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ANALYTICAL TASK SUMMARY REPORT

J.D. Kuenzly
Rein Grabbi

TRW Systems Group
One Space Park
Redondo Beach, Calif. 90278

DECEMBER 1973

INTERIM REPORT

FOR PERIOD MARCH - APRIL 1973

Prepared for
GODDARD SPACE FLIGHT CENTER
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16. Abstract

The objective of the "Study of Monopropellants for Electrothermal Thrusters" program is to determine the feasibility of operating small thrust level electrothermal thrusters with monopropellants other than MIL-grade hydrazine. The work scope includes analytical study, design and fabrication of demonstration thrusters, and an evaluation test program wherein monopropellants with freezing points lower than MIL-grade hydrazine are evaluated and characterized to determine their applicability to electrothermal thrusters for spacecraft attitude control.

Results of propellant chemistry studies and performance analyses have indicated that the most promising candidate monopropellants to be investigated during this program are monomethylhydrazine, Aerozine-50, 77% hydrazine-23% hydrazine azide blend, and TRW formulated mixed hydrazine monopropellant (MHM) consisting of 35% hydrazine-50% monomethylhydrazine-15% ammonia. It is recommended that these monopropellants be used during the Evaluation Test Program Task of this program.

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PREFACE

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1.0 INTRODUCTION

This report summarizes the analytical studies performed in support of the "Study of Monopropellants for Electrothermal Thrusters" program. The studies were performed to identify, evaluate and characterize propellants with freezing points lower than MIL-grade hydrazine which would be applicable to electrothermal thrusters for spacecraft attitude control. The work performed during this program period included an extensive literature search, propellant chemistry studies, performance analyses, recommended approach to Design and Fabrication, and a detailed test plan for the Evaluation Test Program. Included in this report are separate topics describing propellant requirements, properties of the various monopropellants, and the selection of candidate propellants for the evaluation test program.

2.0 PROPELLANT REQUIREMENTS

Among the various monopropellants, hydrazine has gained the widest acceptance for spacecraft low-thrust propulsion systems. However, the relatively high freezing point of 1.53°C (34.75°F) inherently restricts use of the propellant and/or complicates the spacecraft's thermal control system. For the purposes of this program, a useful monopropellant is one which has a freezing point lower than that of MIL-grade hydrazine and which may provide improvements in performance or density impulse. While not specifically stated in the Statement of Work, the consideration of various propellants for spacecraft applications also requires that equal importance be given to propellant properties related to materials compatibility, thermal stability, shock sensitivity, toxicity, handling, and transfer. These propellant requirements have been summarized and are presented in Table 1. They are representative of requirements for a system whose thrust functions are typical for spacecraft attitude control and station keeping applications. The assignment of more exact requirements is difficult without detailed analyses of the needs for a specific mission.

Imposition of these characteristics may represent a set of partially contradictory requirements which must be reasonably satisfied by the condidate propellants. Each requirement has therefore been graded as "requirement" or "goal", depending on whether the characteristic is a firm requirement or a design goal which may be compromised.

The requirement of the propellant freezing point less than that of hydrazine has been amplified to include a design goal of -17.8°C (0°F) or lower. This value is a reasonable lower temperature limit which may be expected in a typical spacecraft application. It also provides a substantial improvement in comparison to hydrazine. Propellant storability, materials compatibility and thermal stability have all been classified as requirements in consideration of typical spacecraft missions lasting five years. Propellant shock sensitivity, toxicity and safety characteristics have also been listed as requirements to be met when selecting propellants for the test program. The criteria in these cases have been assumed to be the need for handling properties and hazard characteristics not worse than those presently established and accepted for hydrazine.

Table 1. Monopropellant Requirements

1. **Ambient Temperature:** maximum	Requirement	51.7°C (125°F)
Freezing Point:	Goal	-17.8°C (0°F)
	Requirement	less than 1.1°C (34°F)
2. **Performance:** Steady state, minimum	Goal	I_{sp} = 1961 N-s/kg (200 sec)
Pulse mode, minimum	Goal	I_{sp} = 1716 N-s/kg (175 sec)
3. **Density (room temperature)**	Goal	1.0 gm/cm^3 or higher
4. **Storability**	Requirement	5 years
5. **Shock Sensitivity**	Requirement	0 cards on JANNAF* card gap test
6. **Materials Compatibility**	Requirement	5 years
7. **Toxicity**	Requirement	No worse than N_2H_4
8. **Safety**	Requirement	Handling and transfer characteristics similar to N_2H_4 (DOD hazard classification Group III)
9. **Thermal Stability**	Requirement	No worse than N_2H_4
10. **Commonality**	Goal	"On-board" propellant in bi-propellant propulsion systems

*JANNAF: Joint Army-Navy-NASA-Air Force

The designation of program "goal" has been chosen for propellant performance, density and commonality. The optimization of each of these characteristics is desirable, but may be compromised if necessary to meet a different propellant requirement.

3.0 PROPELLANT PROPERTIES

The survey of monopropellant substitutes for hydrazine provides a large number of low freezing point candidates. A considerable amount of research and development has been expended in efforts to develop suitable monopropellants. This work included studies of hydrogen peroxide, organic nitrates, nitro paraffins and hydrazine derivatives such as monomethylhydrazine and unsymmetrical-dimethylhydrazine. Efforts to lower the freezing point of hydrazine have led to the evaluation of binary monopropellants utilizing hydrazine with the afore named hydrazine derivatives as well as inorganic salts such as nitrates and azides. The freezing point of hydrazine is also depressed by the addition of amines (ammonia, aniline), alcohols and water. Similar studies have been conducted with hydrazine based ternary and quaternary mixtures. A large variety of these is feasible using the additives considered for binary mixtures. All such mixtures characteristically exhibit a freezing point lower than that of hydrazine. However, the freezing point depression is associated with significant physical property and performance changes. The basic propellant selection criteria applicable to this study requires the simultaneous control of the mixture's properties, performance and freezing point. The additional propellant properties requiring evaluation are vapor pressure, viscosity, density impulse, decomposition temperature, boiling point and detonation propagation.

The task of propellant selection has been simplified by a preliminary screening of monopropellants and the rejection of obviously unsuitable candidates. The following propellants have been considered unsatisfactory for use on this program because of violating one or more of the requirements specified in Table 1:

a) hydrogen peroxide: this propellant has a high freezing point of -0.6°C (31°F). The decomposition and thermal stability characteristics are unsuitable for extended periods of storage.

b) hydrazine nitrate: mixtures of hydrazine and hydrazine nitrate impose stability and handling-safety problems more severe than hydrazine. Standard JANNAF* card gap and drop

*JANNAF: Joint Army-Navy-NASA-Air Force

weight tests have shown a value of zero cards and negative results, respectively, for mixtures up to 16% hydrazine nitrate. Standard ICRPG* detonation propagation tests have resulted in partial propagation in 6.35 mm (0.25 inch) tubing at 23°C (91.4°F) and 20% hydrazine nitrate concentration. The non-volatile residues are definitely shock sensitive. The presence of nitrate ion in the hydrazine nitrate blends promotes chemical reactions with materials and rapid burning.

c) Other inorganic salts with the exception of azides: mixture freezing point can be depressed with the addition of hydrazine sulfide, cyanide, perchlorate, fluoride or carbonate. Performance and physical data on these mixtures are limited or non-existent and none of these has apparently been considered as a likely monopropellant.

d) Organic nitrates: n-propyl nitrate has a drop-weight shock sensitivity of 7.0 kg-cm. The corresponding value for hydrazine is 120 kg-cm (minimum). Ethyl nitrate may be added to reduce the shock sensitivity of n-propyl nitrate, but improvements in performance are not expected. Other organic nitrates such as methyl nitrate and diethylene glycol dinitrate exhibit shock sensitivity similar to that of nitroglycerin.

e) nitro paraffins: nitromethane has a freezing point of -28.5°C (-19.3°F) and can provide a density impulse** of approximately 2452 N-s/kg (250 sec) at 25°C. The high combustion temperature of 2177°C (3950°F) and oxygen bearing decomposition products (H_2O, CO_2, CO) preclude its use as a monopropellant. The anticipated temperatures are in excess of noble metal alloy limits. Although refractory metals (Re, etc.) have sufficient thermal capability, their reaction

* ICRPG: Inter agency Chemical Rocket Propulsion Group
**Density impulse is expressed as the product of specific impulse (N-s/kg or $\frac{\text{lbf-s}}{\text{lbm}}$ = sec) and the propellant specific gravity at a specified temperature

with CO_2 and H_2O will result . adverse material degradation.

Tetranitromethane is undesirable by virtue of its high freezing point of 13.3°C (56°F). The addition of freezing point depressants increases the explosive sensitivity to unacceptable levels.

The propellants not excluded by the preliminary screening are grouped into three major categories: 1) hydrazine derivaties such as monomethyl-hydrazine (MMH) and unsymmetrical-dimethylhydrazine (UDMH); 2) binary mixtures of hydrazine with its derivatives, hydrazine azide, ammonia or water; and 3) hydrazine based ternary mixtures using the same constituents. The performance, physical and safety characteristics for these propellants are summarized in the following discussion:

1) Hydrazine Derivatives. This group includes monomethylhydrazine, unsymmetrical-dimethylhydrazine and Aerozine-50. The latter, a 50-50 blend of N_2H_4 and UDMH, is included with the other monopropellants because it is a unique propellant ofen used in bi-propellant propulsion. The performance and physical properties of these propellants are compared to hydrazine in Table 2. The following characteristics are considered: freezing point, density, vapor pressure, viscosity, specific impulse, density impulse and adiabatic flame temperature. The data, in general, are for ambient room conditions. The temperature dependence of propellant density, vapor pressure and viscosity is shown in Figures 1, 2 and 3, respectively. The safety, storage and handling characteristics are summarized in Table 3. The following characteristics are considered: shock sensitivity, detonation propagation, thermal stability, long term storability, toxicity, safety and materials compatibility. The specific test methods and rating scales for these properties are described in Appendix A.

2) Binary Mixtures. This category considers the binary monopropellant characteristics which result from blending hydrazine with UDMH, MMH, water, ammonia, hydrazine azide and hydrazine nitrate. The latter is included for informative reasons although it has been excluded by the preliminary screening.

Table 2. Performance and Physical Characteristics of Pure Monopropellants

CHARACTERISTIC	UNITS	PROPELLANT N_2H_4	MMH	UDMH	AERO-50
1. Freezing Point	°C (°F)	1.53 (34.75)	-52.2 (-62)	-57.2 (-71)	-5.6 (22)
2. Density (25°C)	gm/cm^3	1.00	0.87	0.79	0.90
3. Vapor Pressure (25°C)	$10^3 N/m^2$ (Torr)	1.89 (14.2)	6.58 (49.5)	22.2 (167)	17.9 (135)
4. Viscosity (25°C)	Poise	0.0091	0.0078	0.0049	0.0081
5. Theoretical Vacuum I_{sp} $P_c = 1.03\ MN/m^2$ (150 psia) $\epsilon = 50$	N-s/kg (sec)	2265 (231)	2206 (225)	2128 (217)	2216 (226)
6. Density Impulse (25°C)	N-s/kg (sec)	2265 (231)	1922 (196)	1677 (171)	1991 (203)
7. Adiabatic Flame Temperature	°C (°F)	816 (1500) $\alpha = 0.72$	785 (1445)	748 (1379)	789 (1453)

$\alpha \equiv$ Fraction of Ammonia Dissociation

Performance Data for MMH, UDMH, and AERO-50 are at Thermodynamic Equilibrium.

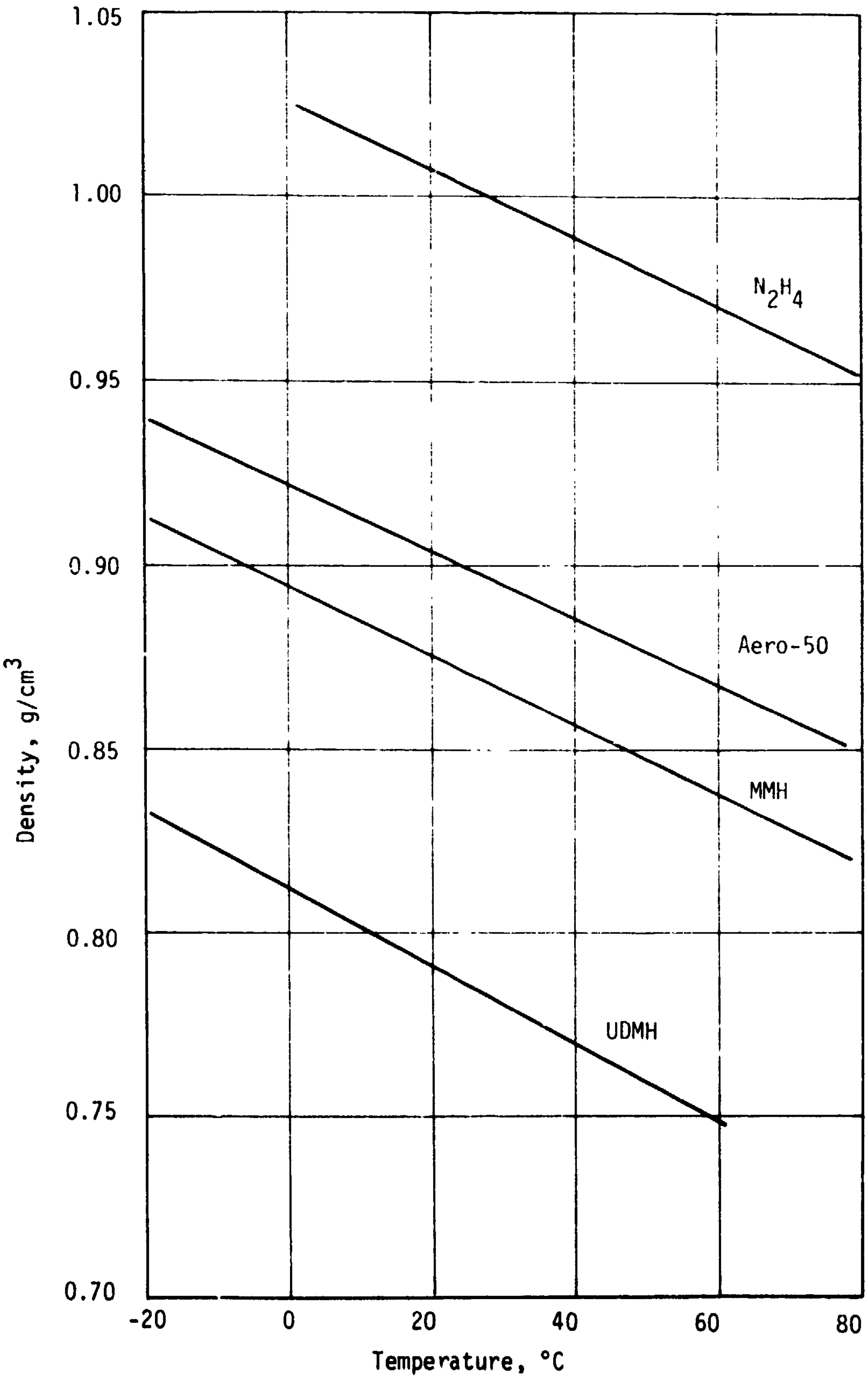

Figure 1. Density of Pure Monopropellants as a Function of Temperature

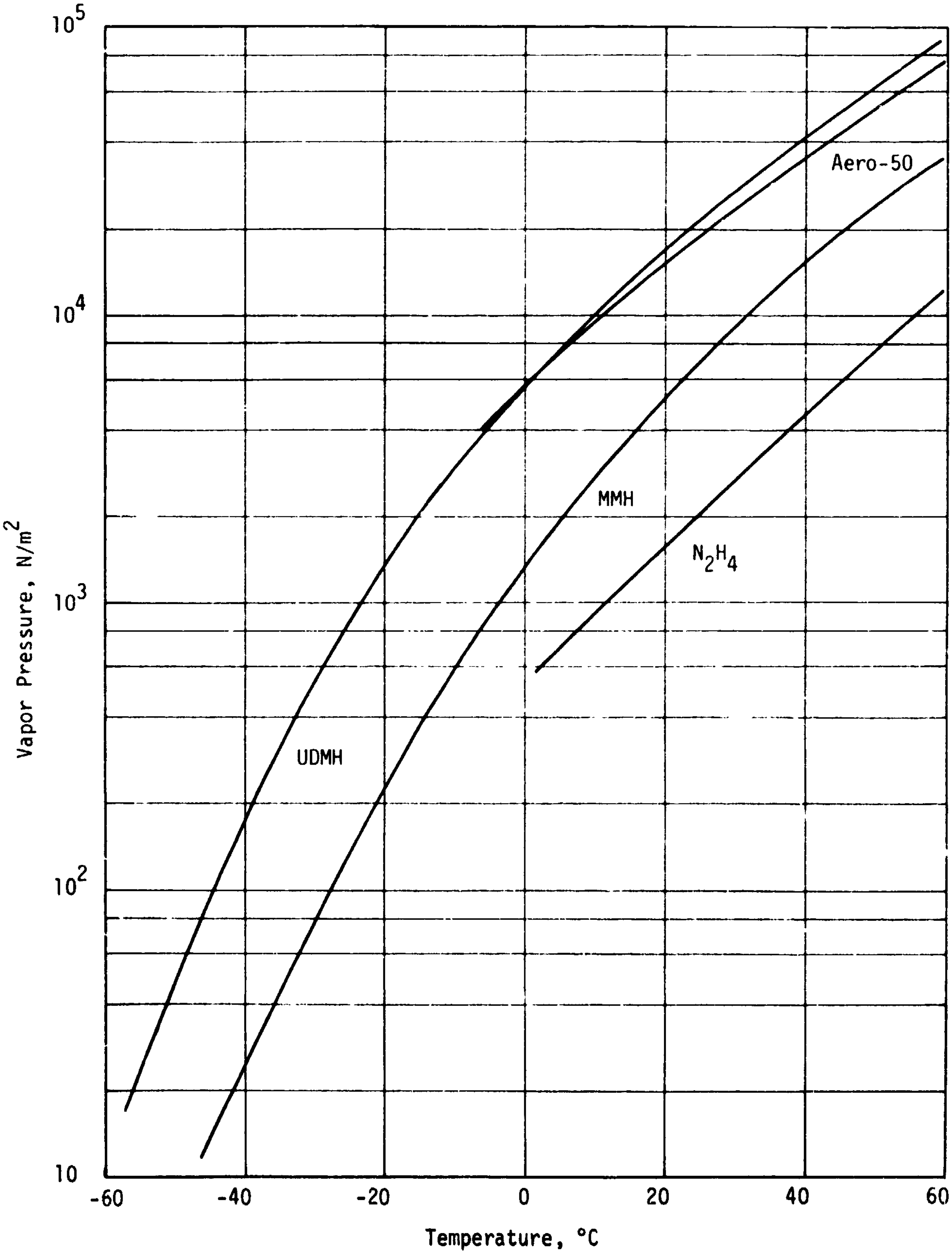

Figure 2. Vapor Pressure of Pure Monopropellants as a Function of Temperature

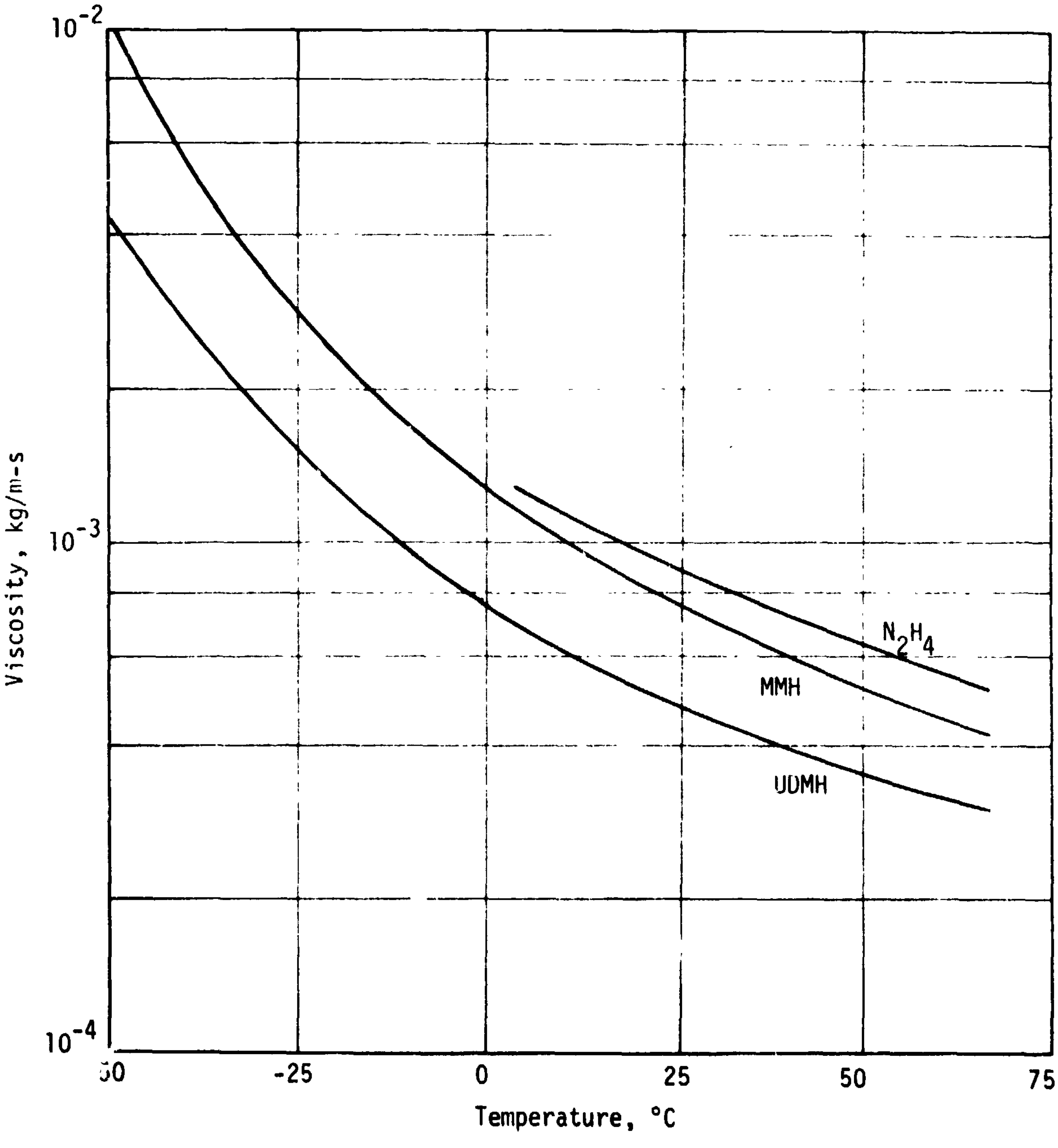

Figure 3. Viscosity of Pure Monopropellants as a Function of Temperature

Table 3. Safety/Storage/Handling Characteristics of Pure Monopropellants

		Propellant			
Characteristic	Test Method	N_2H_4	MMH	UDMH	AERO-50
Shock Sensitivity	Drop-weight	120 kg-cm (minimum)	N/A	N/A	N/A
	JANNAF card gap	0	0	0	0
Detonation Propagation	Standard ICRPG	No propagation in 0.64 cm line at 23°C	No propagation	No propagation	No propagation
Thermal Stability	Differential Scanning Calorimeter	172°C	N/A	N/A	N/A
	Standard ICRPG	168°C	N/A	N/A	N/A
Long Term Storability	Gas Evolution Rate	1.19×10^{-4} cc_{NTP}/kg-min	6.89×10^{3} N/m^2-day at 71.1°C 6061 aluminum	68.9 N/m^2-day at 71.1°C 5250 aluminum	N/A
Toxicity	MAC* (PPM for 8 hr)	1.0	0.5	0.5	0.5
Safety/Handling	DOD Hazard	Group III	Group III	Group III	Group III
	ICC Rating	Corrosive liquid	Flammable liquid	Flammable liquid	Flammable liquid
Materials Compatibility**	Aluminum alloys	A	A	A	A
	300 CRES	A&B	A	A	A
	Titanium alloys	A	A	A	A

*MAC-Maximum Allowable Concentration
**Compatibility classifications are listed in Table 7
N/A - Not available

Propellant performance and physical property (25°C) data are summarized in Table 4 for mixtures of hydrazine with hydrazine azide, ammonia, hydrazine nitrate and MMH, respectively. Corresponding safety, storage and handling characteristics appear in Table 5. The mixture compositions are typical of those considered for propulsion applications.

The freezing point, density, specific impulse, and density impulse dependence on propellant composition are illustrated in Figures 4-7, respectively. The freezing point of hydrazine is lowered by all additives in this section (Figure 4). The minimum freezing point, -17.5°C (0.5°F), of hydrazine-hydrazine azide mixtures occurs at the eutectic composition of 77% N_2H_4 - 23% N_5H_5. The density is increased by the addition of water, hydrazine azide or hydrazine nitrate, whereas, additions of ammonia, MMH or UDMH decrease mixture densities. The specific and density impulse data shown in Figures 6 and 7 were computed for a chamber pressure of 1.034 MN^*/m^2 (150 psia) and expansion to vacuum through a nozzle having an area ratio of 50 to 1. The TRW Rocket Chemistry Computer Program was used to obtain the performance parameters in Figures 6 and 7. The data are for adiabatic thermodynamic equilibrium. The fraction of dissociated ammonia at equilibrium corresponds to the maximum possible. An analysis of the kinetic environment in most thrusters reveals that thermodynamic equilibrium is rarely achieved. Hydrazine thrusters are designed to provide a minimum amount of ammonia decomposition. Higher performance results when the energy of ammonia dissociation is retained to increase the hydrazine decomposition product enthalpy. The effect of ammonia dissociation on performance is best illustrated by assuming the condition of frozen flow. The hydrazine decomposition product compositions and phases are arbitrarily fixed and no consideration is given to equilibrium. The performance parameters are expressed as a function of ammonia dissociation fraction, α. The decomposition of hydrazine may be described by

$$3N_2H_4 \longrightarrow 4\,(1-\alpha)NH_3 + (2\alpha + 1)\,N_2 + 6\alpha H_2 \qquad (1)$$

The corresponding descriptive decomposition reaction for hydrazine azide (N_5H_5) is

$$3N_5H_5 \longrightarrow 5(1-\alpha)NH_3 + (2.5\alpha + 5)\,N_2 + 7.5\alpha H_2 \qquad (2)$$

*MN/m^2 = mega-newtons per square meter ($10^6 N/m^2$)

Table 4. Performance and Physical Property Characteristics of Pure Binary Monopropellants

CHARACTERISTIC	UNITS	PROPELLANT		
		77% N_2H_4 23% N_5H_5	80% N_2H_4 20% NH_3	72% N_2H_4 28% HN
1. Freezing Point	°C (°F)	-17.5 (0.5)	-15 (5)	-17.8 (0)
2. Density (25°C)	gm/cm^3	1.08	0.92	1.12
3. Vapor Pressure (25°C)	10^3 N/m^2 (Torr)	1.33 (10)	424 (3192)	N/A
4. Viscosity (25°C)	Poise	0.02	N/A	0.015
5. Theoretical Vacuum I_{sp} $P_c = 1.03$ MN/m^2 $\epsilon = 50$	N-s/kg (sec)	2256 (230)	2148 (219)	2471 (252)
6. Density Impulse (25°C)	N-s/kg (sec)	2432 (248)	1971 (201)	2765 (282)
7. Adiabatic Flame Temperature	°C (°F)	816 (1500)	766 (1410)	921 (1690)
		$\alpha = 0.92$	$\alpha = 0.7$	Equilibrium

N/A = Not available

Table 5. Safety/Storage/Handling Characteristics of Pure Binary Monopropellants

		Propellant Mixture		
Characteristic	**Test Method**	N_2H_4 - NH_3	N_2H_4 - $N_2H_5NO_3$	N_2H_4 - N_5H_5
Shock Sensitivity	Drop-weight	120 kg-cm (minimum)	N/A	120 kg-cm (23% HA)
	JANNAF card gap	0	0 up to 25% HN	0
Detonation Propagation	Standard ICRPG	Not available No propagation expected	Partial propagation in 0.64 cm tubing at 23°C (40% HN)	No propagation in 0.64 cm tubing at 23°C
Thermal Stability	Differential scanning calorimeter	N/A	N/A	Endotherm 168°C Exotherm 182°C
	Standard ICRPG	N/A	N/A	Exotherm 129°C (Peak 177°C)
Long Term Storability	Gas evolution rate	N/A	N/A	5.73×10^{-3} cc_{NTP}/kg-min 60°C, 23% N_5H_5
Toxicity	MAC(PPM for 8hr)	1.0	1.0	1.0
Safety and Handling	DOD Hazard	Group III	Group III up to 25% HN Group IV above 25% HN	Group III
	ICC rating	Corrosive liquid	Corrosive liquid up to 25% HN	Corrosive liquid
Materials Compatibility	Aluminum alloy	A	A or B	A
	300 CRES	A or B	A or B	A or B
	Titanium alloy	A	A or B	A

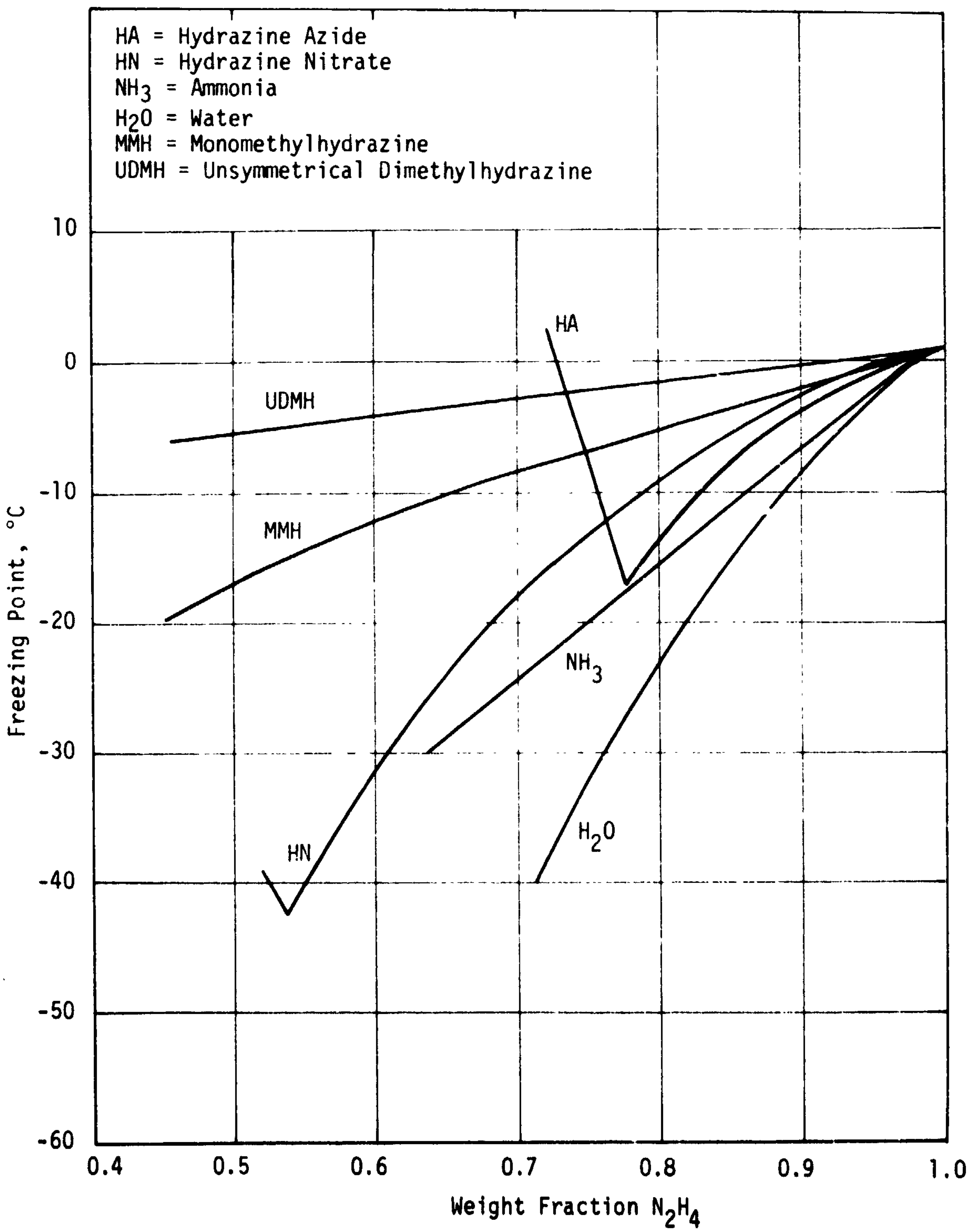

Figure 4. Freezing Point Temperatures of Pure Binary Monopropellants

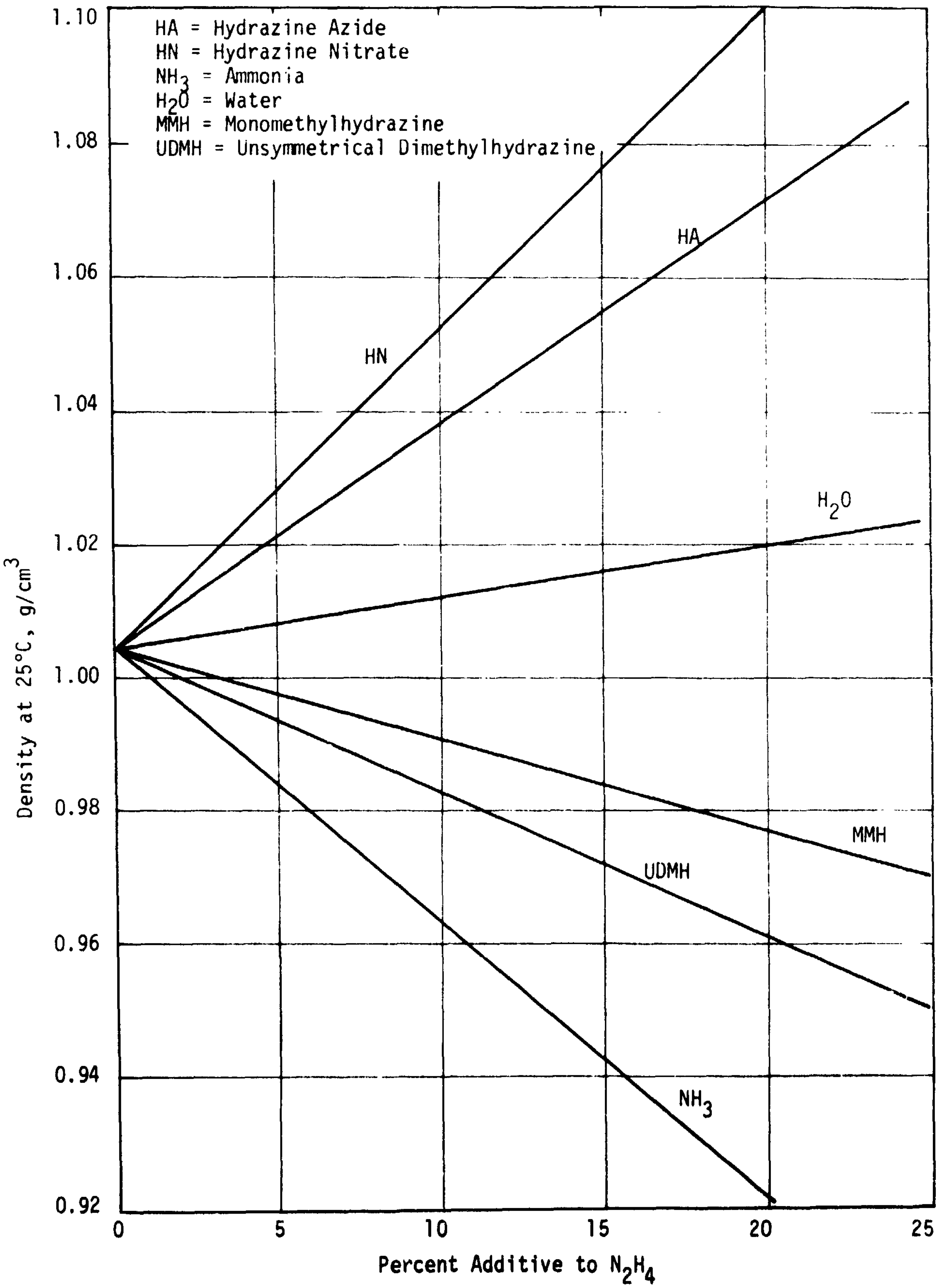

Figure 5. Density of Pure Binary Monopropellants

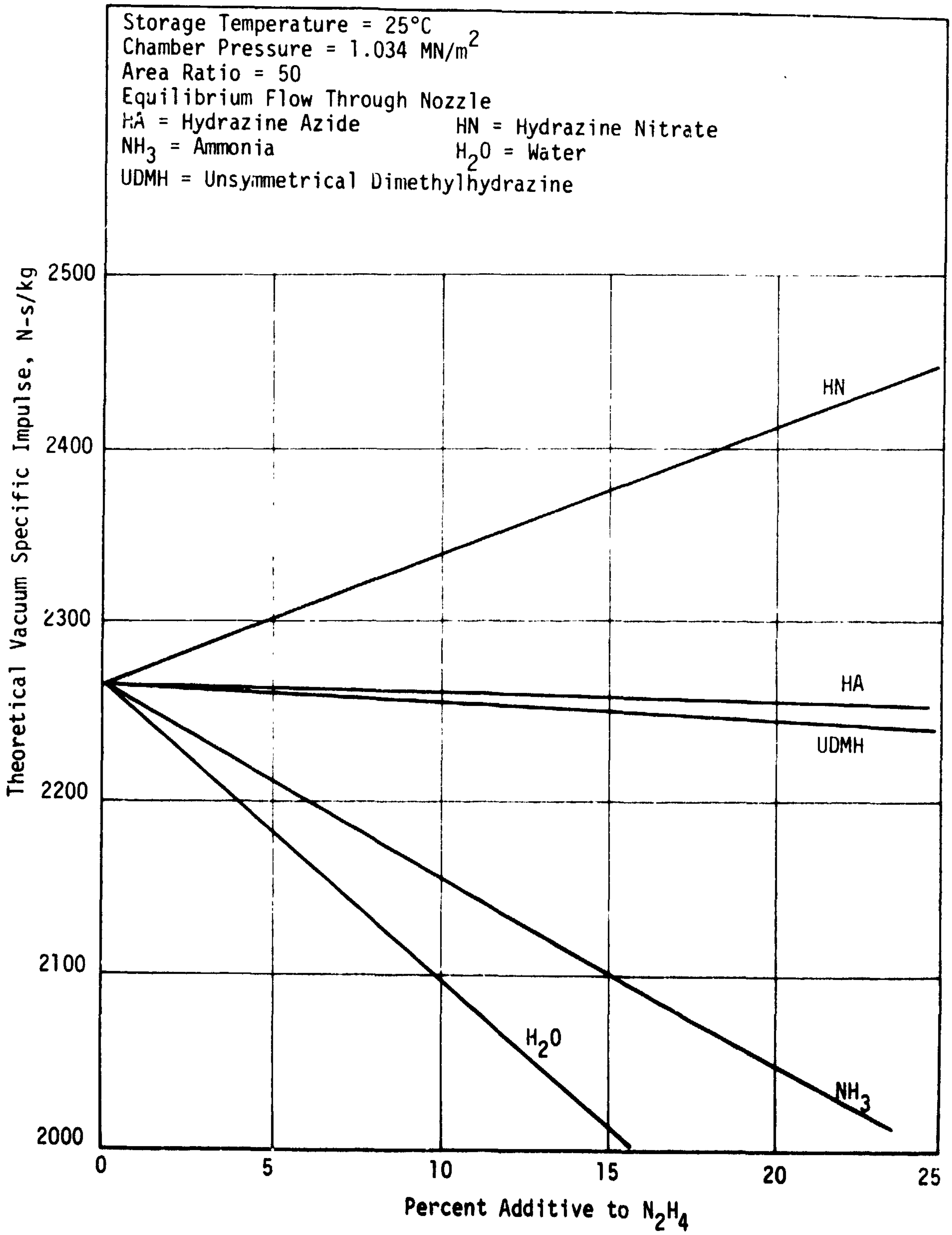

Figure 6. Theoretical Vacuum Specific Impulse of Pure Binary Monopropellants

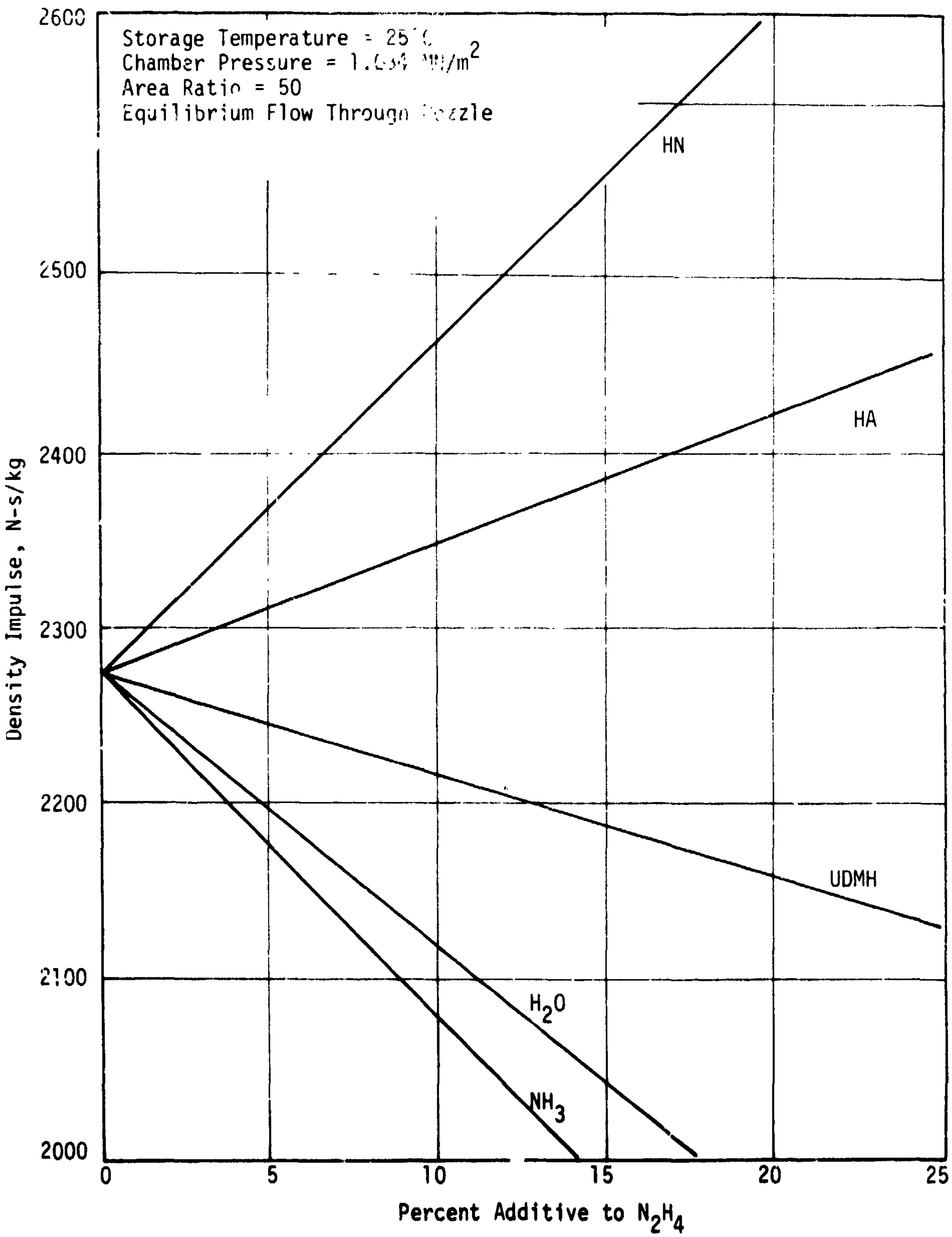

Figure 7. Density Impulse of Pure Binary Monopropellants

The effect of ammonia decomposition on the performance of azide blends is illustrated in Figure 8 (specific impulse) and Figure 9 (density impulse). Pure hydrazine is included as a comparison. Only data for practical ammonia decomposition fractions are shown ($\alpha \cong 0.3$ to 0.8).

3) Ternary Mixtures. This group includes three component mixtures of hydrazine, MMH, UDMH, hydrazine azide, ammonia and water. The performance and physical properties of three mixtures are shown in Table 6. A comparison of the two hydrazine - hydrazine azide based ternary blends illustrates the trade-off between freezing point and performance for nearly equal additions of ammonia (7%) and water (8%). The mixture containing water (freezing point = -20°C or -4°F) has a density impulse 7.8% below that of hydrazine, whereas, the mixture containing ammonia (freezing point = -18°C or -0.4°F) has a 6.1% increase in density impulse. A freezing point of -53.9°C (-65°F) is realized for the MHM blend while retaining performance levels similar to that of the hydrazine-hydrazine azide-water mixture. Figure 10 compares the theoretical vacuum specific impulse as a function of ammonia dissociation of the two N_2H_4-N_5H_5 ternary blends with that of hydrazine. The lower combustion temperatures of the ternary blends should result in a smaller percentage of dissociated ammonia in actual engine operation. The relative difference in operating performance between hydrazine, N_2H_4 - N_5H_5 - H_2O and N_2H_4-MMH-NH_3 should be reduced to less than 5%.

Although numerous other ternary blends could be formulated from the six components considered in this section, the three blends presented appear to be the best compromise between freezing point depression and performance.

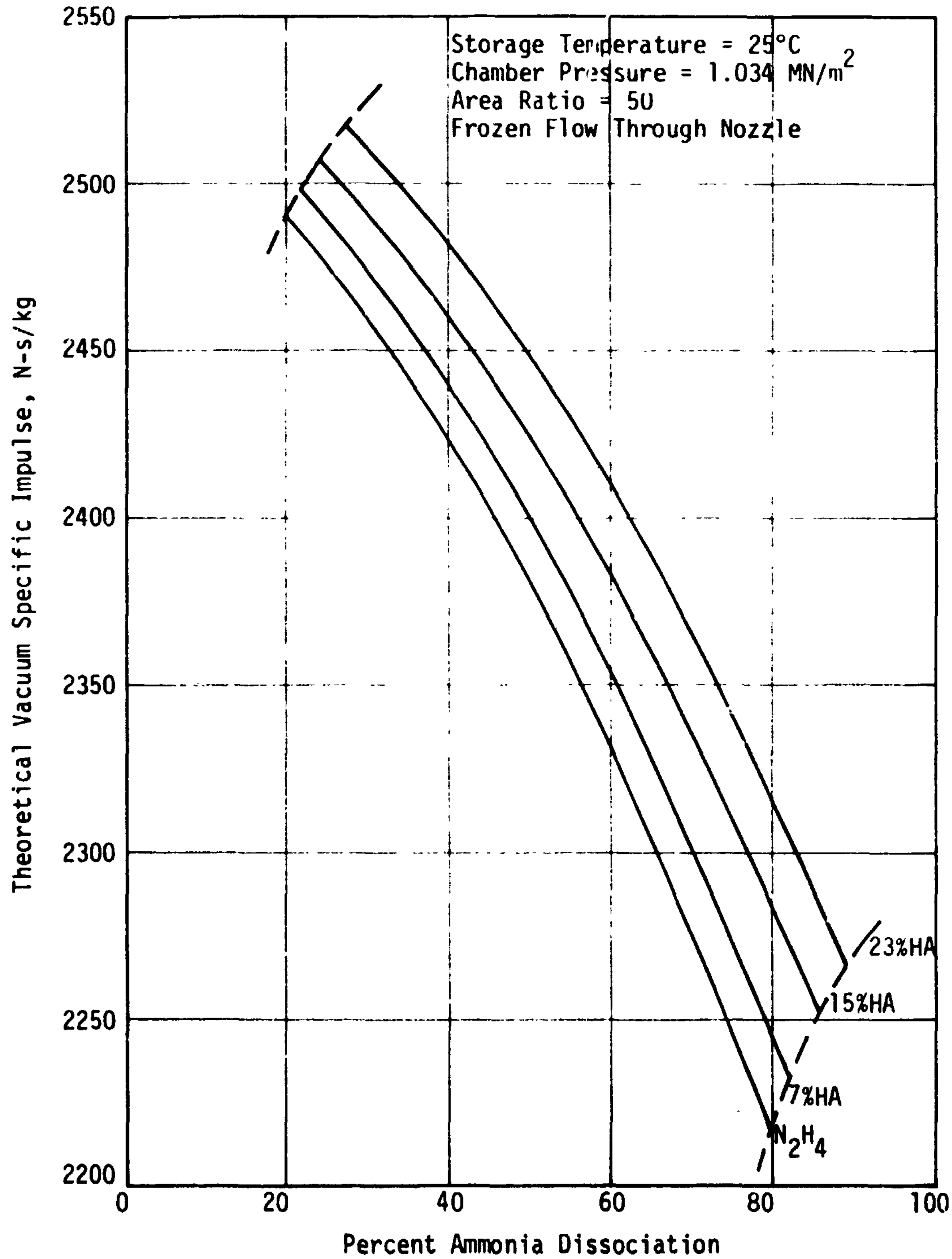

Figure 8. Theoretical Vacuum Specific Impulse of Hydrazine-Hydrazine Azide Mixtures as a Function of Ammonia Dissociation

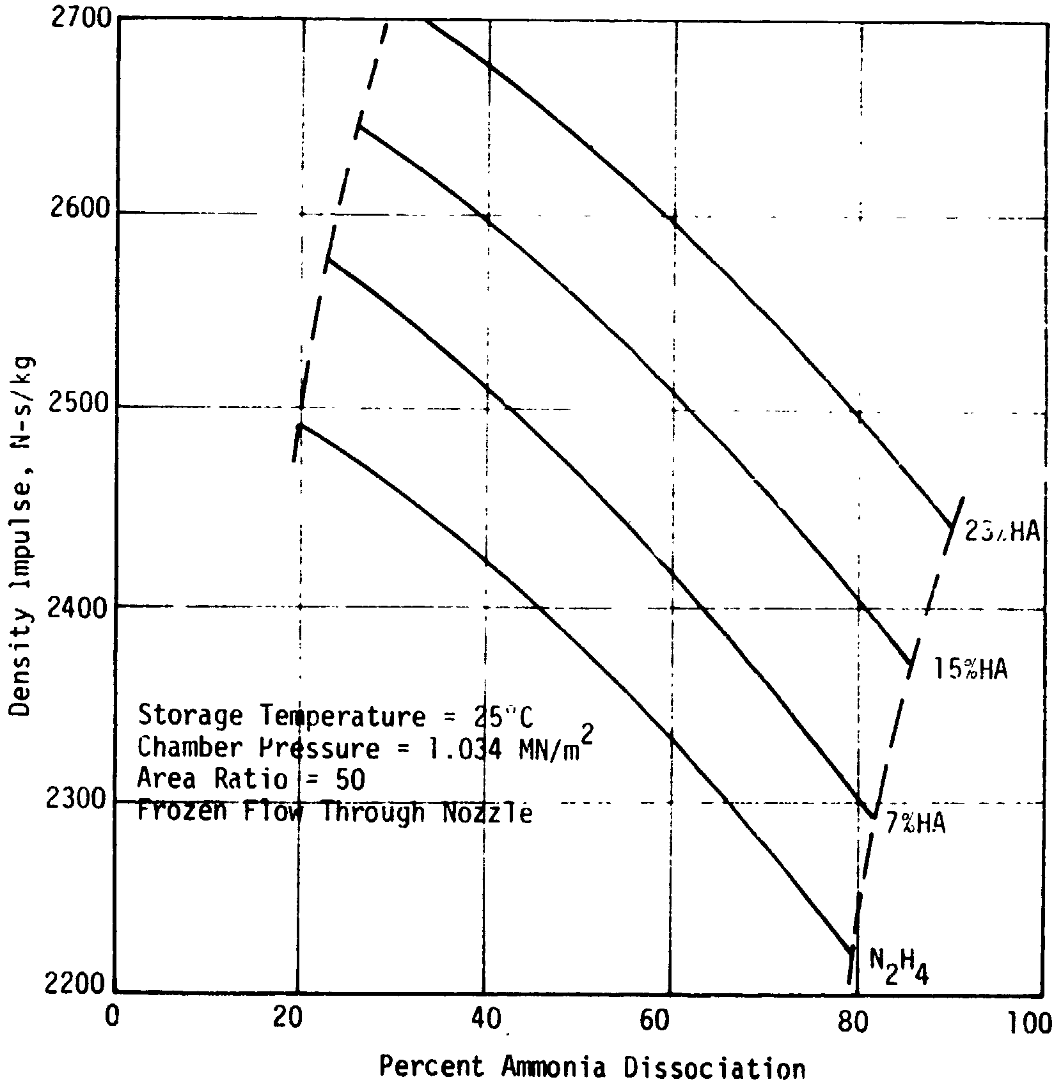

Figure 9. Density Impulse of Hydrazine-Hydrazine Azide Mixtures as a Function of Ammonia Dissociation

Table 6. Performance and Physical Property Characteristics of Pure Ternary Monopropellants

CHARACTERISTIC	UNITS	PROPELLANT N_2H_4	1	2	3
1. Freezing Point	°C (°F)	1.53 (34.75)	-18 (-0.4)	-20 (-4)	-53.9 (-65)
2. Density (25°C)	gm/cm^3	1.00	1.1	1 06	1.0 (est)
3. Vapor Pressure (25°C)	10^3 N/m^2 (Torr)	1.89 (14.2)	111 (836)	1.46 (11)	343 (2584)
4. Viscosity (25°C)	Poise	0.0091	N/A	0.02	N/A
5. Theoretical Vacuum I_{sp}	N-s/kg (sec)	2265 (231)	2177 (222)	1971 (201)	1961 (200)
P_c = 1.03 MN/m^2 (150 psia)					
ϵ = 50					
6. Density Impulse (25°C)	N-s/kg (sec)	2265 (231)	2403 (245)	2089 (213)	1961 (200) (est)
7. Adiabatic Flame Temperature	°C (°F)	816 (1500)	810 (1490)	804 (1480)	804 (1480) (est)
		α = 0.72	α = 0.65	α = 0.65	α = 0.65

1. 74% N_2H_4 - 19% N_5H_5 - 7% NH_3
2. 75% N_2H_4 - 17% N_5H_5 - 8% H_2O
3. MHM, 35% N_2H_4 - 50% MMH - 15% NH_3

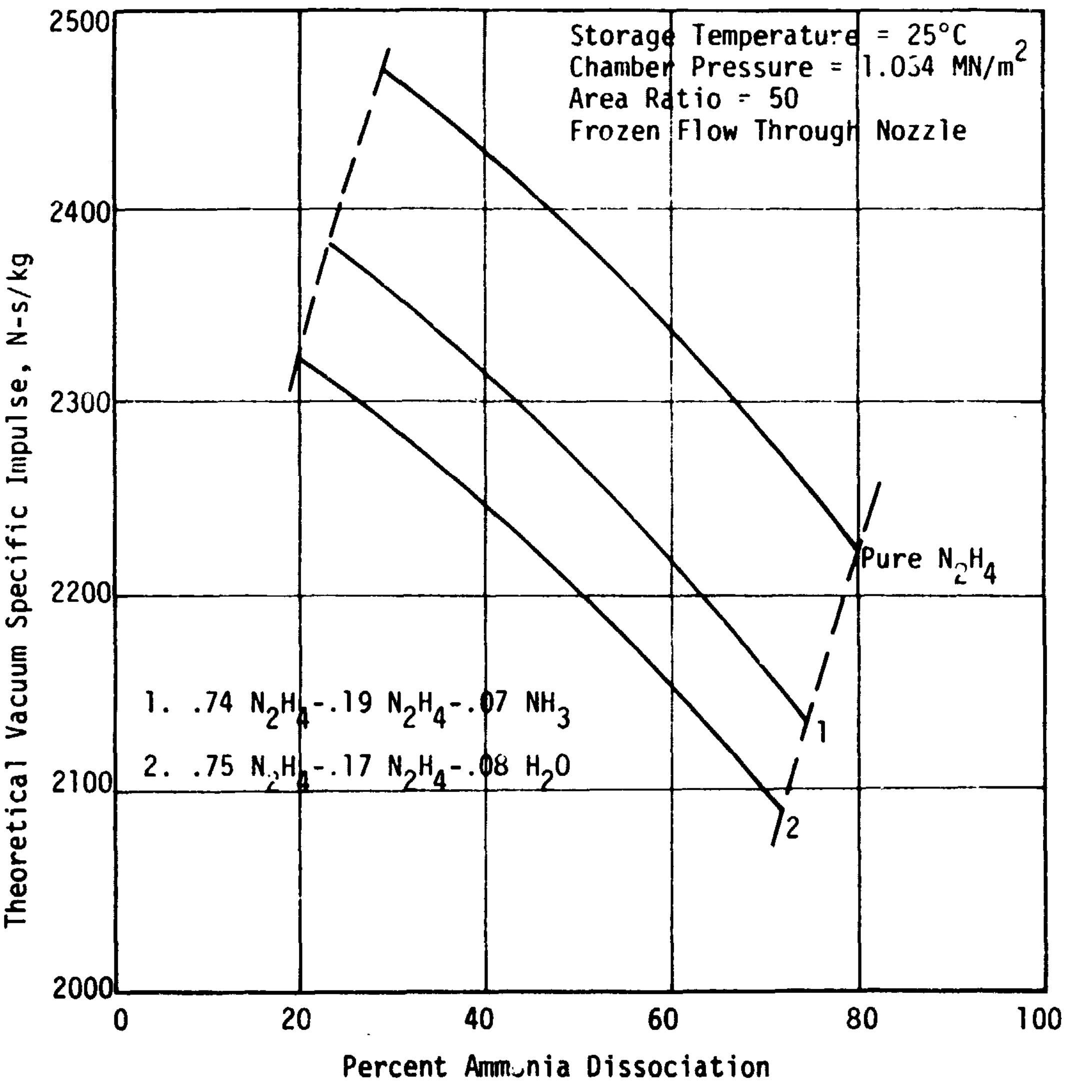

Figure 10. Theoretical Vacuum Specific Impulse of Pure Ternary Monopropellants as a Function of Ammonia Dissociation

4.0 PROPELLANT SELECTION

Four candidate monopropellants have been selected for the evaluation test program by the evaluation and review of the properties presented in Section 3 subject to the requirements and goals as defined in Section 2. This section describes the rational in recommending the following monopropellants: a) monomethylhydrazine, b) Aerozine-50, c) 77% hydrazine-23% hydrazine azide, d) TRW formulated mixed hydrazine monopropellant of 35% hydrazine - 50% monomethylhydrazine - 15% ammonia.

The two hydrazine derivatives, MMH and UDMH, are attractive by virtue of very low freezing points [-52.2°C (-62°F) and -57.2°C (-71°F), respectively], theoretical values of specific impulse near that of hydrazine (< 5% below), and of being "on board" in many spacecraft for use in high thrust bi-propellant systems. However, both propellants perform poorly with catalytic thrusters. Carbon deposition from propellant decomposition has led to rapid clogging, poisoning and degradation of the catalyst bed. Large concentrations of MMH and UDMH are required to significantly depress the freezing point of hydrazine (Figure 4). Consequently, electrothermal thrusters utilizing these mixtures may also have problems associated with carbon deposition. However, the potential advantages of low freezing point and high theoretical performance warrant their selection for the evaluation test program. Carbon accumulation in the thrust chamber can be best evaluated by using one propellant unmixed or "pure," and the other blended with hydrazine. The logical selections are Aerozine-50 (50% N_2H_4 - 50% UDMH) and MMH. Aerozine-50 has the advantage of being a commonly used bi-propellant. The total carbon content of both propellants is identical. This will allow a better evaluation of degradation effects attributable to carbonaceous propellants.

Binary mixtures obtained from blending hydrazine with ammonia or water exhibit -17.8°C (0°F) freezing points at additive concentrations of 21.5% (NH_3) and 17% (H_2O). However, the large loss of density impulse (11% for H_2O, 20% for NH_3) excluded them from further consideration. The eutectic blend of 77% N_2H_4 - 23% hydrazine azide offers a substantial performance increase over hydrazine and has an acceptable freezing point of -17.5°C (0.5°F). Previous TRW experience with catalytic thrusters using azide blends has been negative. Higher thruster temperatures and a more severe nitriding environment resulted in premature catalyst, thrust chamber and injector failures. These adverse characteristics will be absent for the electrothermal thruster; no catalyst (such as Shell 405) is used, and the thruster design allows the fabrication of noble metal alloy components capable of withstanding the higher temperature environment. For these reasons, the eutectic hydrazine-hydrazine azide mixture is warranted for evaluation in the test program phase.

Performance levels of the N_2H_4 - N_5H_5 - NH_3 ternary mixture are similar to those of the binary N_2H_4 - N_5H_5 blend. The degree of self-pressurization (0.11 MN/m^2 or 16.2 psia) and slightly lower freezing point of -18°C (-0.4°F) is not considered significant enough to include this ternary blend in addition to or in lieu of the binary azide mixture.

The N_2H_4 - N_5H_5 - H_2O mixture has a freezing point (-20°C or -4°F) below the program goal. The performance characteristics of this blend have been severly compromised by a slight reduction in freezing point when compared to the other ternary azide blend. Ignition delay times are increased by the addition of water to hydrazine fuels. The trade-off between performance and freezing point of the ternary azide - water mixture results in an unacceptable candidate for the scope of this program.

The TRW formulated ternary blend (MHM), 35% N_2H_4-50% MMH-15% NH_3, has numerous advantages that offset the reduction in specific impulse (≈ 13% below N_2H_4). The MHM has a density impulse comparable to the derivatives of hydrazine, has no solid exhaust products or condensable combustion species. Faster start transients are expected for the MHM blend than mixtures containing water. Thus, the MHM blend is a logical candidate for the evaluation test program.

A test plan for the evaluation of the selected monopropellants appears in Appendix B.

5.0 NEW TECHNOLOGY

No new technology was developed during the analytical studies phase of the "Study of Monopropellants for Electrothermal Thrusters."

6.0 PROGRAM FOR THE THRUSTER DESIGN AND FABRICATION TASK

This section describes the basic approach to the Task II thruster design and fabrication.

6.1 DESIGN

The thruster design is based on the Electrothermal Hydrazine Thruster (EHT) developed by TRW for NASA/GSFC on NASA Contract No. NAS5-11477. This thruster was designed to operate with MIL-grade hydrazine at a steady state thrust of 0.089 N (0.020 pound) and 0.689 MN/m^2 (100 psia) feed pressure. The design parameters for the present thruster are:

1) Thrust: 0.344 $\pm$ 0.0267N (75 $\pm$ 6 millipounds) at 1.724 MN/m^2 (250 psia) nominal feed pressure
2) Vacuum specific impulse: 1961 N-s/kg (200 sec) steady state (goals)
   1716 N-s/kg (175 sec) pulsed mode
3) Pulse duration: 0.050 second to steady state
4) Pulse mode duty cycle: that typical for attitude control including "wheel dump"
5) Holding power: 5 watts maximum
6) Nominal voltage: 24 to 32 vdc
7) Maximum steady state on-time: 30 hours
8) Total number of pulses: 3×10^5
9) Weight: to be determined
10) Size: to be determined

A preliminary design layout for the demonstration thruster is illustrated in Figure 11. A threaded connection will replace the braze joint between the thrust chamber and nozzle. This configuration satisfies the anticipated need for convenient inspection, cleaning, and if necessary, replacement of the screen pack. Changes in screen geometry can be readily implemented and the characteristic chamber length, L^*, may be optimized by varying the length of the nozzle inlet section.

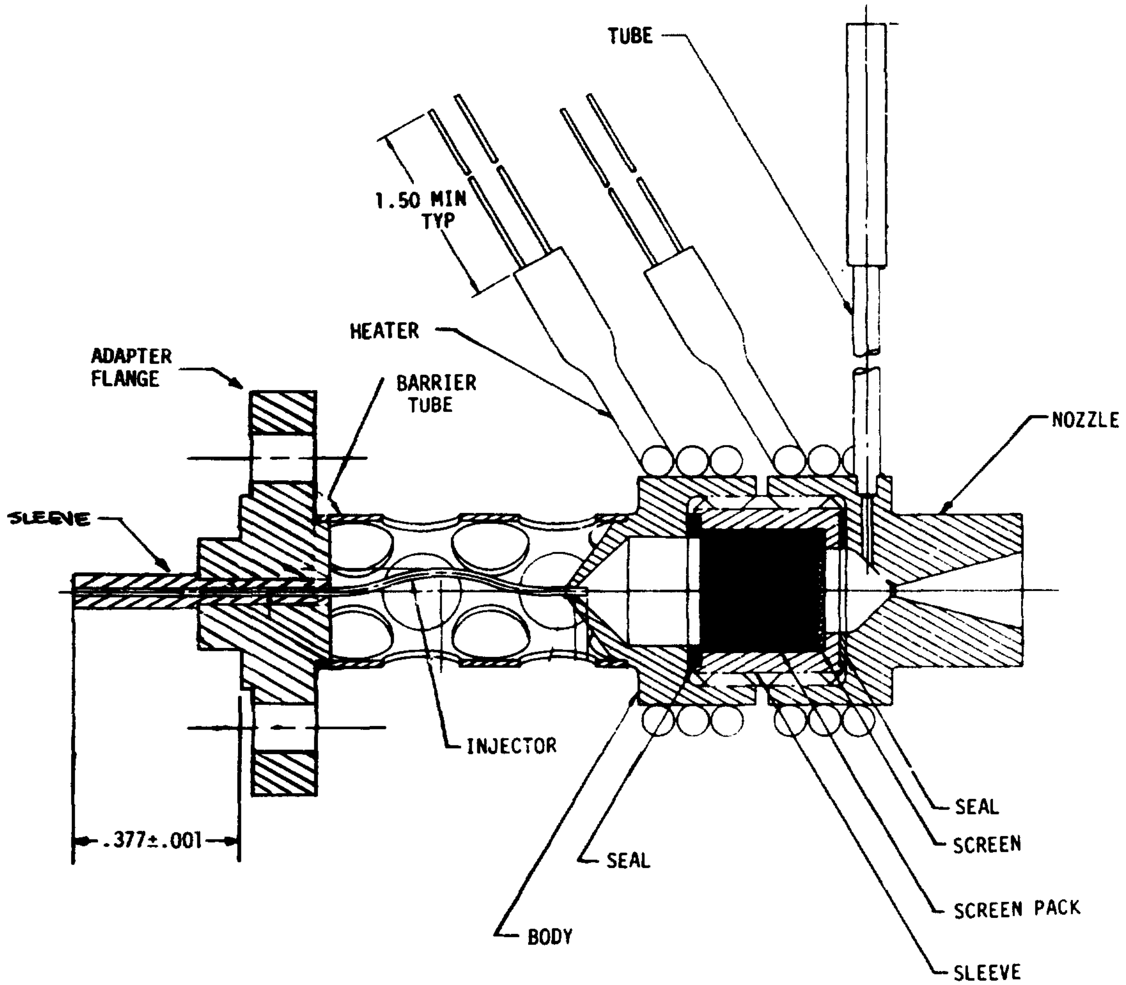

Figure 11. Demonstration Thruster

The thruster design will use construction materials similar to those of tle EHT. The thrust chamber and injector tube will be of Haynes 25, and the screen pack a Haynes 25 and platinum composite. The chamber heater and thruster insulation will also be similar to those used on the EHT.

6.2 FABRICATION

Five thruster assemblies of the initial design will be fabricated for the untested candidate propellants. Additional assemblies will be fabricated (within schedule and budget restrictions) depending on the performance test results and subsequent design changes. The fabrication techniques for the proposed design have been developed and no problem areas are expected.

7.0 CONCLUSIONS

Numerous low freezing point hydrazine substitutes for monopropellant propulsion are readily available. However, the majority of these propellants are unsuited for the overall objectives of the "Study of Monopropellants for Electrothermal Thrusters." Four propellants were identified that do not require an excessive trade-off between freezing point and performance. They are monomethylhydrazine, Aerozine-50, 77% hydrazine - 23% hydrazine azide blend, and TRW formulated mixed hydrazine monopropellant of 35% hydrazine - 50% monomethylhydrazine - 15% ammonia. The four candidate propellants selected offer the opportunity to expand the technology base of monopropellant propulsion. The thruster design will allow operation on carbonaceous fuels, high combustion temperature azide blends and contaminated propellants that are not compatible with the more conventional catalytic thrusters.

APPENDIX A

A.1 SHOCK SENSITIVITY

The two standard methods of determining shock sensitivity are the drop-weight and JANNAF card gap tests.

The drop-weight test for liquids assumes that an explosion is initiated by the adiabatic compression of the gas volume present with the sample. A small amount (0.030 cc) of propellant is enclosed in a 0.060 cc cavity formed by a steel cup, an elastic ring and a steel diaphragm. A piston rests on the diaphragm and contains a vent hole which is blocked by the steel diaphragm. A weight is dropped onto the piston. Explosion is indicated by a ruptured diaphragm and loud noise. The sensitivity value for a given sample is the potential energy (height x weight) at which the probability of explosion is fifty percent.

The standard JANNAF card gap test assembly consists of a 25.4 mm (1-inch) diameter by 76.2 mm (3-inch) long schedule 40 steel cup with a 0.051 mm (0.002-inch) polyethylene film mounted in the bottom of a cardboard support assembly. A 50 gram tetryl pellet is placed below and touching the polyethylene bottom; a blasting cap is placed below and touching the tetryl pellet. The test liquid is placed in the cup and a 101.6 mm x 101.6 mm x 9.5 mm (4-inch x 4-inch x 3/8-inch) cold-rolled mild steel plate is placed, unattached, atop the cup. The tetryl charge is detonated by activation of the blasting cap. Test liquid detonation due to the hydrodynamic shock from the tetryl charge produces a 25.4 mm (1-inch) diameter hole in the mild steel witness plate. No plate damage is observed with non-detonable materials (e.g. water). Results are expressed as the number of cellulose acetate cards that must be placed between the tetryl donor charge and the cup bottom such that the donor shock will be sufficiently attenuated to give a 50% statistical chance of test material detonation.

A.2 DETONATION PROPAGATION

Standard ICRPG detonation propagation tests are performed by containing the test liquid in a section of 6.35 mm (1/4-inch) 347 stainless steel tubing having a 0.89 mm (0.035-inch) wall thickness. The tube fits into a reservoir through a 25.4 mm (1-inch) diameter opening. A 50-gram pentolite booster is used with a number 8 electric blasting cap to detonate the reservoir fluid. The criterion for a positive test is the complete destruction of the 6.35 mm (1/4-inch) acceptor tube.

A.3 THERMAL STABILITY

Propellant thermal stability is measured by the standard ICRPG thermal stability test and by differential scanning calorimetric methods. Results of the standard tests are regarded as practical values and the differential scanning calorimetric test results are considered as limiting values. Only the standard ICRPG test will be described.

The ICRPG test fixture consists of a stainless steel cylinder which has a 5.59 mm (0.22-inch) diameter and is 38.1 mm (1.5-inches) long. The bottom is closed and a compression-fitted shielded thermocouple is employed. The fixture is charged with 0.5 cc of propellant and closed at the top with a 0.076 mm (0.003-inch) thick SS diaphram. The assembly is then placed in a bath which is heated at a constant rate of 10°C/min. A second thermocouple and an X-Y recorder are connected with the sample thermocouple so as to yield a plot of differential temperature (sample temperature minus bath temperature) versus bath temperature. Exothermic reactions appear as positive peaks, while endothermic reactions appear as negative peaks. The results are reported in terms of the temperature at which significant thermal activity is observed.

Long term thermal storability is measured by the rate of gas evolution over a specified period of time. Results are usually given for a particular material in units of psi/day.

A.4 TOXICITY

Exposures are expressed as concentration and exposure duration for exposure to vapors in the air; and as dosages referred to as a fraction of body weight for ingestion. In tests on animals, the lethal dosage is defined as that which kills 50 percent of the test subjects. The dosage is expressed as LD_{50} in milligrams of substance per kilogram of body weight (mg/kg). The concentration of vapors in air is expressed in terms of parts of vapor per million parts of air (ppm).

A.5 MATERIALS COMPATIBILITY

The compatibility classification is based on the rating scheme recommended by the Defense Metals Information Center. Table 7 presents the rating scheme used in this report.

Table 7. Materials Compatibility Classification

CLASS	CORROSION RATE mm/YEAR	DECOMPOSITION	USAGE LIMITATIONS
A	Less than 0.0254	None	No limitations. Typical use involves constant contact with the fuel. Metals can be considered for long term storage.
B	.0254 to 0.127	Slight degradation over a period of time.	Restricted to transient or limited contact. Not recommended for long term storage.
C	0.127 to 1.27	Limited decomposition may occur on contact.	May be used in areas where brief contact can occur. Not recommended for use where contact occurs regularly.
D	More than 1.27	Considerable decomposition may occur. May cause ignition or explosion.	Metals are totally unsuitable for use under any conditions. Contact may create a hazardous condition.

APPENDIX B

TRW
SYSTEMS GROUP
ONE SPACE PARK • REDONDO BEACH, CALIFORNIA

CODE IDENT 11982

TITLE

TEST PLAN
FOR THE STUDY OF MONOPROPELLANTS
FOR ELECTROTHERMAL THRUSTERS

DATE 1 December 1973
Revision 1

NO.

SUPERSEDING: 1 May 1973

PREPARED FOR:

NASA/Goddard Space Flight Center
Greenbelt, Maryland 20771
Contract No. NAS5-23202

PREPARED BY: Rein Grabbi
Rein Grabbi

APPROVAL SIGNATURES:

CK Murch 2 Dec 73
C. K. Murch DATE

DATE

DATE

DATE

DATE

DATE

SYSTEMS 1391 REV. 3-67

B.1 SCOPE

B.1.1 Equipment to be Tested. The equipment to be tested shall be an engineering model electrothermal thruster assembly designed to be operated with various monopropellants. This equipment shall be referred to as the thruster unit.

B.1.2 Test Objective. The tests outlined in this plan are conducted to determine the feasibility of operating small thrust level electrothermal thrusters with monopropellants other than MIL-grade hydrazine.

B.1.3 Test Description. The tests described in this Test Plan consist of these specified in Paragraphs B.3.1 through B.3.6 and as outlined in Table B1 of this plan. The test sequence shall not necessarily be as shown in Table B1.

TABLE B1

TEST SUMMARY

Test Description	Applicable Paragraph
1. Acceptance Tests	B.3.1
2. Baseline Performance Tests	B.3.2
3. Propellant Analysis	B.3.3
4. Preliminary Performance Tests	B.3.4
5. Performance Optimization Tests	B.3.5
6. Thruster Characterization Tests	B.3.6

B.2 CONDITIONS

B.2.1 Facility. The tests outlined in this plan shall be conducted at the contractor's facility.

B.2.2 Referenced Documents. The following documents of the exact issue shown, or the latest issue in effect, form a part of this Test Plan to the extent specified herein. Where differences occur between documents referenced and the detail content of Section 3 of this specification, the requirements of this specification shall apply.

SPECIFICATIONS

Military

MIL-P-26536C	Propellant, Hydrazine
MIL-P-27402A	Propellant, Aerozine-50
MIL-P-27404A	Propellant, Monomethylhydrazine
MIL-P-27406	Anhydrous Ammonia
MIL-P-26504A	Propellant, Unsymmetrical Dimethylhydrazine

TRW Systems

PR2-2K	Cleaning of Fluid System Components

DRAWINGS

TRW Systems

TBS	Electrothermal Thruster, Study of Monopropellants

B.2.3 Test Fluids. Test fluids shall be as follows:

B.2.3.1 Hydrazine propellant per MIL-P-26536

B.2.3.2 Aerozine-50 propellant per MIL-P-27402

B.2.3.3 Monomethylhydrazine propellant per MIL-P-27404

B.2.3.4 Hydrazine - hydrazine azide propellant blend

B.2.3.5 TRW mixture of hydrazine monopropellants

B.2.3.6 Nitrogen gas per MIL-P-27401

B.2.3.7 Isoproplyl alcohol per TT-I-735

B.2.3.8 Distilled water

B.2.4 Equipment Handling. Continuous precaution shall be taken to preserve and maintain cleanliness of the unit.

B.2.5 Safety and Propellant Handling. Appropriate precautions shall be taken when handling propellants. Full consideration shall be given to the toxic and flammable nature of the propellants. Initial tests with propellants other than hydrazine shall be conducted at sea-level ambient until full confidence in safe operation has been ascertained.

B.2.6 Measurement Accuracy. Measuring instruments used to determine functional parameters values (such as voltage, frequency, pressure, etc.) shall indicate true values with an accuracy determined by the tolerance allowed for the parameter variation itself, such that the measuring instrument shall not introduce an uncertainty greater than ten percent of the allowable variation of the measured parameter. However, no such measurement accuracy shall be required to exceed 0.5 percent of the required value of the parameter unless otherwise specified.

B.2.7 Test Tolerance. Except as specifically noted in the Test Methods, test tolerances for all test condition measurements shall be as follows:

a)	Temperature	plus or minus 2.8°C (5°F) to 93.3°C (200°F) plus or minus 5% above 93.3°C (200°F)
b)	Pressure	plus or minus 2%
c)	Time	plus or minus 5%, plus or minus 1.0 ms for pulse length
d)	Thrust	plus or minus 5%
e)	Propellant Flow	plus or minus 5%

B.3 TEST METHODS

B.3.1 Acceptance Tests

B.3.1.1 Inspection. Each thruster shall be visually examined to verify that the unit meets the requirements of workmanship and dimensions per the applicable engineering drawings.

B.3.1.2 External Leakage. The external leakage of each thruster shall be measured when pressurized with gaseous nitrogen at maximum operating pressure. No indication of leakage is allowed when probed with "SNOOP".

B.3.2 Baseline Performance Tests. Each thruster shall have its baseline performance determined with MIL-grade hydrazine. These tests shall be performed at an altitude chamber pressure below $1.33 \times 10^3 N/m^2$ (10 Torr). The thrust chamber heater voltage shall be set at nominal, and the chamber temperature allowed to stabilize. The thruster shall then be fired continuously for one (1) minute. (Note: Break-in pulses are permitted on a new thruster prior to performance tests.) The propellant inlet pressure shall be set at three different levels to cover the design range of the thruster. After thruster temperature stabilization at the holding level, the thruster shall be fired for approximately 20 consecutive pulses of 50 millisecond duration at one (1) second intervals. The thruster shall be instrumented to measure the following parameters as a mimimum:

a) chamber pressure
b) propellant inlet pressure
c) chamber temperature
d) propellant flow rate
e) thrust level

B.3.3 Propellant Analysis. Each propellant utilized shall be subjected to chemical analysis.

B.3.4 Preliminary Performance Tests. The following propellants shall be used to determine thruster performance:

a) a hydrazine-hydrazine azide blend
b) 50-50 blend of UDMH and hydrazine (Aerozine-50)
c) monomethylhydrazine
d) a hydrazine-MMH-ammonia blend

All initial tests with propellants not previously used with the electrothermal thruster shall be performed at sea level in a facility considered safe in relation to possible fire and explosion hazards. The sequence of tests and selection of thruster units shall be determined at the time of the testing. Test duration shall be determined from the performance data of individual propellants. Thruster characteristics shall be determined over a range of inlet pressures and chamber holding temperatures selected. Each thruster will be disassembled at regular intervals for inspection, and, if required, cleaning. The thrusters shall be instrumented according to the requirements of Paragraph B.3.2.

B.3.5 Performance Optimization Tests. Thruster design changes will be incorporated as suggested by preliminary test data. Each modified thruster design shall be retested with the specific propellant to determine the affect of the design change. Any new thruster configuration resulting from optimization for a specific propellant shall also be re-evaluated with the other test propellants. The extent of the optimization tests shall be determined after the evaluation of previous test data. A program goal will be to achieve a thruster design applicable to several different monopropellants in addition to hydrazine.

5.3.6 Thrust Characterization Tests. The one (or more) optimized thruster configuration(s) determined from previous testing shall be tested for pulse mode operation with each of the selected propellants. Injection pressure, pulse duration, duty cycle and holding temperature variations shall be evaluated within schedule and budget limitations.