

N71-33234

CASE FILE

NASA CR - 121456



SRI Report No. 951581-11

CHEMICAL AND METALLURGICAL ANALYSES OF
6AL-4V TITANIUM TEST SPECIMENS EXPOSED
TO HYDRAZINE (N_2H_4) LIQUID PROPELLANT

Prepared for:

Jet Propulsion Laboratory
California Institute of Technology
Pasadena, California 91103

JPL Technical Cognizance: L. R. Toth

Contract No. 951581
Under NAS7-100



STANFORD RESEARCH INSTITUTE
Menlo Park, California 94025 • U.S.A.



STANFORD RESEARCH INSTITUTE
Menlo Park, California 94025 · U.S.A.

SRI Report No. 951581-11

April 15, 1971

Final Report on TDM 69X08200 / October 1, 1969 to April 1, 1971

CHEMICAL AND METALLURGICAL ANALYSES OF
6AL-4V TITANIUM TEST SPECIMENS EXPOSED
TO HYDRAZINE (N_2H_4) LIQUID PROPELLANT

Prepared for:

Jet Propulsion Laboratory
California Institute of Technology
Pasadena, California 91103

JPL Technical Cognizance: L. R. Toth

Contract No. 951581
Under NAS7-100

By: W. E. Tolberg, R. T. Rewick, and M. P. Dolder

SRI Project PYD 6063

Approved:

Marion E. Hill, Director
Chemistry Laboratory

C. J. Cook, Executive Director
Physical Sciences Division

Copy No. 73

ABSTRACT

Under TDM 69X08200, JPL Contract No. 951581, SRI Project PYD 6063, test capsules containing N_2H_4 and Ti(6Al-4V) were analyzed both chemically and metallurgically for decomposition and corrosion. A high chloride and carbon impurity was found in the N_2H_4 . Freon TF used as a degreasing solvent was shown to react with N_2H_4 forming hydrazine monohydrochloride. It is speculated that the monohydrochloride has caused both the corrosion of the titanium alloy and the decomposition of some of the hydrazine. Further analysis of the test capsules will not give true corrosion properties of the Ti(6Al-4V) alloy in N_2H_4 . The Freon TF cleaning procedure must be either eliminated or altered to ensure complete removal of the carbon-chlorine containing cleaning solvent. The recommendation is made that N_2H_4 be analyzed by the more accurate iodate method. Future capsules should be improved by the addition of break seals which would allow for final analysis on a vacuum line.

CONTENTS

ABSTRACT ii

I INTRODUCTION 1

II DISCUSSION OF RESULTS 2

 A. Hydrazine Analysis 2

 B. Control Capsule Analysis 4

 C. Test Capsule Analysis 4

 1. Analysis of Water-Insoluble Solids 7

 2. Analysis of Water-Soluble Solids 8

 3. Reaction of Freon TF and N_2H_4 8

 4. Analysis of Ti(6Al-4V) Test Specimen 13

 5. Atomic Absorption Analysis 23

III CONCLUSIONS AND RECOMMENDATIONS 26

REFERENCES 27

I INTRODUCTION

This report covers work on the analysis of hydrazine test capsules performed by Stanford Research Institute beginning October 1, 1969 and ending April 1, 1971 under JPL Contract No. 951581 entitled "Chemistry Support Services."

The task covered by TDM 69X08200 involves the analysis of four Ti(6Al-4V) specimens, serial numbers S/N 20-0057, S/N 21-0059, S/N 22-0061, and S/N 24-0065. These specimens had been stored in hydrazine (N_2H_4) liquid propellant at 110°F in sealed glass capsules. Extensive chemical analysis of the N_2H_4 in each vial was carried out to determine propellant properties, impurities, and the extent of visible decomposition. Metallurgical analysis was carried out for evaluation of material compatibility.

II DISCUSSION OF RESULTS

A. Hydrazine Analysis

As a preliminary investigation, we analyzed hydrazine samples from JPL stock from which the test capsules were filled. Three samples were taken in duplicate from a half-filled barrel and were labeled top, middle, and bottom. The hydrazine was analyzed by a glc method using Carbowax 400 on a Chromosorb T support. From this analysis we found that the N_2H_4 contained three detectable impurities, NH_3 , H_2O , and aniline. The results are found in Table I. The results are not given for the bottom of the barrel sample B since it was contaminated during preliminary analysis procedures.

In the glc method used here, peak areas were measured and related to concentration. Thus the results given in Table I all totaled very nearly 100%, a fact that may be misleading. However, only four peaks were observed in the chromatographs, meaning that if other impurities were present, elution occurred simultaneously with the known peaks. None of the minor peaks, NH_3 , H_2O , or aniline seemed large enough to contain more than a trace of impurity so that the only possibility for significant coincidence was at the hydrazine peak.

The JPL specifications required chloramine-T as the method of hydrazine analysis. The N_2H_4 stock samples were analyzed by the chloramine-T method and the results are found in Table II. A third analysis was made by the iodate titration of N_2H_4 , and the results are also found in Table II. Whereas the chloramine-T and glc methods have the potential for giving low results (N_2H_4 is unstable in slightly basic medium and at higher temperature in the presence of metals and organic material), in the iodate procedure, decomposition is minimized because the analysis is conducted under strong acid conditions. Several literature references indicate a preference for the iodate¹⁻⁴ and glc⁵⁻⁷

Table I

HYDRAZINE ANALYSIS BY GLC

		NH ₃ (%)	H ₂ O (%)	Aniline (%)	N ₂ H ₄ (%)	Totals (%)
Top of Barrel	A	1.14	0.33	0.12	98.40	99.99
	B	1.14	0.47	0.21	98.17	99.99
Middle of Barrel	A	1.10	0.39	0.26	98.34	100.09
	B	1.06	0.64	0.20	98.10	100.0
Bottom of Barrel	A	1.45	0.43	0.19	97.94	100.0

Table II

HYDRAZINE ANALYSIS RESULTS

		Chloramine-T (%)	Glc (%)	Iodate (%)
Top of Barrel	A	97.93	98.40	99.04
	B	97.85	98.17	98.24
Middle of Barrel	A	97.85	98.34	98.44
	B	97.93	98.10	98.58
Bottom of Barrel	A	97.91	97.94	98.57

methods for the determination of N_2H_4 , whereas those procedures which must be conducted under basic conditions (chloramine-T) can give low results.¹ However, we followed the JPL specifications and used the chloramine-T method of N_2H_4 analysis.

B. Control Capsule Analysis

Three control capsules were sent to us by JPL which contained only hydrazine. The control capsules, S/N 35, 33, and 27, were analyzed for gas-phase decomposition, hydrazine concentration, and residue.

Each capsule contained four strain gauges as a pressure monitoring system. Room temperature readings were taken of the strain gauges, which are found in Table III. All the capsules were then broken in a vacuum-tight rupture vessel specifically designed for them after the gauge material was removed. Since the gauge material was found to cause further N_2H_4 decomposition, only initial strain gauge readings could be taken.

The off gases were analyzed by mass spectrometry. The results in Table IV show only nitrogen except for capsule S/N 33, where widely varying mass spectra result probably from presence of some N_2H_4 . After chloramine-T analysis, see Table V, samples of the colorless liquid N_2H_4 were evaporated to dryness and found to contain a residue of around 60 ppm. The emission spectra of this residue are found in Table VI.

C. Test Capsule Analysis

Test capsules S/N 20, 21, 22, and 24 contained N_2H_4 which had turned greenish-black and contained some black solids along with the Ti(6Al-4V) test strips. Strain-gauge readings for the test capsules are found in Table III. The conversion of the μV readings to pressure units were obtained through calibration curves supplied by JPL. The corresponding pressure was found to be extremely high, ranging from 128 to 235 psig. This pressure buildup corresponds to a significant N_2H_4 decomposition.

Table III

STRAIN GAUGE READINGS

Capsule S/N	35	33	27	24	22	21	20
Test Specimen	/	/	/	0065	0061	0059	0057
Voltage	430 μ V	280 μ V	560 μ V	325 μ V	480 μ V	1.42mV [†]	561 μ V
Temperature ($^{\circ}$ C)	--	--	--	22.8	22.5	22.5	23.0
Corresponding Pressure (psig)	--	--	--	156.25	235.29	--	128.08

[†] The high reading was caused by a bubble under one strain gauge.

Table IV

GAS-PHASE DECOMPOSITION PRODUCTS

Capsule S/N	35	33	27	24	22	21	20
Test Specimen	/	/	/	0065	0061	0059	0057
Ir Spectrum	--	--	--	NH ₃	NH ₃	NH ₃	NH ₃
Mass Spectrum (%)							
N ₂	95	2.7	99	54.16	91.06	80.05	82.20
NH ₃	--	33	--	44.19	8.94	19.94	17.76
Ar	--	0.5	0.9	--	--	--	--
H ₂	--	--	--	1.64	--	--	--
H ₂ O	--	55.3	--	--	--	--	--
Residue	--	9.5	--	--	--	--	--
Cooling Temp ($^{\circ}$ C)	-36	-36	-36	-36	-36	-78	-196

Table V

ANALYSIS OF LIQUID HYDRAZINE IN TEST CAPSULES

Capsule S/N	35	33	27	20	21	22	24
Test Specimen	/	/	/	0057	0059	0061	0065
N ₂ H ₄ (%)	98.45	97.98	97.56	†	90.15	94.1	90.3
Total Wt of N ₂ H ₄ and Decomposition Products (g)	--	--	--		21.76	21.26	19.57
N ₂ H ₄ Corrected for Solids (%)	--	--	--		92.6	96.6	92.9
N ₂ H ₄ Decomposed ‡ (%)	--	--	--		5.4	1.4	5.1
Residue (ppm)	--	59	57		--	--	--
Insolubles Present (%)	--	--	--		0.78	0.99	0.88
Solubles Present (%)	--	--	--		1.13	2.86	2.87

† Capsule shattered on breaking.

‡ Based on average analysis of control capsules.

Table VI

EMISSION SPECTRA OF RESIDUE FROM CONTROL CAPSULES

Capsule S/N	33	27
Si	0.01%	0.007%
Mg	0.002	<0.001
Fe	0.01	<0.01
Cu	0.002	0.003
Na	0.1	<0.05
Ca	0.01	0.008
Cr	<0.003	0.003
Ba	<0.01	<0.001
B	0.005	<0.005

Upon removal of the strain gauges, the capsules were broken in the vacuum-tight rupture vessel described earlier. The gas-phase analysis was done by infrared and mass spectrometry. The results, found in Table IV, are consistent in that N_2 and NH_3 are present in all capsules. In S/N 24, some H_2 was detected, which leaked when evacuated, thus accounting for its varied mass spectral results.

After a capsule was broken, the rupture vessel containing the capsule was opened in a dry box and the capsule removed. In all cases only the neck of the ampule was broken except with capsule S/N 20 in which the entire ampule shattered, thus eliminating this capsule from any further analysis.

The N_2H_4 contained in the test capsules was greenish-black; small amounts of dark insoluble material were also present. Infrared analysis of the liquid phase of capsules S/N 21, 22, and 24 showed only N_2H_4 and traces of NH_3 .

The total weights of N_2H_4 and decomposition products in the capsules are recorded in Table V. Liquid samples containing some solid material were diluted with distilled H_2O . At this point a gray flocculent material precipitated from these solutions.

1. Analysis of Water-Insoluble Solids

Infrared spectra were taken of the gray insolubles obtained from capsules S/N 21, 22, and 24. The solids were mixed in a 350-mg matrix of KCl and pressed into transparent disks. The spectra showed strong -OH and/or -NH absorption with a broad band beginning at about 1000 cm^{-1} and a smaller absorption band at 1615 cm^{-1} , which is possibly H_2O . Other smaller bands were seen but could not be assigned due to low peak intensity.

Emission spectrographic and elemental analyses of the water-insoluble solids are found in Table VII. These results indicate that the material consisted mainly of the elements Ti, Al, and H.

X-Ray diffraction patterns obtained of the gray powders using $\text{CuK}\alpha$ radiation failed to reveal any lines. These observations indicate that the sample is amorphous. After the samples were heated at 750°C for 1.5 hours, the insoluble solids from capsules S/N 21, 22, and 24 showed weight losses of 19.5, 17.1, and 18.2%, respectively. If $\text{Ti}(\text{OH})_4$ existed, which it does not,⁸ a weight loss of 31.1% should have occurred. X-Ray analysis of the samples after heating showed definite patterns for TiO_2 . The data, coupled with ir analysis, indicate that the solids obtained by H_2O dilution might be hydrous TiO_2 .

2. Analysis of Water-Soluble Solids

Aliquots of the green supernatant liquid were evaporated to dryness and white solids were obtained in all test capsules studied. This white solid was analyzed by infrared spectroscopy and X-ray diffraction methods and was found to consist mainly of $\text{N}_2\text{H}_4\text{HCl}$. The elemental and emission spectrographic analysis of this material is compiled in Table VIII. The soluble solids obtained from capsule S/N 24 were sufficient, after other tests, to titrate with chloramine-T, and the $\text{N}_2\text{H}_4\text{HCl}$ concentration was found to be 64.76%. The total N_2H_4 content of the capsules after correction for the weight of soluble and insoluble material is recorded in Table V.

As seen in Table VIII, the solids obtained from the water-soluble fraction had a very high carbon and chloride concentration. There are two possible sources for the chloride concentration, one is the Ti(6Al-4V) coupon and the other is Freon TF used as a degreasing agent in the test capsules. The Freon TF is the only major source of carbon contamination; aniline is initially present in N_2H_4 in trace amounts.

3. Reaction of Freon TF and N_2H_4

Freon TF contamination might have been introduced into the capsule during the cleaning procedure described in JPL SPEC GMZ-50521-GEN-A.⁹ The cleaning procedure states in step 4.9.1 that the capsule shall be rinsed twice with Freon TF and each time the solvent shall be poured out. The

Table VII

ANALYSIS OF WATER-INSOLUBLE MATERIAL

Capsule S/N	20	21	22	24
Test Specimen	0057	0059	0061	0065
Emission Spectrograph				
Ti	†	P.C. ‡	P.C. ‡	P.C. ‡
Al		6.0%	0.7%	18.0%
V		4.5	0.8	0.35
Si		0.35	0.5	0.4
Cu		0.1	0.07	0.02
B		0.1	0.06	0.05
Mg		0.01	0.03	0.001
Fe		0.25	0.015	0.08
Ca		0.008	0.002	0.015
Cr		0.003	--	0.015
Pb		0.01	--	--
Ni		0.02	--	--
Zn		0.03	--	--
Elemental Analysis				
C	†	Trace	None	Trace
H		1.61%	0.29%	2.23%
N		None	None	3.45
Cl		None	--	0.31

† Capsule shattered on breaking.

‡ P.C. = principal constituent.

Table VIII

ANALYSIS OF WATER-SOLUBLE MATERIAL

Capsule S/N	20	21	22	24
Test Specimen	0057	0059	0061	0065
Emission Spectrograph				
Ti	†	12.5%	0.35%	0.7%
Al		2.5	0.25	0.15
B		--	0.2	--
Na		--	0.15	--
Fe		0.005	0.025	--
V		0.25	0.02	0.025
Cu		0.15	0.007	0.01
Ca		0.005	0.007	<0.001
Zn		--	0.006	--
Cr		--	0.005	--
Si		0.05	--	--
Mg		0.003	0.004	--
Ba		--	0.001	--
Ag		--	--	<0.001
Pt		--	--	0.3
Elemental Analysis				
C	†	19.36%	9.44%	8.83%
H		6.35	7.28	7.58
Cl (free)		31.01	30.21	39.58
Cl (total)		29.26	30.69	---
N		36.23	39.38	41.61

† Capsule shattered on breaking.

capsule shall be then allowed to air dry. Then in step 4.10 the specification states "immediately after cleaning, the open end of the capsule neck shall be plugged with a clean plastic plug...". This procedure leaves the drying time of the capsule open to the discretion of the technician. On September 3, 1969, JPL Procedure No. EP504516 REV. B was issued which allows for pumping the capsule dry of Freon TF. However, this revised procedure was issued after test capsules S/N 20, 21, 22, and 24 were filled and sealed. Therefore JPL SPEC GMZ-50521-GEN-A was followed for the test capsules which we analyzed.

In duplicating this cleaning procedure, we used a 70-cc test tube and a plastic plug. We rinsed the test tube twice with Freon TF, poured the solvent out, and allowed the tube to air dry. Dry in this case was the absence of any visible signs of liquid Freon TF. The capsule was then plugged and allowed to stand for ten minutes. Visual observation of the plugged test tube still indicated that it was dry. However, when the capsule was unplugged, a definite odor of Freon TF was noted. We feel, therefore, that this cleaning procedure leaves a residue of Freon TF vapor and/or liquid.

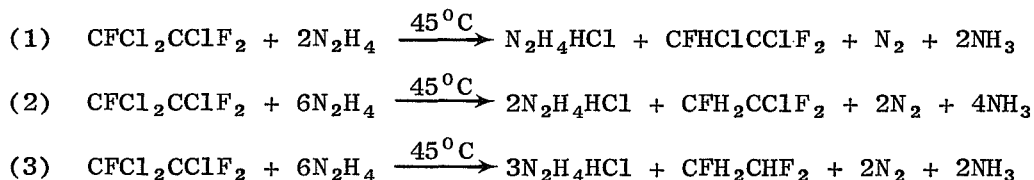
A calculation was made to determine if a vapor phase of Freon TF in the test capsule could produce the chloride concentration that was found experimentally. Using the JPL specifications, we estimated that a test capsule would have a sealed volume of 90 cc; a room temperature vapor phase of Freon TF in this volume could produce 0.15 g of chloride. Experimentally, however, we found that the test capsule chloride concentration ranged from 0.07 to 0.2 g. We felt, therefore, that within limits of the calculation Freon TF can be the source of the chloride contamination; provided, of course, that a reaction occurs between hydrazine and Freon TF vapors.

In attempts at establishing the reaction of Freon TF and hydrazine, we first determined that neat hydrazine and neat Freon TF contained no free Cl^- . Both room temperature and 45°C (113°F) reactions were run with liquid hydrazine and liquid Freon TF. Results indicate that at room temperature only a trace of free Cl^- is liberated whereas at 45°C a substantial residue of $\text{N}_2\text{H}_4\text{HCl}$ was formed. This establishes the

reaction of liquid Freon TF and liquid N_2H_4 at $45^\circ C$; however, under test capsule conditions, Freon TF is most likely present in the gas phase.

Liquid Freon TF was placed in a round-bottom flask and the liquid poured out. The Freon TF vapors remaining in the flask varied from 250 to 450 mg. In the process of obtaining a vapor phase of Freon TF, we noted that a drop of Freon TF collected in the flask. This drop of liquid Freon TF remained after ten minutes of open air evaporation, and only continued inversion of the flask removed the liquid phase. After the vapor phase of Freon TF was weighed, N_2H_4 was added to the flask with a hypodermic syringe, and the system was closed and heated to $45^\circ C$. The N_2H_4 remained colorless at $45^\circ C$ for two hours, and then the solution began to turn a pale yellow. The reaction was allowed to continue for five hours after which it was cooled to room temperature. Evaporation of an aliquot of the yellow N_2H_4 gave a solid residue identified as N_2H_4HCl by ir analysis. This confirms the reaction between Freon TF vapors and liquid N_2H_4 .

We have observed N_2H_4HCl in all Freon TF- N_2H_4 reactions. In the N_2H_4 -Ti(6Al-4V) test capsules (S/N 21, 22, and 24) we observed N_2H_4HCl along with N_2 and NH_3 . Because no fluoride has been detected, we are assuming that the C-F bonds are not being attacked and therefore we propose the following N_2H_4 decomposition reactions:



The products, $CFHClCClF_2$, CFH_2CClF_2 , and CFH_2CHF_2 , have not been observed in the off gases or in the solid residue. However, as noted in Table VIII, a definite carbon concentration was found in capsules S/N 21, 22, and 24, indicating that some further reaction of $CFHClCClF_2$, CFH_2CClF_2 , and CFH_2CHF_2 had occurred. We found no carbon concentration in the residue of neat N_2H_4 , which indicated that the carbon is likely due to the Freon TF.

The NH_3/N_2 mole ratios in Eqs. (1), (2), and (3) are 2/1, 2/1, and 1/1, respectively. However, the mass spectra of the test capsule off gases give NH_3/N_2 ratios of 1/4, 1/4, 1/10, and 1/1 for test capsules S/N 20, 21, 22, and 24, respectively. The low NH_3 value is due to its appreciable solubility in liquid N_2H_4 . Therefore, at this time we cannot determine which reaction (1, 2, or 3) the N_2H_4 -Freon TF is undergoing.

4. Analysis of Ti(6Al-4V) Test Specimen

Upon removal of the hydrazine and its reaction products from each capsule, the titanium strips were also removed and analyzed by a variety of methods. Figures 1 through 4 show photographs of the titanium test specimens after removal from the glass capsules. In all samples a demarcation line across the middle of the sample showed the N_2H_4 liquid level. Below this line is a mottled portion which has been exposed to liquid hydrazine. The surfaces of the mottled portions were covered irregularly with flaky black films. The upper portion of the test specimens, exposed to gases of N_2H_4 , did not have this powdery surface. Some physical properties of the test specimens are found in Tables IX and X.

The black powder from the mottled portion of the test specimens was scraped off and analyzed by various methods. The results are found in Tables XI and XII. Ir and X-ray data indicate that the black powder is a hydrous TiO_2 compound; the gray precipitate obtained by water dilution of the N_2H_4 was also. However, emission spectrographic results (Table VII) indicate that the water-soluble material of capsules S/N 22 and 24 is low in vanadium while the emission spectra of the black powder (Table XI) indicate that these samples are very low in aluminum and relatively high in vanadium. It appears that the leaching process is not consistent, and overall patterns are not readily apparent from the samples studied.

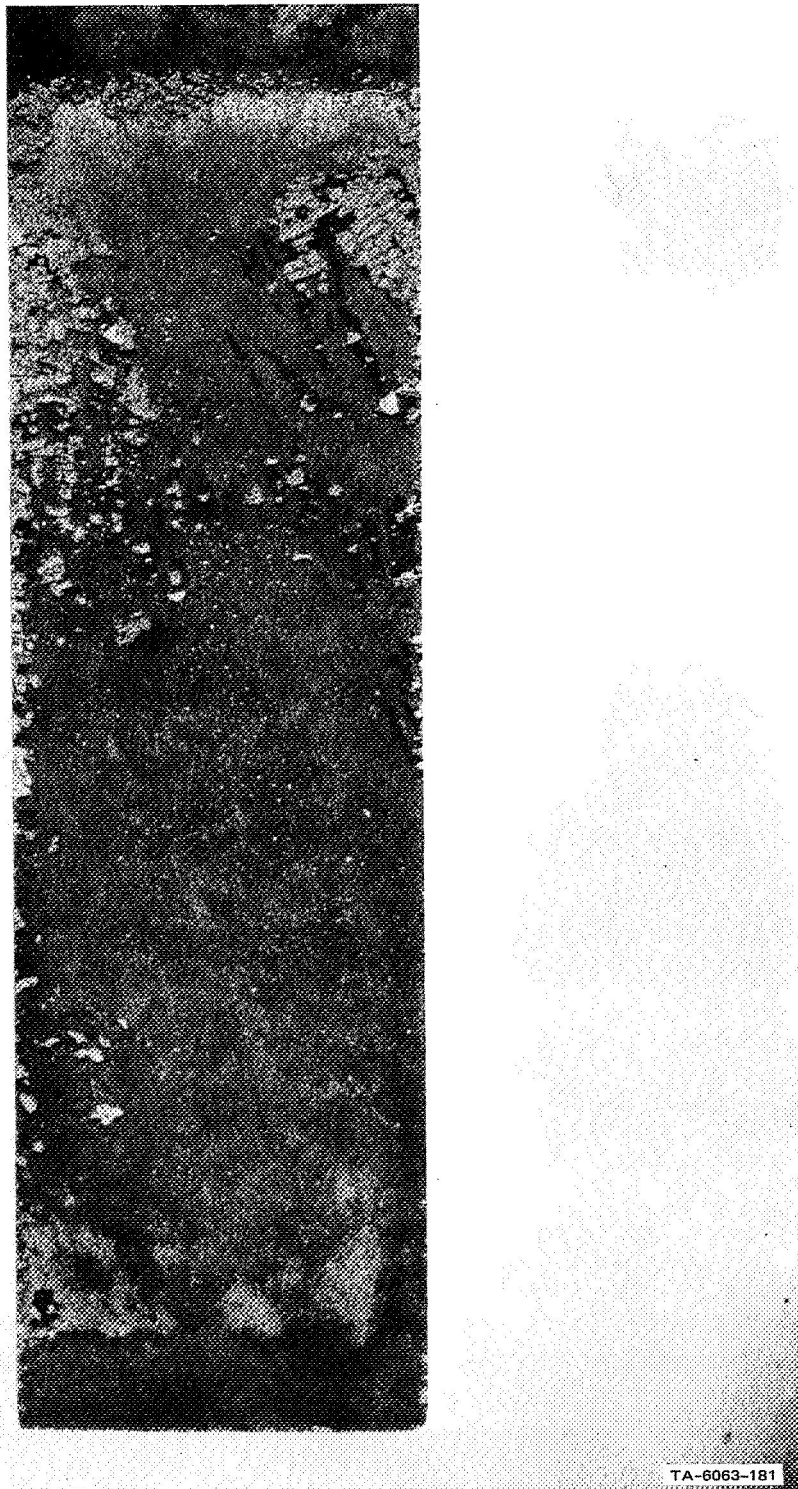
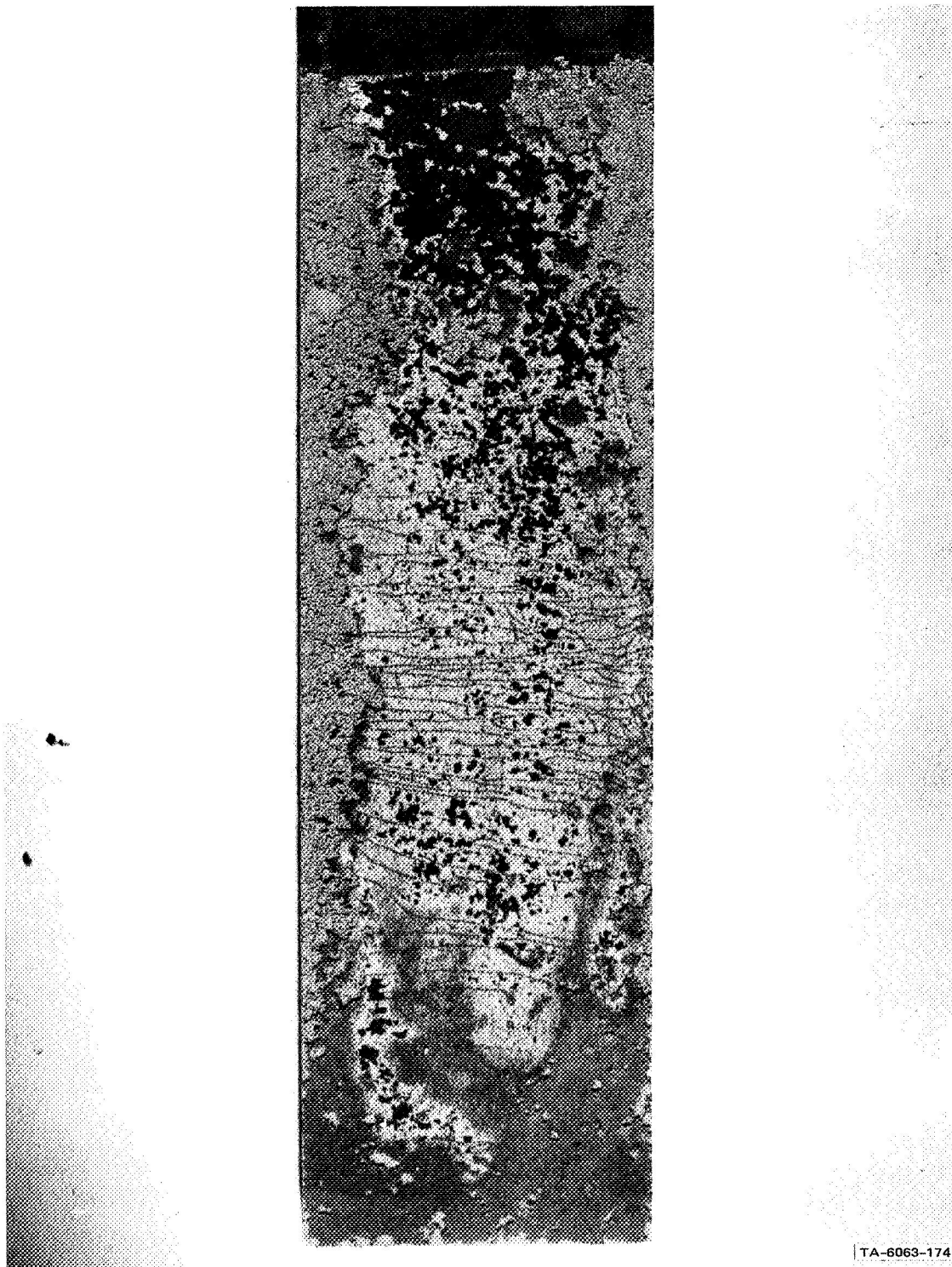


FIGURE 1 SURFACE OF TEST SPECIMEN NO. 0065 EXPOSED TO LIQUID N_2H_4 IN CAPSULE S/N 24



TA-6063-174

FIGURE 2 SURFACE OF TEST SPECIMEN NO. 0061 EXPOSED TO LIQUID N_2H_4
IN CAPSULE S/N 22



TA-6063-180

FIGURE 3 SURFACE OF TEST SPECIMEN NO. 0059 EXPOSED TO LIQUID N_2H_4
IN CAPSULE S/N 21

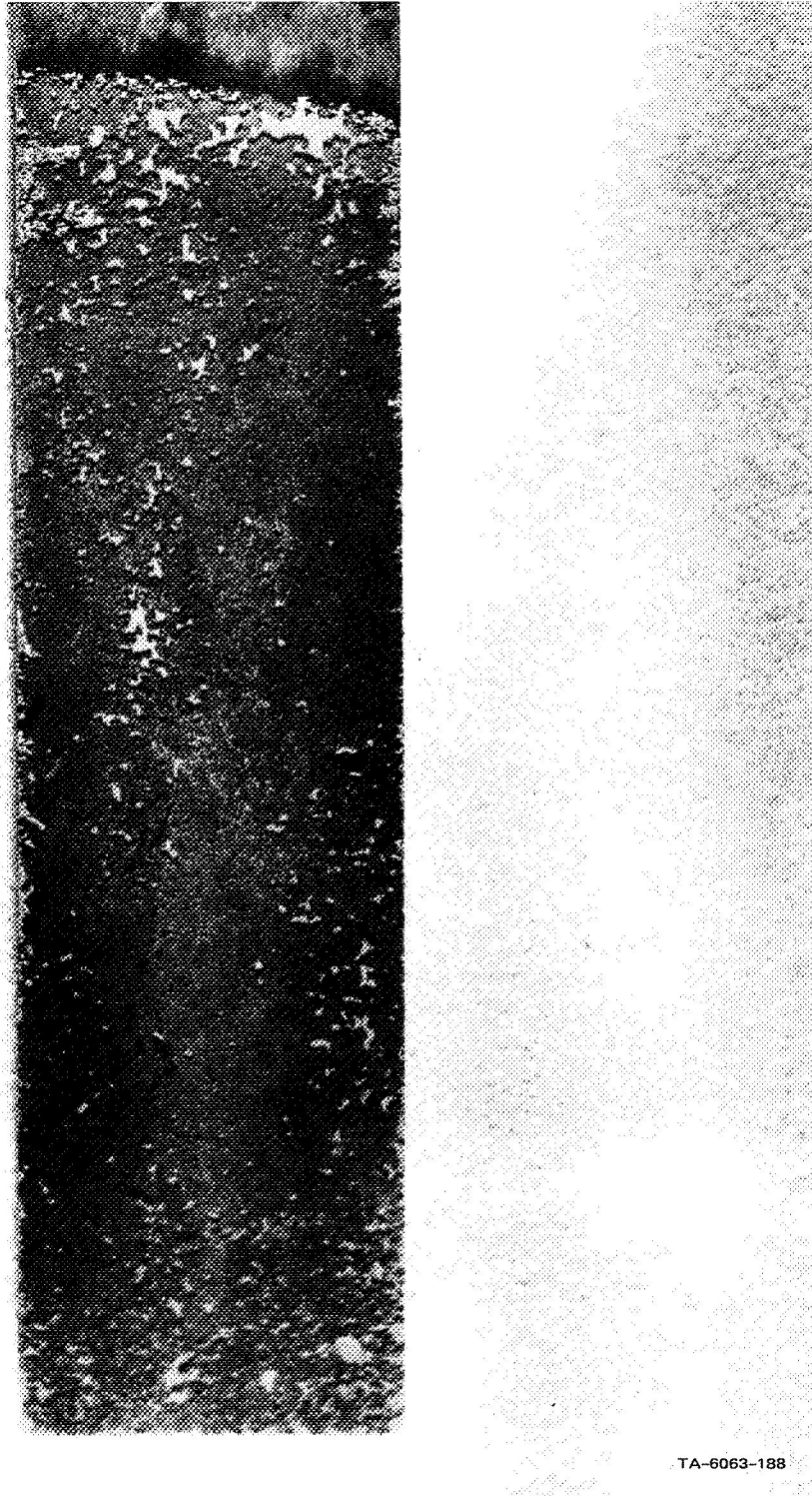


FIGURE 4 SURFACE OF TEST SPECIMEN NO. 0057 EXPOSED TO LIQUID N_2H_4
IN CAPSULE S/N 20

Table IX

PHYSICAL CHARACTERISTICS OF TITANIUM
TEST SPECIMENS BEFORE REACTION WITH HYDRAZINE

Capsule S/N	20	21	22	24
Test Specimen	0057	0059	0061	0065
Weight (g)	3.2451	3.2421	3.2415	3.2627
Length (in.)	2.9869	2.9882	2.9871	2.9908
Width (in.)	0.4974	0.4982	0.4984	0.4981
Thickness (in.)	0.0304	0.0304	0.0304	0.0305

Table X

PHYSICAL CHARACTERISTICS OF TITANIUM TEST SPECIMENS
AFTER REACTION WITH HYDRAZINE

Capsule S/N	20	21	22	24
Test Specimen	0057	0059	0061	0065
Weight (g)	3.1940	3.1950	3.1760	3.2081
Weight Lost (g)	0.0511	0.0471	0.0655	0.0546
Length (in.)	2.994	2.995	2.996	2.999
Width (in.)	0.498	0.497	0.496	0.498
Thickness (in.)	0.031	0.031	0.030	0.031
Immersion Depth (in.)	1.771	1.765	1.737	1.691
Total Surface Area (in. ²)	3.198	3.194	3.182	3.204
Surface Area Exposed to N ₂ H ₄ (in. ²)	1.905	1.895	1.842	1.820

Table XI

EMISSION SPECTROGRAPH OF BLACK POWDER ON TITANIUM STRIP

Capsule S/N	20	21	22	24
Test Specimen	0057	0059	0061	0065
Ti	P.C.†	P.C.†	P.C.†	P.C.†
V	5.0%	4.0%	10.0%	7.0%
Al	0.3	0.5	0.5	0.75
Fe	0.15	0.25	0.08	0.3
Si	0.06	0.15	0.5	0.4
Cu	0.08	0.05	0.05	0.015
Cr	0.03	<0.005	0.007	0.003
B	0.01	0.01	0.03	0.08
Mg	0.001	0.01	0.25	0.004
Mn	<0.001	<0.001	0.02	0.003
Mo	0.03	0.05	0.01	0.03
Pb	0.005	--	--	0.007
Sn	0.006	--	--	--
Ni	0.006	--	0.007	0.003
Ca	<0.003	--	0.015	<0.002
Ba	--	--	0.06	--
Sr	--	--	--	0.005
Ag	--	--	0.01	--

† P.C. = Principal Constituent

Table XII

ELEMENTAL ANALYSIS OF BLACK POWDER ON TITANIUM STRIP

Capsule S/N	20	21	22	24
Test Specimen	0057	0059	0061	0065
C	<1%	<1%	2.1%	3.96%
H	2.29	2.13	2.44	2.44
Cl	0.0	0.0	0.0	0.0
N	2.93	2.62	1.61	1.88

In the process of cutting strips from the titanium alloy it was noted that the metal exposed to the liquid N_2H_4 had become brittle and could now be broken by hand. However, the metal that was exposed to the vapors retained its metallic properties and had to be cut with tin snips. It is thus evident that the titanium alloy had undergone some physical change while standing in liquid N_2H_4 .

Samples of the test specimens above and below the liquid phase were analyzed by emission spectroscopy. The results, found in Tables XIII and XIV, seem to differ from the theoretical amounts of 6%Al and 4%V expected for Ti(6Al-4V). A sample of virgin Ti(6Al-4V) was analyzed by atomic absorption (see below), and the starting concentrations of (Al and V) were more accurately determined. From the atomic absorption work we determined that emission spectrographic analysis is not accurate to the degree required.

X-Ray diffraction patterns were taken of samples exposed to liquid hydrazine only. These X-ray patterns are found in Table XV. Differences occur between the two halves of the strips depending apparently upon a gaseous or liquid exposure to hydrazine. Most Ti(6Al-4V) alloys are known to contain both α (hexagonal close packed) and β (body-centered cubic) phases. The results indicate that the β phase is present in the titanium sample exposed to liquid N_2H_4 , but no β -phase titanium is present above the liquid level. The α -phase titanium is present both above and below the hydrazine liquid level. This is not the case for the lower half of S/N 22, in which only the α phase is found. It is difficult to explain this α - and β -phase discrepancy without knowing the past histories of the titanium test samples. However, this α - and β -phase discrepancy is very likely to be a surface phenomena since X-ray analysis does not penetrate more than a few angstroms.

As shown earlier, the chloride contamination could arise from the cleaning solvent Freon TF. However, the possibility also exists that the Ti(6Al-4V) alloy contributed some chloride contaminants. The standard preparation of Ti involves reduction of $TiCl_4$,

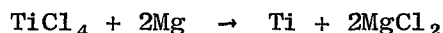


Table XIII

EMISSION SPECTROGRAPH OF Ti(6Al-4V)
 ABOVE THE LIQUID HYDRAZINE

Capsule S/N	20	21	22	24
Test Specimen	0057	0059	0061	0065
Ti	P.C. †	P.C. †	P.C. †	P.C. †
V	3.0%	4.0%	6.0%	3.0%
Al	6.0	4.0	5.5	7.0
Fe	0.2	0.2	0.15	0.2
Si	0.08	0.015	0.1	0.005
Cu	0.002	0.002	0.002	0.005
Cr	<0.003	--	0.001	--
Mg	<0.001	--	0.001	--
Ca	--	--	<0.001	--
Mn	<0.001	<0.001	--	0.003
B	<0.01	--	--	--

† P.C. = Principal Constituent.

Table XIV

EMISSION SPECTROGRAPH OF Ti(6Al-4V)
 BELOW THE LIQUID HYDRAZINE

Capsule S/N	20	21
Test Specimen	0057	0059
Ti	P.C. †	P.C. †
V	3.0%	4.0%
Al	5.5	5.5
Fe	0.25	0.15
Si	0.08	0.02
Cu	0.002	0.005
B	<0.01	--
Mn	<0.001	<0.001
Cr	<0.003	--

† P.C. = Principal Constituent.

Table XV
X-RAY ANALYSIS OF Ti(6Al-4V) TEST SPECIMENS

Capsule S/N	21	21	22	24	24
Test Specimen	0059	0059	0061	0065	0061
Sample	A [†]	B [‡]	A [†]	A [†]	B [‡]
	d ^o Å I	d ^o Å I	d ^o Å I	d ^o Å I	d ^o Å I
	2.54 vw	2.53 w	2.51 vw	--	2.53 w
	2.34 vw	2.33 w	2.31 w	--	2.31 vw
	2.23 w	2.22 m	2.21 w	--	2.21 w
	1.72 m	1.72 m	1.71 m	1.72 m	1.71 m
	1.60 vw	--	--	1.60 w	--
	1.53 vw	--	--	--	--
	1.46 s	1.46 s	--	1.46 s	1.46 s
	1.33 w	1.32 w	1.32 w	--	1.32 w
	1.25 vw		--	--	--
	1.24 vw	1.24 vw	1.24 vw	--	--
	0.98 vw	0.98 vw	--	--	--

† Polished lower half of Ti test specimen.

‡ Polished upper half of Ti test specimen.

Thus any chloride remaining in the Ti lattice could be eluted by the hydrazine, leaving in its place lattice holes or TiH_4 impurities. The reaction of hydrazine with the impurity would account, at least in part, for the chloride found in the hydrazine and would also account for the changes in physical properties found in the test specimens below the liquid level. Several samples of the Ti test specimens above the encapsulated liquid N_2H_4 level were combined for a chloride analysis, on the assumption that gaseous N_2H_4 would not remove the chloride present. Results of the analysis indicated the chloride content of the test specimens to be less than 0.02%. Samples of virgin Ti(6Al-4V) were obtained for a chloride analysis. Two of these samples, 515-B and 914, were cut into small pieces, a total weight of 5.0521 g, and dissolved in aqueous HF according to Codell's method¹⁰ for chloride analysis. Analysis showed that less than 0.016% Cl^- ($<0.0008g$) was present in the 5-gram sample of virgin Ti(6Al-4V). The chloride concentration found in the hydrazine test capsules was almost 200 times greater than that found in virgin Ti(6Al-4V). Therefore, we conclude that the titanium test strip is not the source of chloride contamination; however, the Freon TF residue is a source of both chloride and carbon impurities.

5. Atomic Absorption Analysis

The emission spectrographs of the Ti(6Al-4V) coupons after exposure to N_2H_4 indicated that the analysis of V and Al varies as much as 2%, allowing no firm conclusions to be made. As a result, we attempted to establish an accurate method for analyzing Al and V in Ti(6Al-4V) using atomic absorption.

Samples of pure Ti, Al, and V were dissolved in HF, HCl, and HCl- HNO_3 , respectively; in addition, samples of virgin Ti(6Al-4V), test specimen 511-B, S/N 20 exposed to liquid N_2H_4 , and S/N 24 exposed to liquid N_2H_4 were dissolved in HF. These standard solutions were then diluted into several concentration ranges and analyzed by atomic absorption. The analytical results are found in Table XVI. It is evident that the V and Al concentrations of the virgin Ti(6Al-4V) sample are well within the Ti(6Al-4V) concentration specifications, but the Ti

Table XVI

ATOMIC ABSORPTION ANALYSIS OF Ti(6Al-4V)

Capsule S/N		20 [‡]	24 [‡]
Test Specimen	511-B [†]	0057	0065
V (%)	4.08±0.1	4.1±0.1	4.0±0.1
Al (%)	6.2 ±0.1	5.7±0.1	5.8±0.1
Ti (%)	92.2 ±0.1	76.3±0.1	86.8±0.1

[†] Virgin Ti(6Al-4V)

[‡] Sampled below the liquid N₂H₄ level.

concentration is at least 2% higher. Atomic absorption analysis is generally accurate for low cation concentrations but less accurate for concentrations greater than 50%. The method, therefore, may be inadequate to measure the Ti present. The Ti standard (99.999%) also may contain some TiO₂. The impurity would lower the Ti standard concentration and would also explain the high Ti concentration found in the virgin Ti(6Al-4V) alloy.

To obtain a more accurate analysis for the alloy, a wet chemical method of analysis was employed on the standard. By the method of Claassen and Visser,¹¹ titanium was reduced to the trivalent state in a cadmium reductor. The reduced titanium was collected in an Fe(III) solution, and the Fe(II) produced was titrated with ceric sulfate using ferrous phenanthroline as an indicator. The results of two samples dissolved in HF showed only that the Ti standard was about 2% low in Ti, which accounts for the 2% Ti excess found in virgin Ti(6Al-4V) by atomic absorption.

We analyzed the remaining pieces of Ti(6Al-4V) exposed to liquid N₂H₄ used in test capsules S/N 20 and 24 for V and Al concentrations by atomic absorption. The results, found in Table XVI, indicate the

V and Al concentrations are almost the same as virgin Ti(6Al-4V), whereas the Ti concentration is greatly reduced and is thus being leached out by either N_2H_4 or a N_2H_4 -Freon TF mixture.

We set up a series of sixteen capsules to study the interaction of Freon TF, hydrazine, N_2H_4HCl , and their combinations with Ti(6Al-4V), Ti, V, and Al. Eight of these capsules, four containing neat Freon TF, Ti, Al, V, and Ti(6Al-4V) and four containing neat N_2H_4 , Ti, Al, V, and Ti(6Al-4V) have been heating at $45^\circ C$ for one month. Visual observation of these eight capsules indicates that neat Freon TF reacts with vanadium at $45^\circ C$ forming a green-yellow coating on the vanadium strips. However, this is the only capsule in which neat N_2H_4 or Freon TF reacted with any of the metal samples contained in the capsules. Due to lack of time, these capsules cannot be studied further, although it would be very interesting to know what reactions take place with N_2H_4HCl and Ti(6Al-4V), Ti, Al, and V.

III CONCLUSIONS AND RECOMMENDATIONS

It is clearly evident that decomposition of the N_2H_4 and corrosion of the Ti(6Al-4V) have taken place in capsules S/N 20, 21, 22, and 24. This decomposition is apparently not due to an interaction of neat N_2H_4 and the Ti(6Al-4V) alloy but to the reaction of N_2H_4 and Freon TF. This reaction forms N_2H_4HCl and other compounds which in turn react with the Ti(6Al-4V) test specimens. It is known that the Ti is being removed from the alloy. The exact Ti species present in the nonaqueous medium is not known; however, water dilution of the N_2H_4 produces a hydrous TiO_2 compound. Further analysis of the test capsules will not give true corrosion properties of the Ti(6Al-4V) alloy in N_2H_4 . The Freon TF cleaning procedure must be either eliminated or altered to ensure the complete removal of the cleaning solvent. We recommend that, if it must be cleaned with a degreasing solvent, the capsule should be blown dry with some inert gas such as argon. This procedure would eliminate any possibility of an external carbon-chlorine contaminant.

Analysis of the N_2H_4 is an important part of this study and, based on our work (Table II), we recommend that the iodate method be used as the standard analytic procedure for N_2H_4 . This recommendation is made since N_2H_4 is more stable in the acidic medium of the iodate reaction, and more accurate results are obtained.

Finally, we recommend for future capsules that the sealing procedure be improved by addition of break seals to the capsules. The break seals will withstand the 200-psi pressures found in capsules S/N 20, 22, and 24 and yet will enable the capsules to be attached to a vacuum line for final analysis. This procedure will also eliminate the need for removing the strain gauges, thus allowing a before and after pressure measurement of each capsule.

REFERENCES

1. Audrieth, L. F., The Chemistry of Hydrazine, John Wiley and Sons, Inc., New York, 1951, p. 153.
2. Malone, H. E. and Anderson, D.M.W., *Anal. Chim. Acta*, 48, 87 (1969).
3. Malone, H. E. and Biggers, R. A., *Anal. Chem.*, 36(6), 1037 (1964).
4. Penneman, R. A. and Audrieth, L. F., *Anal. Chem.*, 20(11), 1058 (1948).
5. Dee, L. A. and Webb, A. K., *Anal. Chem.*, 39, 1165 (1967).
6. Jones, R. M., *Anal. Chem.*, 38, 338 (1966).
7. Kuwada, D. M., *J. Gas Chromatogr.*, March 1963, 11.
8. Cotton, F. A., and Wilkinson, G., Advanced Inorganic Chemistry, 2nd Ed., John Wiley & Sons, Inc., New York, 1966, pp. 802-3.
9. JPL Specification GMZ-50521-GEN-A, "General Specification Long Term Compatibility Testing with Hydrazine."
10. Codell, M., Analytical Chemistry of Titanium Metals and Compounds, Interscience Publishers, Inc., New York, 1959, pp. 286-7.
11. Claassen, A. and Visser, J., *Rec. Trav. Chim. Pays-Bas*, 60, 213 (1941).