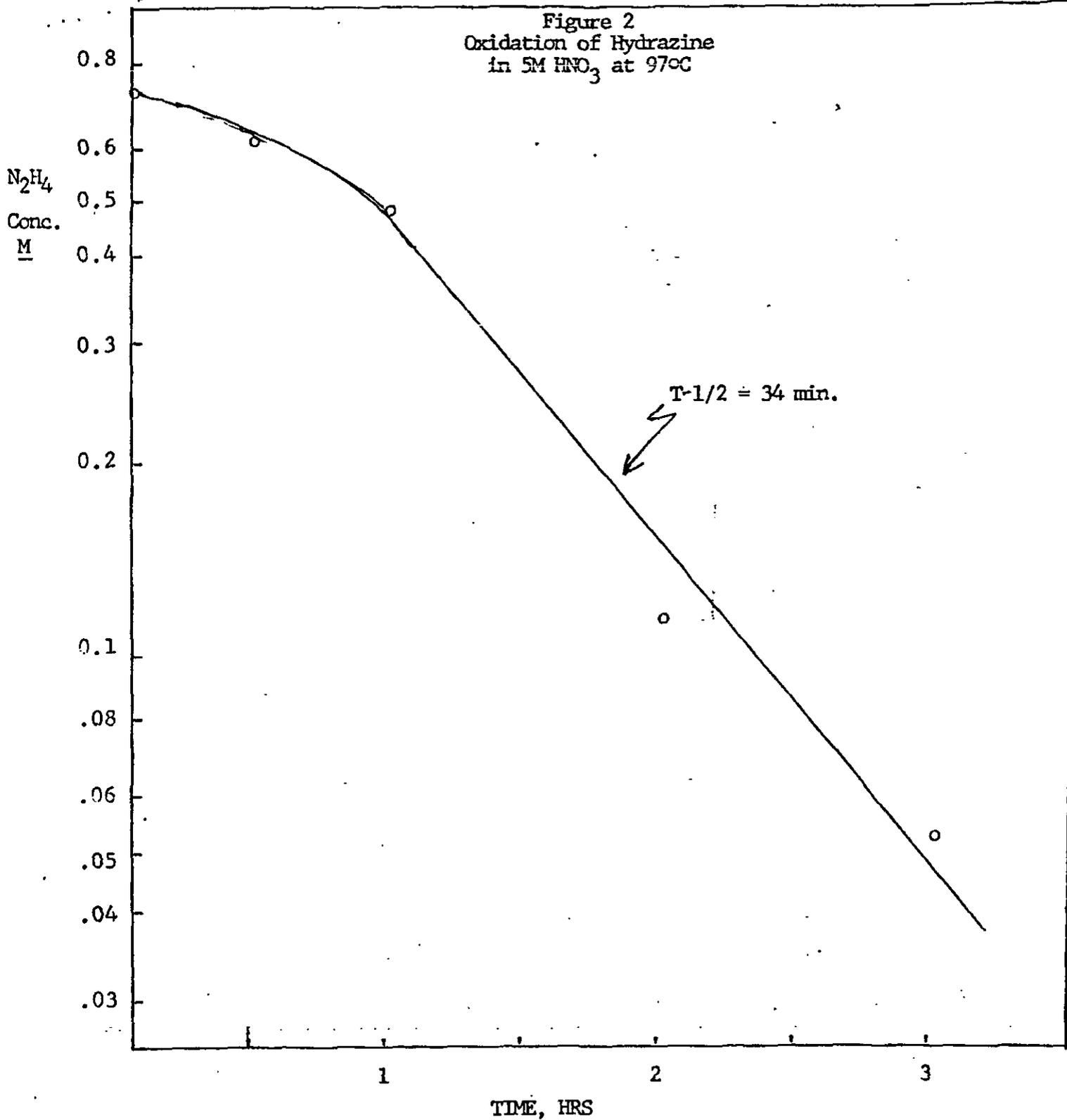


Figure 2  
Oxidation of Hydrazine  
in 5M HNO<sub>3</sub> at 97°C



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Figure 3  
Oxidation of Hydrazine  
in  $5M HNO_3 - 10^{-3}M Fe$  at  $100^\circ C$

$N_2H_4$   
Conc.,  
M

0.1

$T_{1/2} = 25 \text{ min}$

TIME, HRS

