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EXHAUST GAS COMPOSITION OF THE F-16 EMERGENCY POWER UNIT

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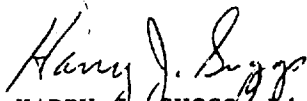
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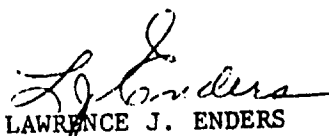
This technical report has been reviewed and is approved for publication.



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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) A study was made of the exhaust gas from the monopropellant hydrazine-fueled emergency power unit (EPU) on the F-16 aircraft. An extractive sampling technique was used to sample for the known exhaust gas components, ammonia, hydrazine, and nitrogen, and to determine if unreacted hydrazine was present. The purpose of the study was to obtain data necessary to evaluate health hazards potential to workers who may be exposed to the exhaust, although an unlikely event. Emphasis was placed on the first minute of operation of the EPU following a cold-start under no-load conditions as the most likely personnel exposure		

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20. ABSTRACT (Continued)

conditions for either planned test firings or inadvertent firings. The amount of unreacted hydrazine was found to be as much as 24 grams per firing, with 65%-95% of this amount emitted in the first thirty seconds of operation. Recommendations for protection of personnel against ammonia and hydrazine are presented.

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EXHAUST GAS COMPOSITION
OF THE F-16 EMERGENCY POWER UNIT

INTRODUCTION

The F-16 is a new single-engine tactical aircraft scheduled to become Air Force operational in early 1979. Since the F-16 is an electronically controlled configuration (fly-by-wire) aircraft, an emergency power unit (EPU) is used to provide short-term electric and hydraulic power for aircraft control. The EPU is fueled with a mono-propellant hydrazine mixture, H-70, which contains 70% hydrazine (N_2H_4), 30% water, by weight.

The introduction of hydrazine to the aircraft flight line scenario has raised numerous questions on environmental and occupational health support requirements. Early discussions with the F-16 Systems Program Office (ASD/YP), Wright-Patterson Air Force Base, Ohio, identified a need to determine the chemical composition of the EPU exhaust gas, to verify theoretical analyses. Specific questions were raised on the quantity of unreacted hydrazine and ammonia in the EPU exhaust gases. Answers to these questions were necessary to develop controls and protective actions to prevent excessive exposure to either of these toxic constituents.

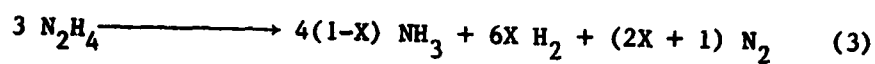
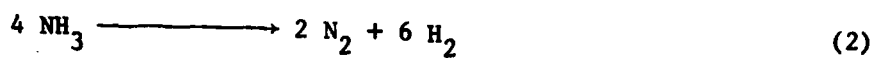
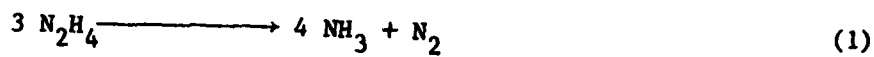
During the week of 23 to 27 January 1978, an analytical team from the Crew Environments Branch, USAF School of Aerospace Medicine, collected a series of exhaust samples during ground-test firings of an installed F-16 EPU. This report describes the test procedures and details the EPU exhaust hydrazine and ammonia emissions.

DESIGN OF THE STUDY

Planned test firings or inadvertent ground firings were known to be largely cold-start runs of short duration under no-load conditions. Inadvertent firings typically have resulted in engine shut-down when the EPU mode selector switch was in the automatic position. The study therefore was designed to collect the exhaust samples following cold-start firings under no-load conditions.

Theoretical reactions of the catalytic decomposition of hydrazine are shown in Table 1. Theoretical gas composition for H-70 is shown in Figure 1 as a function of X, the fraction of ammonia dissociated in reaction 2. The value of X for the F-16 EPU was unknown at the start of the investigation, but was determined to be approximately 0.5 (50% ammonia dissociation).

TABLE 1. REACTIONS OF THE CATALYTIC DECOMPOSITION OF HYDRAZINE



Where X = fraction of NH_3 dissociated.

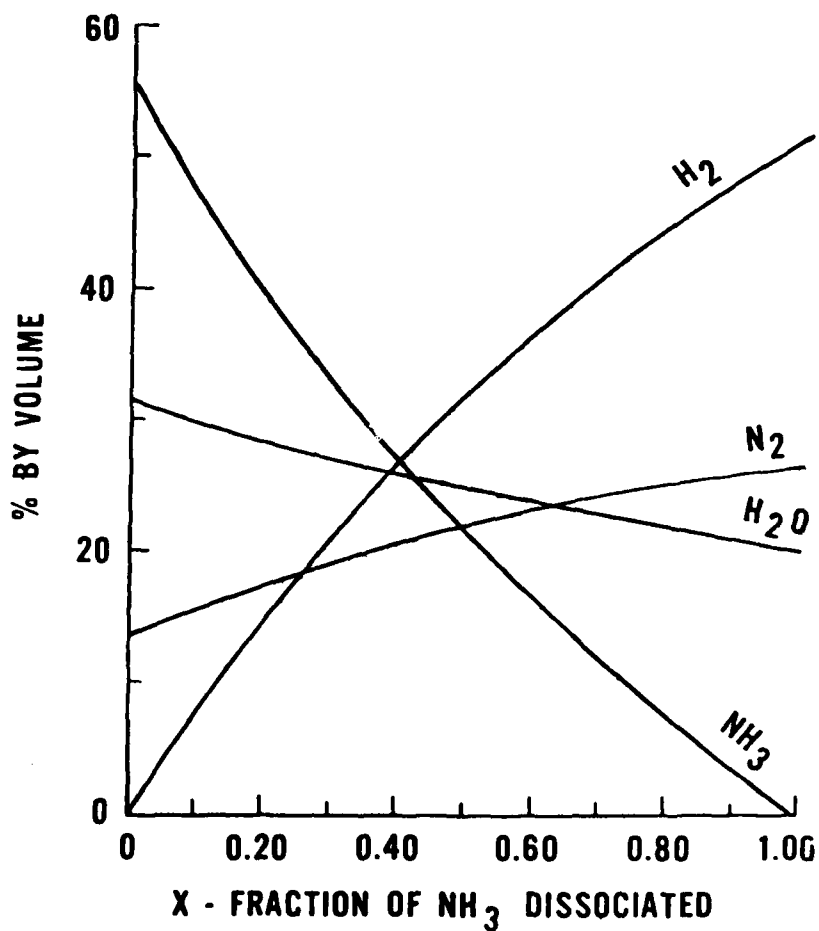


Figure 1. Theoretical exhaust products from catalytic decomposition of H-70.

Under no-load conditions, the EPU operates in a pulsed manner at approximately two pulses per second. Because water in the fuel does not enter into the decomposition reactions, the exhaust gas has a very high water vapor content and hence a high dew point. The exhaust gas is discharged from the F-16 aircraft through a 3-in (7.62 cm) duct opening, flush with the aircraft skin near the wing root and directed vertically downward. Maximum gas temperature was expected to be about 800° F (430° C). These combined factors created somewhat adverse conditions for extractive sampling. However, since in situ measurement techniques were not available within the required time frame, an extractive sampling method was devised and briefly laboratory tested before the study was undertaken.

The extractive sampling train, shown schematically in Figure 2, employed an evacuated tank (approximately 7½ liters) to draw sample through the train, to collect noncondensable gases in the sample, and to contain that gas sample for subsequent analysis. The tanks were alternatively replaced with a vacuum pump, in which case the noncondensable gases were not collected. A limiting orifice was used to maintain a known sampling rate of approximately 1 l/min. Two impingers, in series, each containing 100 ml of 2N sulfuric acid were placed in an ice bath and used to trap ammonia, hydrazine, and water. Solenoid valves before and after the impingers were remotely actuated to start and stop sample flow at predetermined times. An electrically heated sample line and nozzle, preheated to 100° C, was used to deliver the sample to the impingers. The sample line led to a manifold that allowed independent operation of five identical sampling trains, in parallel. Samples were collected from each of the five trains concurrently or sequentially as desired. Exhaust gas temperature was measured with a type J, iron-constantan thermocouple located alongside and flush with the sample nozzle.

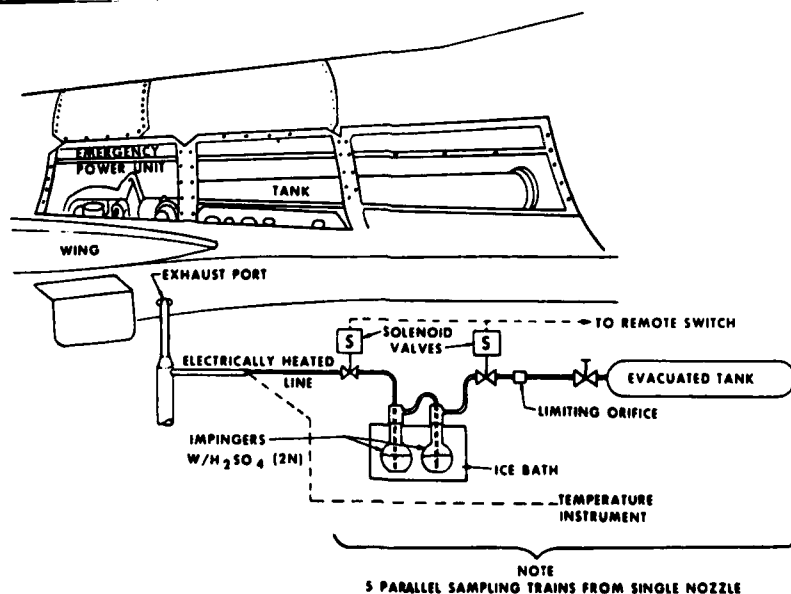


Figure 2. Schematic diagram of exhaust gas sampling train.

The sampling time interval for each sampling train for the six EPU tests is shown in Figure 3. Lines, in the figure, indicate the time of on-stream sample collection for each of the five samples in each test. Only four samples were collected in test 1. Sets A and B indicate tests with two different emergency power units installed in the aircraft. Set A was run on 24 Jan 1978 with EPU S/N 76-103, and Set B on 26 Jan 1978 with EPU S/N 76-107. The first test in each set was run after the EPU had stood overnight at ambient temperature (about 5°C). Between the two subsequent tests in each set, the catalyst bed was purged with gaseous nitrogen and cooled to touch. However, neither EPU was instrumented to measure catalyst temperature, making actual bed temperature unknown at the beginning of subsequent restarts.

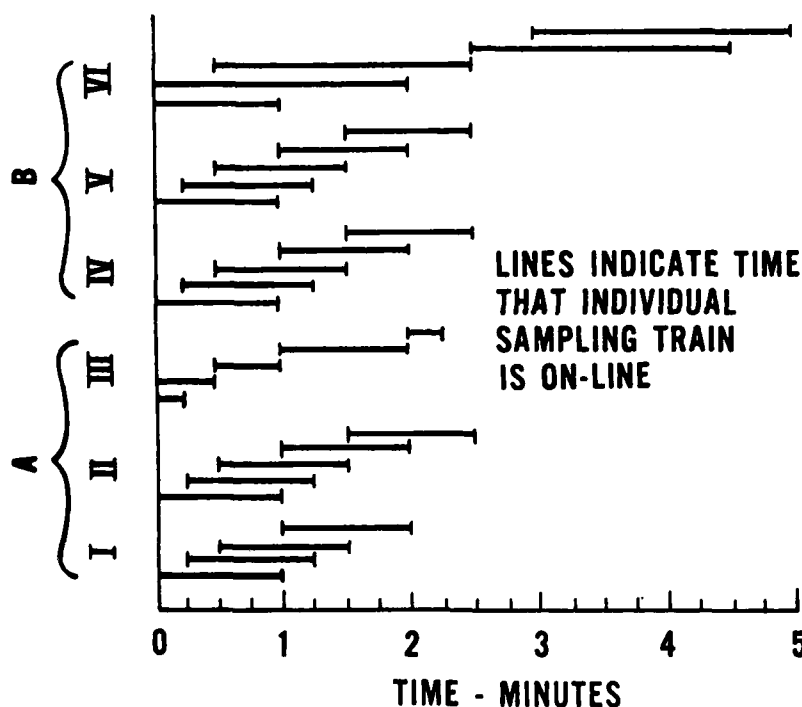


Figure 3. Sampling sequence.

Impingers were weighed before and after each test to determine total condensibles collected. Impinger samples were spot analyzed in the field to verify sample collection, but all samples were returned to the laboratory at Brooks AFB for final analysis. The p-dimethylaminobenzaldehyde (PDAB) colorimetric method (1) was used for hydrazine. Preliminary testing showed that ammonia did not interfere in the hydrazine method. Assay for ammonia was done with Nessler's reagent (2).

RESULTS

Exhaust Gas Temperature

The temperature profiles for two typical EPU tests are shown in Figure 4, as a function of time. Before the completion of the first run, it was apparent that EPU operation was not as had been expected. During run I the exhaust temperature rose rather gradually to around 500°F (260°C) then, at about 1-3/4 min into the run, the temperature increased rapidly to approximately 1200°F (650°C) just as the planned 2-min run was terminated. Run II resulted in the same phenomenon (Fig. 4) except that the rapid temperature rise started 1-1/2 min into the run and leveled off at around 1300-1400°F (700-760°C), the upper range of the type J thermocouple. Prior to run III, contractor engineers installed a 0-2000°F (-20-1100°C) thermocouple on the sample probe, taping the bare wire junction at the exhaust exit plane. During run III the contractor-installed thermocouple indicated a maximum temperature of nearly 1600°F (870°C). Run III was terminated before the planned 2-1/2 min time when flame (afterburning) was seen in the exhaust gas.

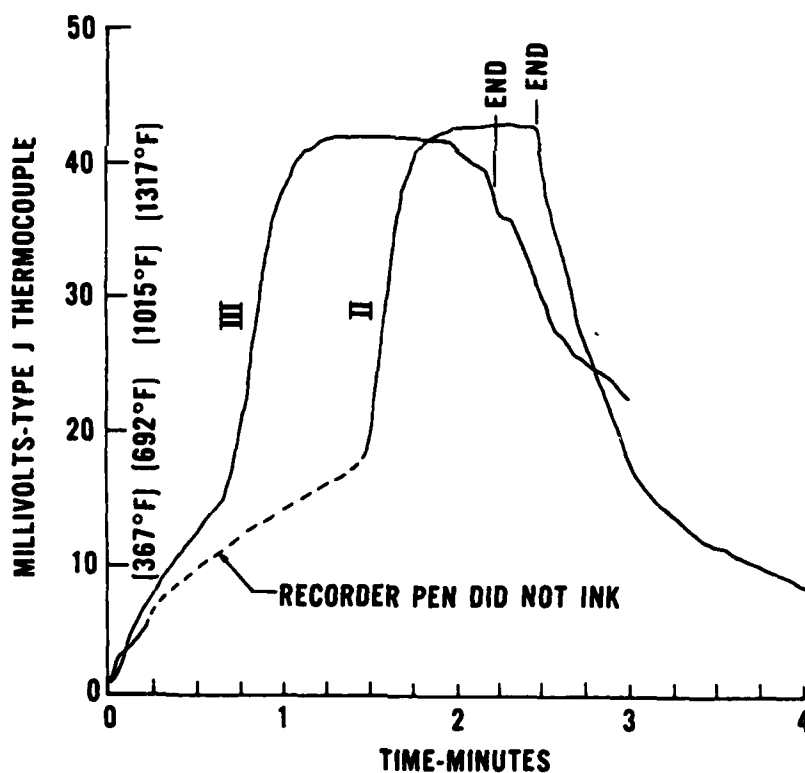


Figure 4. Exhaust gas temperature profile.

After considerable discussion of the findings from the first three tests, the contractor made the decision to exchange EPU S/N 76-103 with one taken from another aircraft. However, runs IV-VI with EPU S/N 76-107 gave essentially the same exhaust gas temperature characteristics. Afterburning was again observed, but usually only after more than 2 min operation.

Hydrazine

Results of hydrazine sampling are shown in Table 2. These results indicated some variability, but there was a clear indication that the hydrazine decreased rapidly with time into the run. Impinger collection efficiency was determined from the ratio of hydrazine in the first and second impingers. All hydrazine samples had a collection efficiency of 95.2% with a standard deviation (σ) of 8.7%.

Significantly greater amounts of unreacted hydrazine were found in runs I and IV. In both cases, these were the first runs made with each of the two different EPU's. Since there had been prolonged cold weather at the time of the test, the catalyst bed temperature was initially between 0°C and 10°C. Between runs, the catalyst bed was purged with gaseous nitrogen; however, in the absence of instrumentation to measure catalyst bed temperature, it is probable that the bed was not cooled to initial run temperatures. This could account for the variability of the hydrazine values and suggests greater hydrazine hazard potential at colder catalyst temperatures.

Ammonia

Results of ammonia sampling are shown in Table 2. These results show little suggestion of either increases or decreases of ammonia with time into the run. Impinger collection efficiency for ammonia was calculated and found to be 88.67% with $\sigma = 15.9\%$.

Gravimetric Determination of Condensibles

The 1-s to 2-min samples gave only a small mass of condensibles, which was a result of measuring a small weight difference (less than 0.5 g) between two rather large weights (about 450 g). This inherently high error determination, coupled with the extremely adverse environmental conditions under which weighings were made, rendered these results of marginal usefulness. They are not included in this report.

Noncondensable Gases

The noncondensable sample gases were collected in evacuated tanks for later laboratory gas chromatographic analysis. The tanks were initially evacuated to 1 Torr. After sampling, pressures were determined with a low volume absolute pressure gauge. Analysis of the tank

TABLE 2. HYDRAZINE AND AMMONIA IN EPU EXHAUST GAS

Run No.	Impinger set No.	Sample time (min)	Hydrazine (μ g)	Ammonia (mg)
I	1	1	10,778	199
	2	1	9,100	231
	3	1	572	180
	4	1	35	164
II	1	1	1,725	152
	2	1	1,350	194
	3	1	690	191
	4	1	51	182
	5	1	14	249
III	1	0.25	1,560	58
	2	0.50	2,650	141
	3	0.50	358	81
	4	1	0	249
	5	0.28	0	58
IV	1	1	3,670	79
	2	1	2,380	232
	3	1	374	135
	4	1	0	94
	5	1	0	68
V	1	1	630	170
	2	1	430	145
	3	1	0	111
	4	1	0	247
	5	1	0	160
VI	1	1	0	177
	2	2	255	244
	3	2	0	281
	4	2	0	283
	5	2	0	372

samples was delayed for several weeks due to laboratory equipment failure. At that time remeasurement of tank pressures suggested some leakage had occurred. Analysis confirmed the presence of oxygen and also suggested hydrogen had been lost. Accordingly, these results are considered suspect and are not reported herein.

Noncondensable Gas Flow Rates

Based on the initial post-sampling pressure measurements of the tanks and the sampling times, flow rates for each sample in runs V and VI were calculated. The average for the ten samples was 0.890 l/min with a σ of 0.218. The limiting orifices had initially been calibrated with air at 1.1 l/min. This value was corrected for molecular weight and temperature, according to:

$$q_2 = q_1 \sqrt{\frac{M_2 T_1}{M_1 T_2}}$$

where q_2 = Actual flow rate, l/min
 q_1 = Calibration flow rate (air at 1.1 l/min)
 M_2 = Molecular weight of actual gas
 M_1 = Molecular weight of calibration gas (air = 29)
 T_2 = Actual temperature $^{\circ}\text{K}$
 T_1 = Calibration temperature (293°K)

By assuming that 50% of the ammonia was dissociated, the average molecular weight of the product gas was calculated to be 12. Substitution of this value for M_2 and the average sampling temperature of 278°K for T_2 , the corrected sample gas flow rate was calculated to be 0.726 l/min, in reasonable agreement with the measured value (based on average post-sampling pressure measurements).

Fuel Consumption

The EPU was not instrumented to determine fuel consumption rate. This value was approximated by determining the weight of fuel consumed during each set of runs and assuming a uniform fuel flow rate over the total lapsed run time. Fuel consumption for the first EPU (Set A) was 4.1 lb/min and for the second EPU (Set B) was 3.5 lb/min.

Determining Emissions and Emission Rates

Since both the weights of condensibles and analyses of noncondensable gases were unreliable, it is impossible to make an overall material balance. Manipulation of real data and theoretically expected values

was necessary to arrive at emission figures. The following procedure was employed.

First, the theoretical ratio of ammonia to noncondensable gas formed (mg/liter) was calculated using equation 3 (Table 1) and plotted against X, the fraction of ammonia dissociated (Fig. 5). The non-condensable gas was assumed to consist only of hydrogen and nitrogen.

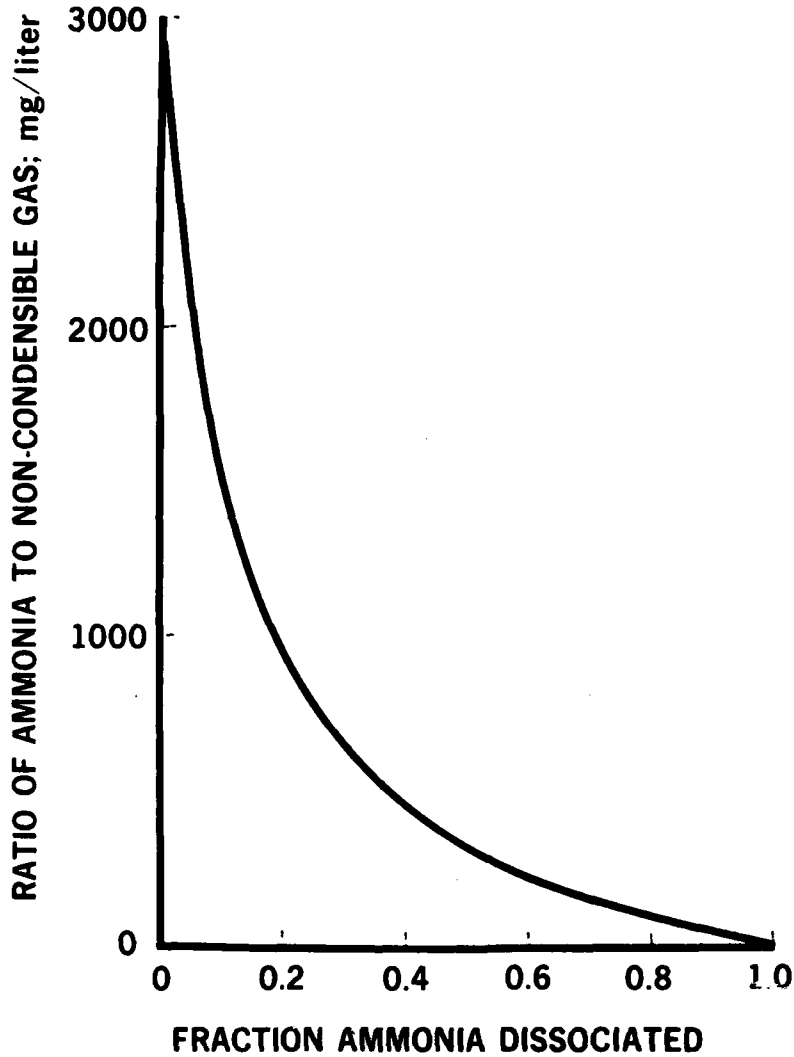
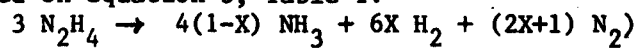


Figure 5. Theoretical ratio of ammonia to noncondensable gas ($N_2 + H_2$) as a function of fraction ammonia dissociated. (Based on equation 3, Table 1:



For each sample, the amount of ammonia trapped (mg) per liter of non-condensable gas sampled (0.726 l/min) was determined. These values were averaged for sample sets A and B, and the results are shown in Table 3. Using Figure 5, the corresponding value of X was determined as indicated in Table 4.

TABLE 3. TOTAL HYDRAZINE AND AMMONIA IN EPU EXHAUST

Set	Run No.	Hydrazine sampling time interval (g)				Ammonia Average (l/min) ^a
		0-30 s	30-60 s	60-120 s	Total	
A	I	22.55	1.50	0.08	24.13	603
	II	2.38	1.43	0.11	3.92	604
	III	5.83	0.84	0	6.67	706
B	IV	8.00	0.44	0.37	8.81	376
	V	1.37	0	0	1.37	515
	VI	0	0	0.56	0.56	475

^aMeasured at 21°C, 1 ATA

TABLE 4. RATIO OF AMMONIA TO NONCONDENSIBLE GASES AND ESTIMATED FRACTION OF AMMONIA DISSOCIATED

Set	mg NH ₃ /liter noncondensable	X, (Fraction NH ₃ dissociated)
A	274, $\sigma = 44$	0.52
B	192, $\sigma = 60$	0.62

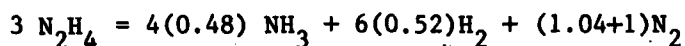
Once a value of X was determined, the theoretical flow rate of noncondensable gas could be determined from the fuel consumption rate and reaction 3 of Table 1, as follows:

Sample Set A: X = 0.52

Fuel flow rate = 4.1 lb/min (70% hydrazine)

$$\begin{aligned}\text{Hydrazine flow rate} &= (4.1)(0.7)(454)/32 \\ &= 40.7 \text{ g-moles/min}\end{aligned}$$

From Equation 3:



$$\begin{aligned}\text{Noncondensable gas ratio} &= (3.12 + 2.04)/3 \\ &= 1.72 \text{ g-moles/g-mole hydrazine}\end{aligned}$$

$$\begin{aligned}\text{Noncondensable gas} \\ \text{flow rate} &= (1.72)(40.7) \\ &= 70.0 \text{ g-moles/min} \\ &= 1596 \text{ l/min at } 5^\circ\text{C}\end{aligned}$$

$$\begin{aligned}\text{Sample ratio} &= 1596/0.726 \\ &= 2198 \text{ or } 2200\end{aligned}$$

A similar calculation for sample Set B gave a sample ratio of 2180. By means of these ratios, the hydrazine and ammonia found in the samples could be extrapolated to the total gas stream, as indicated in Table 3.

DISCUSSION OF RESULTS

The higher-than-expected exhaust gas temperatures experienced in the A set of runs led to speculation that the EPU was not operating properly. When the same temperature patterns were observed in the B set with a different EPU, it became more likely that the operation was in fact normal even if unexpected. The temperature and exhaust composition data indicated only minor difference between the two EPU units.

The variability in the results was not altogether unexpected for a field extractive sampling method, considering the adverse sampling parameters. Additional sampling by this method is considered unlikely to refine the results to any great extent. If additional refinement is needed, in situ optical methods should be explored. Laser Raman spectroscopy would appear to be a promising technique, but our laboratory is not equipped to do such work.

EVALUATION OF POTENTIAL EXPOSURES

The EPU exhaust gas presents potential exposure to both ammonia and hydrazine. By all realistic scenarios, there is little likelihood of multiple firings at any one location and on a given day, except in test programs such as the one described in this report. For either planned or inadvertent outdoor ground firings, the duration would probably be of no more than 30 s. Under normal meteorological conditions, one might expect elevated concentrations of ammonia and hydrazine to persist for a matter of 3 to 5 min. For this condition, consideration of 8-hour time-weighted average (TWA) standards are inappropriate since relatively massive exposures during this short period of time--assuming no exposure for the remainder of the day--would result in average exposure well below standards. For this reason short-term or excursion limits must be used to evaluate exposures.

Table 5 shows appropriate standards currently applicable in the Air Force. Note that the last column of Table 5 shows odor threshold values, which for both materials, are higher than even the short-term limits. Hence, odor cannot be used to give warning of overexposure.

The ratio of ammonia to hydrazine short-term limits is approximately 70:1, whereas the ratio of ammonia to hydrazine in the actual exhaust varied from 20:1 to 49:1 at 30-s duration. Hydrazine therefore appears to be the controlling material. This is unfortunate since ammonia can be measured in air easier than hydrazine, and at the higher ratio would be an indicator of potentially unsafe hydrazine concentrations.

Concentrations of ammonia in the immediate vicinity of the exhaust, while not measured directly, were probably greater than 1000 ppm. Concentrations this high are so irritating to man that he will not remain in the area of exposure unless he is physically restrained. Hence, massive worker exposures to ammonia are unlikely. Of concern, however, are those areas where the ammonia is present but cannot be detected by odor, or those areas where the ammonia is not in high enough concentration to cause great discomfort. Meteorological conditions are extremely important in determining the extent of these potential exposure zones. For unfavorable conditions, the exposure zone can extend to beyond 50-100 m downwind.

TABLE 5. AMMONIA AND HYDRAZINE EXPOSURE LIMITS

<u>Contaminant</u>	<u>8-h TWA</u>	<u>Short-term or excursion limit</u>	<u>Odor threshold</u>
Ammonia	25 ppm (18 mg/l)	35 ppm (27 mg/l)	50 ppm
Hydrazine	0.1 ppm (0.13 mg/l)	0.3 ppm (0.39 mg/l)	3-4 ppm

If the EPU were accidentally fired in a closed hangar, even of moderate size, the concentration of ammonia and/or hydrazine could quickly build up to unacceptable levels throughout the structure. In this case, high concentrations could persist for much more than 3 to 5 min, depending on the ventilation rate for the hangar. The experience to be gained in the climatic test at Eglin (April-May 1978), where the EPU exhaust will be ducted outside the hangar, will be valuable in determining if venting is a permissible procedure for indoor firings.

RECOMMENDATIONS

To arrive at realistic recommendations, we must consider both deliberate planned firings and inadvertent firings. Planned firings may be defined as routinely occurring events (tests) which require planned actions to preclude excessive exposure. Inadvertent firings, by contrast, may be defined as accidents which require general cognizance of their probability as well as preplanned actions both to prevent the accident and to minimize injury if the accident should occur.

For routine, planned ground hot firings:

1. Minimize or eliminate requirements for such firings.
2. Do not conduct planned ground firings inside closed hangars unless ducting the exhaust gas outside the building is feasible and effective.
3. Develop outdoor siting/meteorological criteria to govern outdoor firings.
4. For area monitoring, use ammonia detection techniques as an indicator of hydrazine. With the hydrazine-ammonia ratios formed, a concentration of over 10 ppm (7.2 µg/l) ammonia would indicate excessive hydrazine exposures. MSA (Mine Safety Appliance Co.) sampling tubes (FSN 6665-00-406-9450) would be appropriate for ammonia detection.
5. Use respiratory protective equipment for any tasks occurring immediately around the aircraft during firing and exclude all other personnel from the potential exposure zone.

For inadvertent ground firings:

1. Develop actions to reduce probability of inadvertent firings-- safety devices, checklists, etc.
2. Conduct training for those individuals potentially exposed, to recognize sound of EPU, odor of ammonia, need to avoid the area, etc.

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