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A PLAN FOR A MATERIAL COMPATIBILITY PROGRAM FOR OXYGEN DIFLUORIDE (OF_2) AND DIBORANE (B_2H_6) LIQUID PROPELLANTS

FINAL REPORT

APRIL 1971

JPL Contract No. 952964

Prepared for

THE JET PROPULSION LABORATORY
Pasadena, California 91103

This work was performed for the Jet Propulsion Laboratory, California Institute of Technology sponsored by the National Aeronautics and Space Administration under Contract NAS7-100

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by

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TRW
SYSTEMS GROUP
ONE SPACE PARK • REDONDO BEACH, CALIFORNIA

FOREWORD

This report was prepared by TRW Systems Group, Redondo Beach, California, and represents the program efforts between 28 August 1970 and 15 April 1971. The work was performed under JPL Contract 952964 for the purpose of developing a plan for a material compatibility program for oxygen difluoride (OF_2) and diborane (B_2H_6) liquid propellants. The program was originated and managed by the Jet Propulsion Laboratory under the technical direction of Mr. O. F. Keller. The TRW Systems Program Manager is Mr. J. R. Denson with overall program management provided by Dr. E. A. Burns, Manager, Applied Chemistry Department.

Substantial support and assistance was provided by Mr. R. N. Porter, Dr. J. A. Neff, Dr. R. S. Ottinger, Mr. C. T. Weekley, and Mr. W. B. Turner.

ABSTRACT

Existing compatibility information on the liquid propellants OF_2 and B_2H_6 was reviewed, but the data did not adequately identify inert materials that have expected high performance and reliability after periods of up to two years storage in mission environments at a temperature of -230°F for a liquid propulsion system in the 1000 lb_f thrust range. Candidate metallic and non-metallic materials were selected for subjection to two years of carefully controlled and documented experimental evaluation in liquid OF_2 and B_2H_6. A test plan was established for the experimental evaluation of candidate materials in a safe and economical manner. Included in the test plan was selection of specimen configuration, specimen combinations, specimen-container-propellant assembly, methods for transporting propellant and specimens, test facility design and operation, and methods for data acquisition and processing.

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1. INTRODUCTION AND SUMMARY

The purpose of this program is to establish availability of technical information that will permit selection of inert materials of construction for a liquid propulsion system, using the propellants oxygen difluoride (OF_2) and diborane (B_2H_6) in the 1000 lb_f thrust range for future space missions. If satisfactory inert materials are not available, a plan is to be established for obtaining the necessary information. Existing compatibility information on the liquid propellants OF_2 and B_2H_6 was reviewed, but the data did not adequately identify inert materials that have expected high performance and reliability after periods of up to two (2) years storage in mission environments at a temperature of -230°F. Candidate metallic and non-metallic materials were selected for subjection to a minimum of two (2) years of carefully controlled and documented experimental evaluation in liquid OF_2 and B_2H_6.

The program details established include selection of specimen configuration and combinations, test container configurations, test assembly and installation, transportation and test initiation and termination criteria. Details were established for data acquisition and processing which utilize computer technology for acquiring and retrieval of data.

1.1 OBJECTIVES

The objective of this program was to advance the technology of materials of construction for a liquid propulsion system in the 1000 lb_f thrust range for future space missions; to determine acceptably inert materials having high performance and reliability after periods of up to two (2) years storage in the mission environments while in contact with liquid oxygen difluoride (OF_2) and diborane (B_2H_6) at a temperature of -230°F; to understand not only the gross but also the subtle implications of extended storage periods of two (2), five (5) and ten (10) years, such as those associated with an advanced mission to the outer planets, and to generate data upon which to base flight commitments.

The available technical information that was available to meet the specific and applied requirements of the objective was acquired and assessed. Because these requirements could not be met, a plan was generated, including related cost estimates, for the purpose of implementing a comprehensive static immersion materials test program with the liquid propellants OF_2 and B_2H_6 at a storage temperature of -230°F. The information presented is in sufficient depth to permit direct implementation with a minimum of technical direction or revision of plans.

1.2 SPECIFIC TASKS

For the purpose of meeting the objective, the program includes the tasks described as follows:

TASK I - COMPILATION AND ASSESSMENT INFORMATION

Current programs which fall within the scope of Tasks II through VI were identified and the extent that these programs provided meaningful technical results of both gross and subtle effects that meet the objectives specified herein was determined, as well as those programs which could be applied with a high degree of confidence to the design of a liquid propulsion feed system using OF_2 and B_2H_6 propellants.

Because adequate existing compatibility information was not available, the remaining tasks were implemented to provide a plan for a material compatibility program.

TASK II - SELECTION OF MATERIALS

A group of candidate materials for static immersion testing with liquid propellants OF_2 and B_2H_6 in the temperature range of -230°F ±30°F was established. The materials selected represent those most likely to be used in an OF_2/B_2H_6 propulsion feed system for an unmanned type spacecraft.

TASK III - TEST PROGRAM DEFINITION

Complete operating details for a compatibility program were established including the following:

(1) Test specimen standard configuration.

(2) Test specimen combinations including unstressed and stressed conditions; mechanical joints such as welding or brazing; dissimilar metals; etc.

(3) Test container standard configuration.

(4) Test specimen-container-propellant assembly and installation in the test facility fixture including special methods and requirements involved.

(5) Transportation handling means and requirements necessary for transporting specimens to or off the test site. Aspects of surface and air transportation were considered.

(6) Immersion test initiation and termination.

TASK IV - ESTABLISH TEST FACILITY REQUIREMENTS

The requirements for the test facility were established including appropriate layout(s) of the facility and engineering information of necessary equipment in sufficient detail to permit subsequent preparation of plans by an architectural and engineering organization.

TASK V - ESTABLISH DATA ACQUISITION AND PROCESSING REQUIREMENTS

The design and requirements for the method of test specimen data acquisition and processing during the subject test were established. This included all detailed information of necessary equipment required for the system.

TASK VI - GENERATE DETAILED TEST PLAN DOCUMENTATION

Pertinent documentation required to implement and accomplish the immersion test program was generated. This will include procedures covering all aspects of the program such as, but not limited to, processing, cleaning, and encapsulation procedures; installation and post-test handling procedures; operational procedures for calibrations, emergencies, hazardous conditions, transportation, and safety considerations for both personnel and facilities.

TASK VII - PROJECT DOCUMENTATION

Complete documentation of the investigations and analyses is provided. Recommendations for future investigations of program areas which are worthy of more extensive investigation are included in the final report.

2. TASK I - COMPILATION AND ASSESSMENT OF AVAILABLE INFORMATION

Compatibility information on the liquid propellants OF_2 and B_2H_6 was compiled and discussed under Contract NAS 7-436, "Advanced Valve Technology".(1) A review of the data compiled under this contract and a review of additional data(2) indicates that a large portion of the propellant-material compatibility data is not applicable to the selection of materials for use in a 1000 lb_f thrust range propulsion system for a future space mission. A summary of these findings is given in the following paragraphs.

2.1 OXYGEN DIFLUORIDE

Oxygen difluoride is a powerful fluorinating and oxidizing agent that is similar to fluorine and the halogens of fluorine. The pure substance is insensitive to mechanical shock and will not detonate when electrically sparked. Its rate of spontaneous thermal decomposition into oxygen and fluorine gas becomes appreciable only above 480°F.

Oxygen difluoride reacts to some degree with all materials considered for construction of a propulsion system. Metals burn in OF_2 if heated by external heat or work to their kindling temperatures. Oxygen difluoride reacts spontaneously with many inorganic and organic substances. When some materials, including certain metals, ice and fluorocarbon plastics, are subjected to impact in the presence of OF_2, reactions of explosive velocity occur.

Compatibility tests(2-8) have been conducted with materials of construction in liquid OF_2. In most cases only the attack on the materials being evaluated was considered and effect on the propellant was neglected.

2.1.1 Metals

The most comprehensive studies performed to date on the corrosion of metals in liquid OF_2 were conducted by McDonnell Douglas Astropower Laboratory.(2) Previous to this investigation Thiokol(3,4) carried out studies of the behavior of a number of alloys exposed to static gaseous and liquid OF_2 which are summarized in Table I. The effect of a rifle ball impact on titanium tanks containing liquid OF_2 was also studied(4);

TABLE I.

RESULTS OF THIOKOL[a] COMPATIBILITY TESTS OF VARIOUS METAL WITH OF_2

	Gaseous OF_2 (Ambient Temperature), 8psia			Liquid OF_2 (-196°C) - Immersed 1/3 of length		
Sample Description[b]	Sample Weight, g	Weight Change g	Visual Observations	Sample Weight, g	Weight Change, g	Visual Observations
SS-301 FH	1.4609	-0.0001	Coating	1.4625	+0.0008	Coating, Minor Pits
SS-304 FH	1.3767	N.1	No Apparent Change	1.3797	-0.0009	No Apparent Change
Maraging AM 367	3.1590	+0.0021	Coating	2.9429	+0.0005	Coating
Maraging AM 355	0.2240	+0.0001	No Apparent Change	0.2155	+0.0013	Coating, Minor Pitting More in Area Exposed to Liquid
Al-2024 T-3	0.3806	+0.0014	Coating	0.3777	+0.0001	Coating, Minor Pitting More in Area Exposed to Liquid, Some Deposits
Al-2024-T-3 Alclad	0.4950	+0.0001	Coating	0.4347	+0.0007	Coating, Minor Pitting More In Area Exposed to Liquid, Some Deposits
Inconel X-750	1.5281	-0.0020	No Apparent Change	1.5053	+0.0007	No Apparent Change
Monel K-500	1.5101	-0.0004	Coating	1.5047	+0.0010	Coating
Monel 400	1.5507	-0.0014	Coating	1.5535	+0.0005	Coating
Titanium 5Al-2.5Sn	0.7993	-0.0012	Stained Spots	0.7935	+0.0001	Stained Spots Developed on Surface
Magnesium AZ 31B, H-24	0.3113	-0.0019	Coating	0.3118	-0.0001	Coating, Increase Depth in Gas Phase
Beryllium Copper 2% Be	1.4720	+0.0003	Coating Slight Discoloration	1.4471	+0.0008	Coating and Discoloration on Surface, More on Area in Contact with Liquid

a Ref. 4 , b 1/2" x 1-3/4 coupons. 2 Week exposures the titanium ignited but did not support combustion. Allied Chemical(5,6) conducted limited studies on the behavior of materials for one day or less when moved slowly in liquid OF_2. These results are summarized in Table II.

The studies conducted by Astropower(2) include impact, closed loop high pressure flow and immersion testing. The method of impact testing was conducted in a device similar to the ABMA open cup tester (7). Aluminum alloys, stainless steels, copper and nickel alloys did not exhibit impact sensitivity with liquid OF_2. Tantalum, titanium alloys 6Al-4V and Ti-Al 10AT, and magnesium alloy Mg HM21A exhibited light-to-extreme reactivity with liquid OF_2. The titanium alloys had only a slight reaction with liquid OF_2 upon impact sensitivity tests. Under high pressure flow testing monel exhibited the greatest resistance of attack of the materials tested. Stainless steel showed some corrosive damage while aluminum alloys showed higher rates of attack. The corrosion rates obtained on the immersion tests were calculated from weight change data. A summary of the Astropower information on corrosion rates is given in Table III.

Muraca(19) suggested that titanium alloys can be protected from impact sensitivity in the presence of OF_2 by coating with electroless nickel plate.

The investigations carried out by Astropower (2),though informative, do not provide data that can be utilized for identifying materials that have high performance and reliability after periods of two years storage in mission environments. The immersion tests in OF_2 were deficient in providing information for the objective of this program for the reasons discussed below:

- Specimens of several different materials were placed in a 316 stainless steel test bomb and supported on a rack using alumina spacers. Because several materials were stored in the same test bomb, the changes in propellant composition were not considered.
- No consideration was given to the effect on sample corrosion reaction products between the propellant and the 316 stainless steel bomb and supporting rack with alumina spacers.

TABLE II

ALLIED CORROSION TEST RESULTS OF[a] MATERIALS IN LIQUID OXYGEN DIFLUORIDE

	Exposure[b] Time (hrs)	Exposure Area (in^2)	Weight Loss (mg)	Corrosion Rate in/yr
Electrolytic Copper	24	2.60	7.0	0.0065
Electrolytic Copper	24	2.60	7.8	0.0072
Phosphor Bronze	25	2.70	5.9	0.0141
Phosphor Bronze	25	2.70	9.9	0.0090
Aluminum 1100	25	2.59	7.6	0.0242
Aluminum 1100	25	2.52	6.9	0.0211
Aluminum 3003	25	2.58	6.1	0.0180
Aluminum 3003	25	2.58	7.3	0.0525
Aluminum 6061	25	2.50	7.7	0.0238
Aluminum 6061	25	2.50	8.7	0.0275
Aluminum 5052	25	2.37	8.1	0.0263
Aluminum 5052	25	2.37	4.2	0.0462
Pure Tin	25	2.72	6.0	0.0948
Pure Tin	25	2.65	5.5	0.2501
Kentanium	24	2.56	3.3	0.0049
Kentanium	24	2.56	4.9	0.0072
Norton HP Alundum	24	4.85	2.9	0.0034
Norton Norbide	24	4.63	2.9	0.0057
Nat'l Carb. CCA-B	24	6.45	+0.5	Gain
Nat'l Carb. CCP-B	24	6.38	+0.2	Gain
Nat'l Carb. CDJ-B	24	6.44	3.5	0.0006
Teflon	5	2.83	+0.7	Gain
Teflon	5	2.69	+0.7	Gain
Genetron VK Polymer	5	2.65	1.8	0.0350
Genetron VK Polymer	5	2.61	2.6	0.0519
Genetron HL Polymer	5	2.68	0.1	0.0019
Genetron HL Polymer	5	2.64	+0.5	Gain
Mylar	5	2.05	+0.5	Gain
Mylar	5	2.03	+0.3	Gain

a - Ref. 5

b - Exposure Conditions:
Temperature: -320°F
Pressure: 15 inches Hg abs.
0.85 ft/sec linear velocity; direction reversed at 0.255 second intervals

TABLE III

CORROSION RATES OF STRUCTURAL MATERIALS: ASTROPOWER[a]

Material & Treatment	Oxidizer Phase	Corrosion Rate, mils/year[b] 1-Day	21-Day	4-Month	12-Month
Aluminum Alloys					
Al 1100-0	L	1.2	.04	.004	.001
	G	0.3	.04	.020	.000
Al 2014-T6	L	0.4	---	.000	.002
	G	0.0	.05	.080	.000
Al 2219-T81	L	1.8	---	.000	.002
	G	0.5	.03	.007	.000
Al 6061-T6	L	0.4	.02	.004	.000
	G	0.2	.01	.004	.002
Al 7075-T6	L	0.4	.09	---	---
	G	0.8	.11	.09	---
Al 7079-T6	L	0.4	.06	.007	.009
	G	0.3	.04	.00	.007
Stainless Steels					
SS301-FH	L	0.3	---	.000	.000
	G	0.8	.01	.005	.001
SS316-A	L	0.2	---	.002	.000
	G	0.1	.01	.000	.000
SS316-FH	L	0.3	---	.001	.000
	G	0.2	.01	.000	.001
SS347-A	L	0.2	---	.002	.002
	G	0.2	.01	.001	.003
SS347-FH	L	0.4	---	.001	.000
	G	0.3	.01	.000	.000
AM350 (850SCT)	L	0.3	---	.005	.000
	G	0.4	.00	.002	.004
PH-15-7Mo (TH 1050)	L	0.4	---	---	.003
	G	0.1	.01	---	.003

(Continued)

a - Reference 2

b - Average of duplicate tests conducted at -110°F and saturation pressure of 450 psi.

TABLE III (Con't)

CORROSION RATES OF STRUCTURAL MATERIALS: ASTROPOWER[a]

Material & Treatment	Oxidizer Phase	Corrosion Rate, mils/year[b] 1-Day	21-Day	4-Month	12-month
Nickel and Copper Alloys					
Nickel 200-A	L	0.1	0.2	.001	.007
	G	0.2	.01	.002	.007
Monel 400-A	L	0.2	.02	.003	.000
	G	0.2	.02	.003	. 01
Inconel X (1300/20 hrs)	L	0.0	---	.002	.001
	G	0.2	.03	.002	.001
Rene' 41/CMR (1400/16 hrs)	L	0.0	---	.001	.001
	G	0.2	.03	.001	.001
Copper-A	L	0.0	.01	.005	.001
	G	0.2	.02	.005	.001
Brass (70-30)-A	L	0.0	.01	.002	.001
	G	0.4	.00	.004	.001
Cufenloy 10-A	L	0.3	.01	.004	.001
	G	0.3	.02	.004	.000
Cufenloy 40-A	L	0.3	.00	.004	.001
	G	0.3	.01	.003	.001

- Immersion testing was conducted at -110°F instead of the -230°F requirement for the 1000 lb_f liquid propulsion system for future space missions. In general, this would not be considered a disadvantage, but in the case of OF_2, it could be a disadvantage because at -110°F a corrosion accelerating impurity could be in the vapor phase while the impurity could be in the liquid phase at -230°F.
- The propellant used contained small unknown amounts of contamination, principally moisture and hydrogen fluoride. The presence of these contaminants to liquid OF_2 increased the surface attack on aluminum, titanium and stainless steel.

2.1.2 Ceramics

Limited tests indicate that sintered alumina (Al_2O_3) and Pyrex glass in liquid OF_2 are insensitive to impact(2). However, any hydrogen fluoride (HF) in OF_2 etches glass according to Equation 1:

$$4\ HF + SiO_2 \rightarrow SiF_4 + 2H_2O \qquad (1)$$

2.1.3 Compliant Materials

Thiokol(9) carried out studies that indicated in addition to the perfluoro materials (Teflon TEF, Teflon FEP and Kel-F-81), vinyl silicone, fluorosilicone and cis 1,4-polybutadiene elastomers were satisfactory for short term applications.

Studies just completed by TRW under Contract NAS 7-770(10) indicate liquid OF_2 compatibility for a compound made from cis 1,4-polybutadiene reinforced with Al_2O_3 and cured by peroxide. This material remains elastomeric down to -150°F and at 110°F was found capable of expelling OF_2 when used as an expulsion bladder. Thiokol(9) conducted thirty-day immersion tests for materials in liquid OF_2 and obtained data for Teflon TEF, Teflon FEP, and Kel-F-81. The data indicated that the polymers swelled slightly in OF_2 but were resistant to the liquid oxidizer for a minimum of thirty days at -110°F. The polymers also exhibited a low brisance in Trauzl block tests while immersed in the liquid oxidizer. Teflon TEF, Teflon FEP, and Kel-F exhibited violent reactions with liquid OF_2 at -110°F when tested in the ABMA impact tester (2). However, these polymers in addition to vinyl silicone and fluorosilicone elastomers have been used with liquid OF_2 for limited applications.

2.2 DIBORANE

Diborane is a liquid at the temperature (-230°F) of interest to this program. Diborane is a reactive reducing compound requiring careful selection of construction materials. Diborane will react with any potential oxidizer including such materials as water, oxygen, some metal oxides(11) and reducible organic oxides. Natural and most synthetic elastomers are not considered compatible because B_2H_6 reacts with the double bonds in these elastomers. Callery Chemical Company(11) reports the work of Winternitz(12) which indicates the following materials of construction were found to be suitable for use with gaseous B_2H_6 on exposure at ambient temperature:

Brass
Lead
Nickel
K Monel
Low Carbon Steel
Stainless Steel
Teflon
Kel-F
Saran
Asbestos - graphite - copper valve packing
Vaseline - paraffin - graphite lubricant

In practice, liquid diborane at -110°F and lower is considered compatible with most metals, Teflon and Kel-F. Some evidence exists that liquid diborane reduces the aluminum oxide on aluminum.(13)

3. TASK II - SELECTION OF MATERIALS

The compatibility information on the liquid propellants OF_2 and B_2H_6 that has been summarized in Section 2, does not adequately identify inert materials that have expected high performance and reliability after periods of up to two years storage in mission environments at a temperature of -230°F. The information found in the literature, though of valuable assistance in eliminating some materials, is deficient because in most cases only the effect of the propellant on the materials of construction was studied for short periods (usually one month or less) at temperatures other than -230°F. The effect of the materials of construction on the propellant was usually not considered nor were the products of corrosion or reaction adequately identified to predict the effect of these products on system operation. Therefore, it is recommended that candidate metallic and non-metallic materials for use in this application be identified and subjected to a minimum of two years of carefully controlled and documented experimental evaluation in liquid OF_2 and B_2H_6 maintained at -230°F.

In most cases it can be assumed that materials compatible with OF_2 will be compatible with B_2H_6. Usually duplicate systems are designed for handling both the oxidizer and fuel. Because adequate compatibility data is not available for materials in OF_2, a reasonable first assumption is that materials of construction used in fluorine service are candidates for liquid OF_2 service. A list of selected materials that have been used in fluorine service is presented in Table IV along with a tabulation of use applications for these materials. Cost considerations require that the list of materials in Table IV be limited to those of greatest interest to the OF_2/B_2H_6 propulsion feed system.

TABLE IV

MATERIALS CONSIDERED FOR USE IN LIQUID OF_2 AND B_2H_6

Material	Applications
A-286	nuts and bolts, springs, shafts
301 Cres	bearing surfaces
302 Cres	bodies, springs, bellows
303 Cres	bodies, nuts and bolts
304 ELC	bodies, springs, bellows, nuts and bolts, diaphrams, tubing (304)
308 Cres	bodies, springs, nuts and bolts
309S Cres	bodies, springs, nuts and bolts
316 ELC	bodies, shafts, tubing (316)
317 Cres	bodies, shafts
321 Cres	nuts and bolts, bellows, bodies, springs, shafts, diaphrams, tubing
347 Cres	nuts and bolts, bellows, bodies, springs, shafts, diaphrams, tubing
410 Cres	bearing surfaces, shafts
422 Cres	shafts
440 C Cres	bearing surfaces
AM 350 Cres	nuts and bolts, springs, bodies
AM 355 Cres	nuts and bolts, springs
17-4 PH (H900 min)Cres	nuts and bolts, shafts
17-7 PH Cres	nuts and bolts, shafts
PH 15-7 MO Cres	shafts
A-356 Al	bodies
1100Al	seals, bearing surfaces
2014 Al	tubing
2017 Al	nuts and bolts
2024 Al	bodies, nuts and bolts
2219 Al	bodies
3003 Al	bodies
5052 Al	bodies, tubing
6061 Al	bodies, bearing surfaces
707S Al	bodies
M 517 Al	bodies
TUNGSTEN CARBIDE	seats in valves, bearing surfaces
Al_2O_3	bearing surfaces, seats in vlaves
CHROMIUM CARBIDE	bearing surfaces
6 Al-4V E4 (b)	bodies, nuts and bolts, shafts
MONEL (400)	bodies, valve seats, springs, nuts and bolts, tubing bellows, diaphrams
K-Monel (K-500)	bellows, nuts and bolts, springs, bodies, shafts, diaphragms
S-Monel (505)	valve seats, bearing surfaces
R-Monel (R-405	tubing, nuts and bolts, valve seats
H-Monel	bodies
Inconel 625	springs, bellows, tubing
Inconel (600)	springs, bellows, tubing

(Continued)

a - ELC grade for welding

b - Extra low interstitial oxygen

TABLE IV (Con't)

MATERIALS CONSIDERED FOR USE IN LIQUID OF_2 AND B_2H_6

Material	Application
Inconel-X (X-750)	nuts and bolts, springs, bellows
Inconel-718	bodies, shafts
Inconel-W (722)	springs
Electroformed Nickel	plating
A Nickel (200)	valve seats
D Nickel (211)	bodies
E Nickel (212)	bodies
Z Nickel or (Duranickel 301)	shafts, springs, diaphragms
Nickel 270	valve seats
OFHC Copper (Alloy 102)	seals, spacers, bearing surfaces
Cufenloy 10	bodies
Cufenloy 40	bodies
Brush 190 (Be Cu)	springs, bellows, flexures, seals, diaphragms
Rene 41	shafts
Hasteloy B	shafts
Hasteloy C	shafts
50-50 TIN-INDIUM	seals
GOLD	corrosion-resistant coating
SILVER	corrosion-resistant coating
TIN	seals
RHODIUM	corrosion-resistant coating
SILVER SOLDER	brazed joints
ALLOY 7	brazed joints
PERMATEX No. 2	thread sealant
KRYTOX	lubricant
SUPER-PURE TEFLON	seals
TEFLON-COPPER LAMINATE	seals
TEFLON-ALUMINUM LAMINATE	seals
COPPER-FILLED TEFLON	seals

Materials recommended for use in an OF_2 and B_2H_6 compatibility study are delineated in Table V together with probable component usage. Table VI lists candidate materials which will be used in stressed configuration, Table VII lists candidate bimetallic couple combination and Table VIII lists candidate welded material. The basis for selecting these materials was the potential use based upon initial design consideration and information supplied by JPL to TRW Systems under Contract NAS7-750, "Thermal Control of a Propulsion System." Because all preliminary designs have not been completed for a propulsion system using the liquid propellants OF_2 and B_2H_6, some materials may not have been identified. Information is especially lacking concerning the selection of a material for construction of a capillary propellant acquisition device.

TABLE V
CANDIDATE MATERIALS FOR STATIC IMMERSION TESTING

Priority	Material	Application
A	A-286 Steel	Bipropellant Valve
A	347 CRES	Bipropellant Valve
A	17-4 PH CRES (H-900 min.)	Vent Valve Fill Valve, Bleed Valve
A	1100 Al	Tank Liner, Fill Valve
A	6061 Al*	Vent Valve, Fill Valve, Bleed Valve
A	Alumina	Vent Valve, Fill Valve, Bleed Valve
A	6Al 4V Titanium*	Vent Valve, Fill Valve, Bleed Valve
A	Inconel-718	Hose, Bipropellant Valve
A	Beryllium Copper (BRUSH 190)**	Bipropellant Valve, Soft Seat
B	303 CRES	Vent Valve, Fill Valve, Bleed Valve
B	Inconel-X(X-750)	Bipropellant Valve
C	301 CRES	Bipropellant Valve
C	321 CRES	Fastener
C	Super-Pure Teflon	Alternate Design Materials
C	Teflon-Aluminum Laminate	Alternative psiga Materials
C	Monel 400	Alternate Design Material
C	316L CRES	Alternate Design Material
C	Rene 41/CMR	Alternate Design Material

*Selection depends on tank material

**Type in parentheses may be preferred

A = Materials of most interest

B = Of interest if no material rated A is suitable

C = Material of interest as possible design alternatives

TABLE VI

CANDIDATE MATERIALS FOR STATIC IMMERSION TESTING UNDER STRESS

A-286 Steel
A 1100 Al
6Al 4V Titanium
Inconel - 718
Beryllium Copper (BRUSH 190)
321 CRES
Welded 321 CRES
A 1100 Al
Inconel - 718

TABLE VII

CANDIDATE MATERIALS FOR STATIC IMMERSION TESTING AS BIMETALLIC COUPLES

Beryllium Copper Vs Inconel - 718
321 CRES Vs a 1100 Al
321 CRES Vs Inconel 714

TABLE VIII

CANDIDATE MATERIALS FOR STATIC IMMERSION TESTING AS WELDED SPECIMENS

6 Al 4V Titanium
321 CRES

4. TASK III - TEST PROGRAM

This task describes the planning of the operational procedures for conducting a detailed compatibility testing program for use with the two liquid propellants over extended exposure durations. It was recognized that the cost of testing will dictate the methods to be employed and limit the number of variables examined in the immersion tests. Variables examined include the number of materials and material combinations, unstressed and degree of stress, replication, testing durations, and post test characterization. The number of materials and material combinations to be studied were the thirty-two (32) identified in Task II as being necessary to provide essential design information (e.g., most probable design usage material and backups). To minimize testing costs, it is recommended that only one stress level should be examined. In addition, replication will be limited to triplicates. This is considered essential to ensure that failure and/or success of a material/propellant combination is repeatable and not just the result of a poorly controlled experiment or an improbable event. If the observed differences among the triplicate samples are beyond those which are expected from inherent errors of testing, confirmatory evaluation can be obtained by either waiting until samples of the same material are removed from test at a later date or one of the samples to be stored a longer period can be removed from testing. To provide meaning to compatibility information which can be utilized to predict long term exposure, it is recommended that the storage durations be limited to 0.1, 0.5 and 1 and 2 years.

The various alternative routes for a test program were assessed for conducting the tests on both 1) a technical-information-generated basis and 2) a cost basis. Details of the methodology for conducting the test program are discussed below.

4.1 TEST SPECIMEN CONFIGURATION

Static immersion of unstressed test specimens in the propellant is most commonly used to evaluate materials for contact with liquid propellants. Testing by static immersion in the propellant will not reveal how the material will behave under mechanical impact or under dynamic stress in propellant. To minimize experimental costs, it is recommended that dynamic testing modes be eliminated from consideration and that the program consist of measuring the compatibility of materials by immersion in the propellant of specimens maintained in static stressed or unstressed condition.

The most common method of evaluating specimens subjected to static immersion in propellants is to first examine the materials visually, under a microscope, and then to measure weight loss or gain for calculation of "average" corrosion rates (expressed as mils per year). This is not a very informative procedure because information is not obtained concerning the effect of OF_2 and B_2H_6 exposure has on the mechanical properties of materials. The changes in strength and ductility in the materials are of primary concern if the materials are to function properly for many system applications. For some materials, although there may be no visible corrosion on the surface, the possibility of solubility, absorption or adsorption of species from the propellants is high. For example, based on unpublished work at TRW, oxygen under some conditions can diffuse into and dissolve in the lattice of titanium causing embrittlement. Adsorbed free halogens are also known to produce stress cracking in titanium.

It is possible that corrosion will take place in a different manner and to a different extent in the vapor and liquid phases, or possibly only at the vapor-liquid interface. At the test temperature, -230°F, most common impurities in OF_2 and B_2H_6 are solids with only limited solubilities in the propellants. In some cases the impurities tend to float to the liquid interface, i.e., carbon dioxide crystals in OF_2 tend to concentrate at the interface. In the gas phase of OF_2, oxygen, if present, will be concentrated with a limited quantity dissolved in the liquid phase. Hydrogen will be concentrated in the gas phase of B_2H_6. On the basis of these considerations a test specimen should have the following characteristics:

- The surface to volume ratio should be large.
- Weight gain or loss measurement should be possible.
- An ability to measure the physical properties independently for specimens stored in vapor and liquid phases is desirable.
- Metallurgical examination should be possible for portions of the specimen exposed to the liquid and vapor phases, as well as the liquid vapor interface.

Test specimens shaped as rods(14), rectangles(15), "dogbones," and double dogbones(2), have been used in compatibility testing. A rod shaped specimen does not provide a large surface to volume ratio and is difficult to prepare and stress in a minimum volume storage container. Therefore, the rod specimen is not recommended for use in this plan. The rectangle shaped specimen meets all the selection criteria listed above, but when submitted to the tensile testing, a break often occurs where the specimen is gripped in the jaws of the testing apparatus.

Although the rectangle specimen could be used, the double dogbone specimen shown in Figure 1 is recommended for the reasons discussed below. Dogbone specimens offer all the advantages of the rectangle specimen except the dogbone is more difficult to fabricate, but is a much more reliable specimen than the rectangle for tensile testing. Except for stressed specimens (see Section 4.2 for explanation) which must have a rectangular shape in order to use the stressing apparatus selected, the double dogbone specimen incorporates the desired characteristics of a test specimen. If separate tensile testing is not required for the portions of the test specimens in the liquid and gas phases of the propellants, the single dogbone specimen can be used as an alternate to the recommended double dogbone.

Metallic test specimens will be prepared by cutting with a band saw the gauge section transversely to the rolling direction; non-metallic specimens will be cut from 0.125-inch thick molded sheets. Welded specimens will be prepared by first welding the sheet stock and then sawing the dogbones from the sheet stock so that the joint traverses the gauge section. All cut edges will be finish-machined. Sheet stock thickness will be 0.030-inch, in order to have a large surface-to-mass ratio and hence, maximize the sensitivity to corrosion.

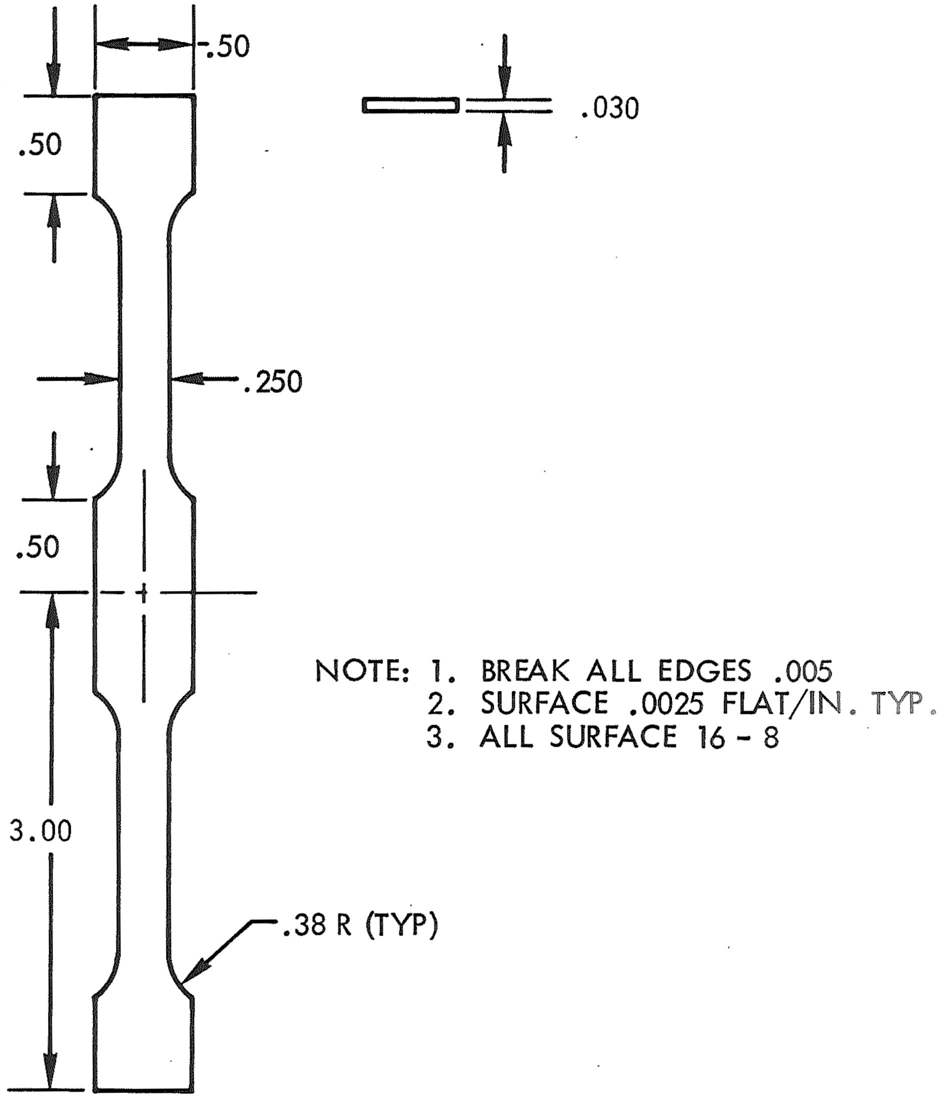


Figure 1. Double Dogbone Test Specimen

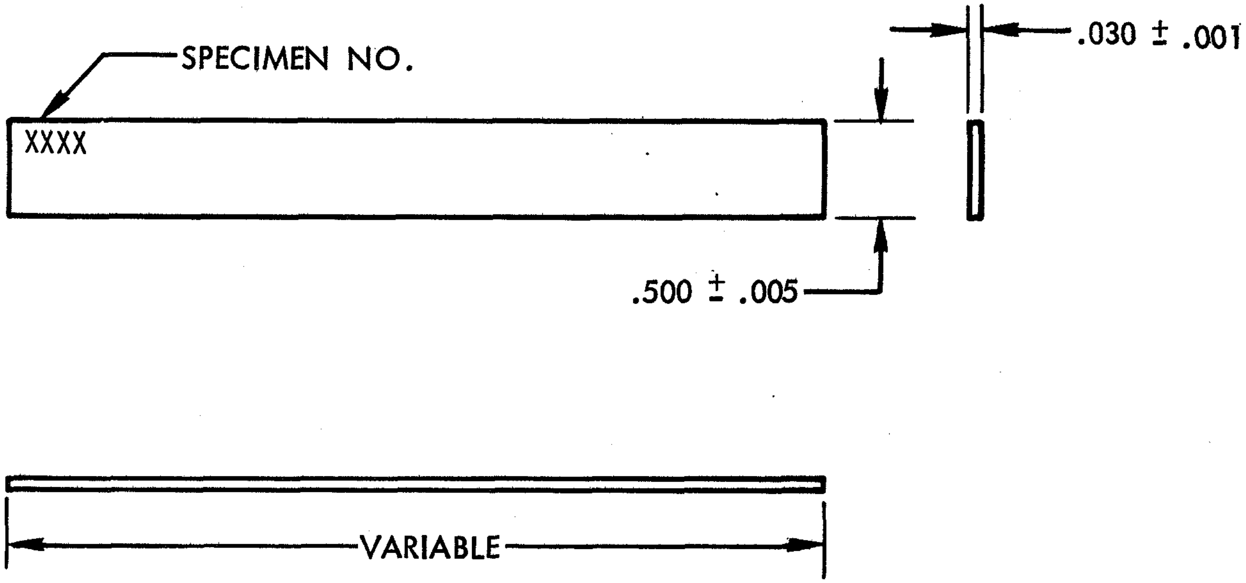
The dogbone or double dogbone specimen cannot be conveniently used in the stressed condition for the reasons given in Section 4.2. The rectangular shaped sample shown in Figure 2 was selected even though this shaped specimen creates a problem in tensile testing, but the advantage of being able to submit the specimen to a desired stress level before static immersion testing, justifies the use of the rectangular specimen.

Post test analysis of the double dogbone specimen will include the following:

- Visual and microscope examination.
- Comparison of weight after propellant exposure to initial weight.
- Sectioning specimen into three parts, 1) dogbone exposed to liquid phase of propellant, 2) small area between the two dogbones exposed to the propellant vapor interface, and 3) dogbone exposed to gas phase of propellant. If a single dogbone specimen is used in place of the recommended double dogbone, separate specimens can be exposed to the vapor and liquid phases of the propellant.
- Tensile testing of "dog-bones" in accordance with ASTM Method E8-57T to obtain stress-strain plots, yield strength, ultimate tensile strength and percent total elongation. The stress-strain relationship provides such properties as elastic modulus, elastic limit, yield point and toughness. The percent total elongation is a measure of the ductility. By determining and comparing the results obtained from tensile tests on the propellant exposed and unexposed material, the effect and severity of the effect on the material by the propellant exposure can be assessed.
- If corrosion has been detected by visual and microscope inspection or by tensile testing, detailed metallographic examination, including examination by the scanning electron microscope, should be performed on the corroded material.
- Residues found on the test specimens or left in the specimen capsules after removal of the specimens should be identified by X-ray diffraction and/or other suitable analytical method to permit identification of the corrosion mechanism.

4.2 TEST SPECIMEN COMBINATIONS

The unstressed specimens, both metallic and non-metallic and specimens with mechanical joints, such as welds and brazed lap joints, present no problem in positioning in the proposed test container. Dielectric couples between dissimilar metals will be achieved by placing two dissimilar metal



NOTE: 1. BREAK ALL EDGES .005
2. SURFACE .0025 FLAT/IN. TYP.
3. ALL SURFACE 16 - 8

Figure 2. Stressed Test Specimen

specimens together and holding them together by means of glass "C" clamps attached to both ends. Glass "C" clamps have sufficient spring force to hold the specimens snugly together.

Stressed specimens present a problem because either the apparatus for stressing the sample must be fabricated from glass or the same material as the specimen, or a dielectric couple between dissimilar materials must be accepted. To avoid dielectric couples between dissimilar materials stressing apparatus manufacture is recommended from the identical materials as the specimens, and glass has been selected for constructing the specimen container (see Section 4.3). With this limitation imposed, the bent-beam specimen becomes attractive. Although bent-beam specimens are relatively simple to use, their stress analysis is quite complex. Haaijer and Loginow(16) established a mathematical analysis used to calculate appropriate specimen dimensions to obtain a desired stress and presented results of tests to verify the mathematical analysis.

Stressing a bent-beam specimen is simple, as shown schematically in Figure 3. Ends of the specimen are forced toward each other so that their original distance L (length of unstressed specimen) is reduced to distance H of the loading jig supports. The specimen is then placed in the jig, and the stressing operation is complete. A summary of the Haaijer and Loginow analysis is presented below:

To determine the strain,

$$\varepsilon = \frac{\sigma}{E} \tag{2}$$

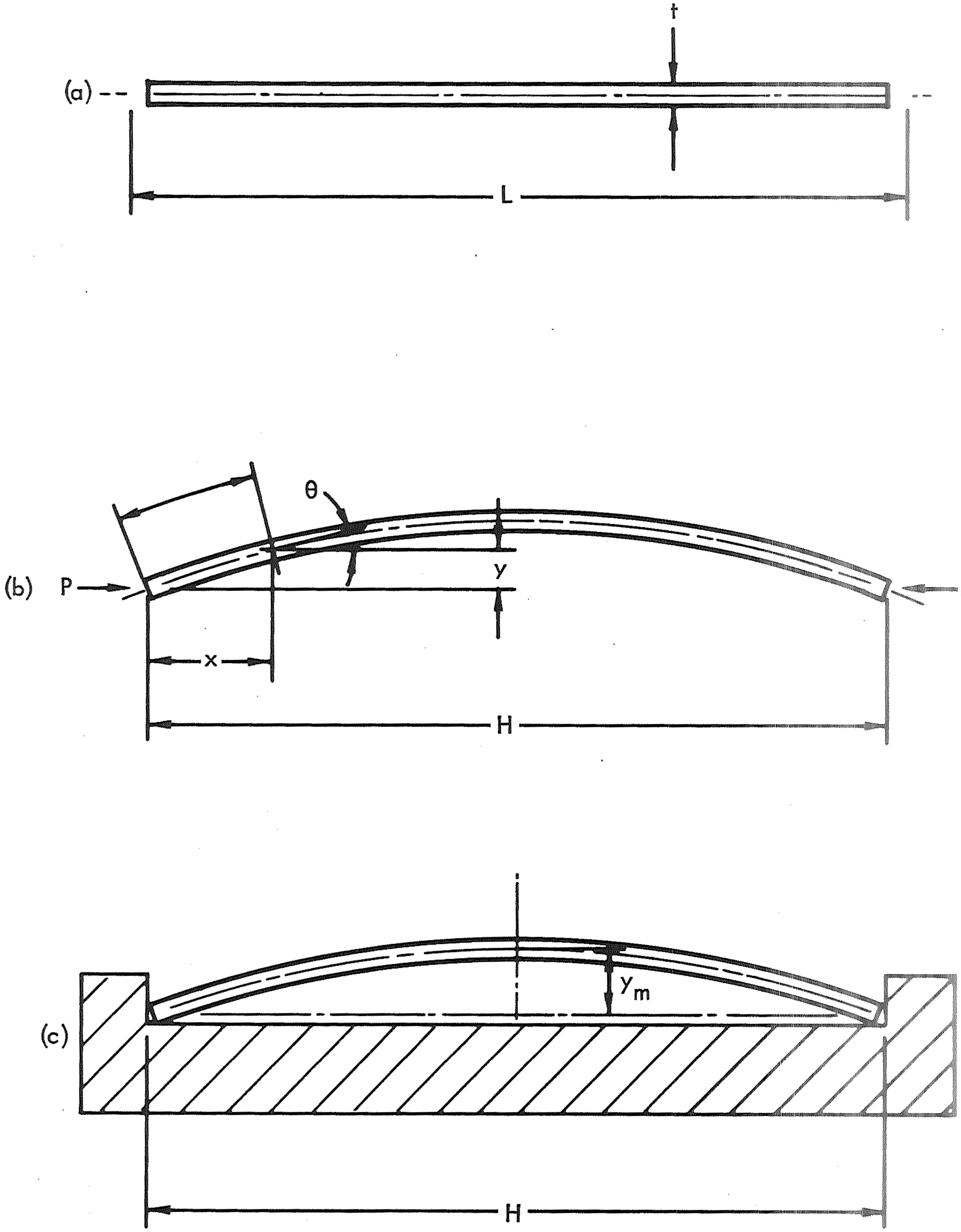


Figure 3. Stressing of Bent-Beam Stress Corrosion Specimen

where

ε = strain

σ = required stress

E = modulus of elasticity

To determine the length (L) of a specimen of known thickness (t) to be stressed in a specimen holder with the distance (H) between the supports to produce the required strain (ε) necessitates the solution of Equations 3 to 5.

$$\varepsilon = \frac{\sigma}{E} = 4[2E(k)-\kappa(k)][\frac{k}{2} - \frac{2E(k)-\kappa(k)}{12} (\frac{t}{H})]\frac{t}{H} \quad (3)$$

$$\frac{L-H}{H} = \frac{2[\kappa(k) - E(k)]}{2E(k) - \kappa(k)} \quad (4)$$

$$\frac{Ym}{H} = \frac{k}{2E(k) - \kappa(k)} \quad (5)$$

where

$$E(k) = \int_0^{\pi/2} \sqrt{1-K^2\sin^2 udu}$$

$$\kappa(k) = \int_0^{\pi/2} \frac{du}{\sqrt{1-k^2\sin^2 u}}$$

k = $\sin \theta_0/2$

Ym = maximum specimen deflection

θ_0 = maximum slope of specimen (at X=0)

u = dummy variable

Haaijer and Loginow expressed Equations 3 and 4 in parametric form and presented the relationship graphically to simplify calculations. Their studies indicated that satisfactory stressed specimen compatibility study could be achieved, using a holder with a span of 4.0-inch for specimens, 0.5-inch wide and 0.03-inch thick.

Arbitrarily, for this compatibility plan, a specimen as shown in Figure 2 and the stressing apparatus shown in Figure 3 will be utilized. The length of specimens for each material will be calculated using the method of Haaijer and Loginow for a holder span of 4.0-inch. The stress value will be limited to the stress of the material at 67-percent of its yield point at 77°F.

4.3 TEST CONTAINER CONFIGURATION

Because the objective of this program is to establish a plan for obtaining long term compatibility data for inert materials in contact with liquid OF_2 and B_2H_6 at -230°F, the plan should provide a means for storage of propellants and inert materials so that interactions between propellants and containers will not invalidate the results of compatibility studies.

Obviously, an ideal container for test specimens cannot be identified. That is, a container that does not introduce any variables into the compatibility test between the propellant and the test specimen. If the best possible test container configuration and material of construction is to be selected, consideration must be given to the following:

- Characterization and possible reactions for both of the propellants with materials to be tested.
- Pressure in specimen containers
- Monitoring of reactions taking place in the specimen containers.

B_2H_6 is manufactured commercially by the reduction of boron halides (BCl_3 or BF_3) or trimethyl borate, $B(OCH_3)_3$. The reduction is accomplished with metal hydrides, either sodium hydride, NaH, or lithium hydrides, LiH. Intermediate complex hydrides are also formed during the hydride synthesis, i.e., sodium borohydride, $NaBH_4$, or lithium borohydride, $LiBH_4$. The solvents used are hydrocarbon ethers; diethyl either, dimethyl eiher of ehtylene glycol, $CH_3OCH_2CH_2OCH_3$, or dimethyl ether of diethylene glycol, $CH_3O(CH_2CH_2O)_2CH_3$.

The reactants, products and solvents, except for boron halides are less volatile than B_2H_6 and can easily be separated from B_2H_6 by simple fractionation. Boron halides react with excess metal hydrides used in the synthesis and are completely removed. The ethers are sometimes reduced to saturated hydrocarbons, methane and ethane, and are trace contaminants in B_2H_6. Callery Chemical Corporation, the major producer of B_2H_6, presently uses the halide method for producing small batches of B_2H_6 (approximately 200 pounds per batch)(17). If demand for B_2H_6 changes, B_2H_6 may be manufactured by reduction of trimethyl borate. Purity of presently supplied B_2H_6 is indicated by Callery Chemical Corporation to be at least 96% with the major impurity being H_2 and traces of hydrocarbons. If allowed to reach near ambient temperatures, B_2H_6 decomposes slowly to produce hydrogen and higher molecular weight and less volatile boron hydrides. To prevent the formation of hydrogen and higher molecular weight pyrolysis products, B_2H_6, after preparation, is stored in mild steel tanks below -20°C. At -20°C about 0.2% B_2H_6 decomposes in one year, but at -33°C the pressure rise in a mild steel tank was approximately 0.1 torr after 100 days(18).

By using vacuum transfer techniques recommended in this plan, the quantities of hydrogen and higher boranes introduced into the specimen containers should be negligible. At the compatibility test temperature of -230°F (-146°C) the pyrolysis reactions should also be negligible, as indicated by the plot of data from (18) in Figure 4 which if extrapolated to -230°F (-146°C) would indicate a pressure rise in a storage tank of approximately 10^{-11} atmosphere after 100 days storage. Therefore, on the basis of the pyrolysis reactions, and no other reactions produce a pressure rise, the pressure rise in specimen containers can be ignored.

The reaction of metal oxides with B_2H_6, a strong reducing agent, has been observed.(13) In this study, 4g of finely divided oxides of stainless steel (produced by placing 316 stainless steel power under a propane-oxygen flame) were placed in a 10 ml 316-stainless steel cylinder along with 3 ml of liquid B_2H_6. After storage for thirty days at -78°C and -20°C, no rise in pressure could be detected in the cylinders with a gauge sensitive to $\pm$0.5 psia, even though the reaction should produce hydrogen as shown in Equation 6 for a metal oxide, MO or in Equation 7 for a metal hydroxide.

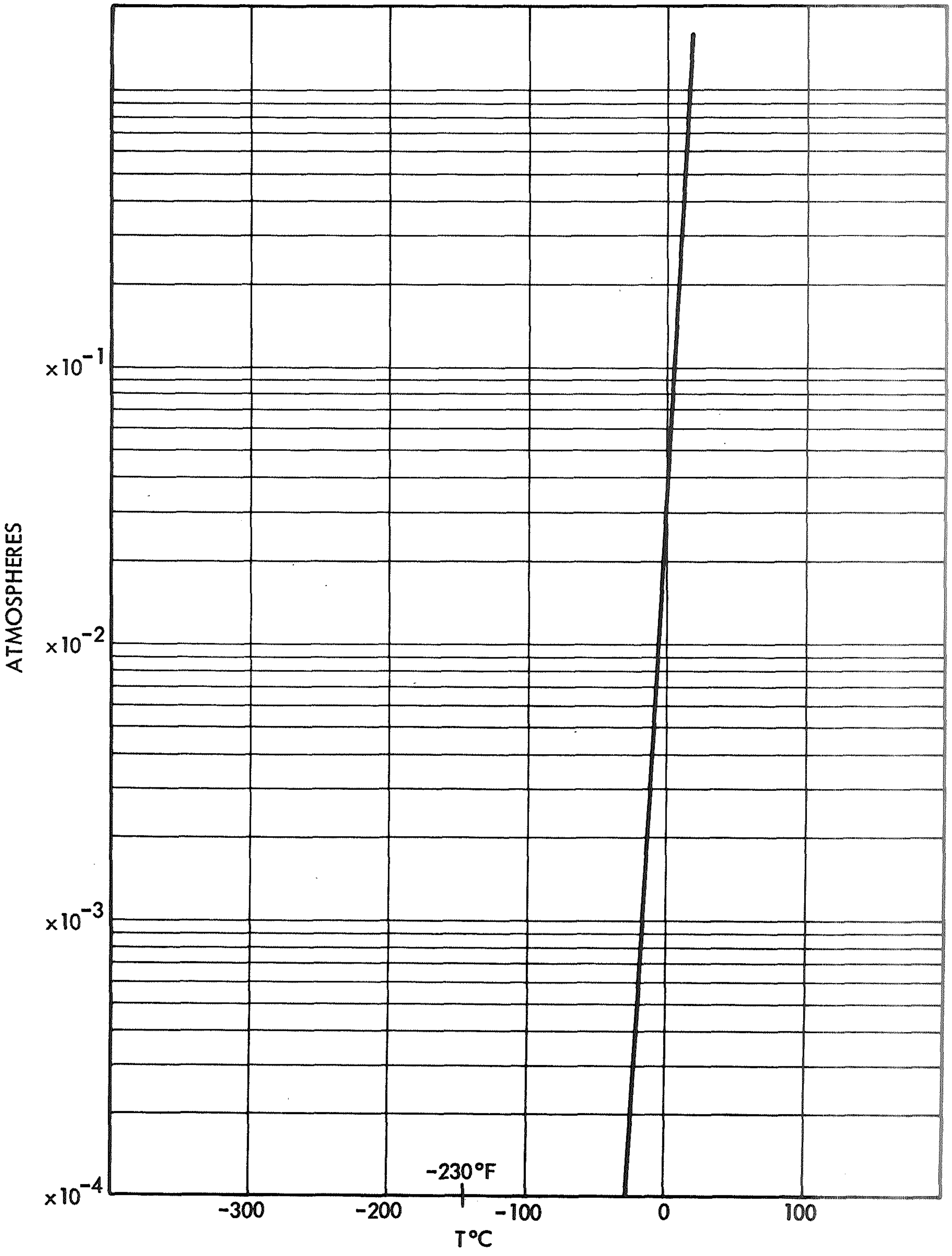


Figure 4. B_2H_6 Decomposition in Storage Tanks after 100 Days

$$3MO + B_2H_6 \rightarrow B_2O_3 + 3H_2 + 3M \qquad (6)$$

$$3M(OH)_2 + B_2H_6 \rightarrow 3M + 2B(OH)_3 + 3H_2 \qquad (7)$$

OF_2 is not commercially manufactured at present, but is supplied by Allied Chemical Corporation from a quantity on hand. Liquid OF_2 is obtained by condensing the gas from the manufacturer's supply tank. The normal impurities are CO_2, HF and SiF_4 which have a limited solubility in liquid OF_2 at -230°F and are solids at -230°F. Another impurity found in OF_2 is CF_4 which is not a solid at -230°F and is soluble at least to a limited extent, in liquid OF_2.

OF_2 can react with metal, M, or metal oxide, MO, surfaces according to Equations 8 and 9. If present as an impurity,HF can react with a metal surface according to Equation 10 and then be reformed according to Equation 11.

$$2OF_2 + 2M \rightarrow 2MF_2 + O_2 \qquad (8)$$

$$2F_2 + MO \rightarrow MF_2 + O_2 \qquad (9)$$

$$2HF + M \rightarrow MF_2 + H_2 \qquad (10)$$

$$2H_2 + OF_2 \rightarrow 2HF + H_2O \qquad (11)$$

If water is present on metal surfaces, HF could be formed according to Equation 12:

$$H_2O + OF_2 \rightarrow 2HF + O_2 \qquad (12)$$

The results of a critical survey performed by Muraca, et al,(19) indicate that fluoride films form almost instantly on most metals when brought into contact with fluorine or any of the fluorine oxidizer such as OF_2. Also, they appear to have the same structure, adherence, flexibility, and corrosion-inhibiting characteristics, regardless of the way in which the fluorine or fluorine oxidant was brought into contact with the metal. Initially, fluorine oxidizers react with clean metal surfaces by a rapid reaction which gradually tapers off to some nearly constant rate approaching zero. On the basis of this information, one can conclude that any large increase in pressure in a compatibility test container will take place initially upon contact of metal surfaces with the OF_2. Dawson, et al,(20) selected metals for compatibility studies with OF_2, steel alloys, aluminum alloys, nickel alloys, titanium alloys, and copper. The specimens (1/4-inch x 1-3/4-inch) were thoroughly cleaned and then sealed in glass ampoules (fitted with metal Bourdon gauges). A pressure of 0.5 atm OF_2 was used for gas-phase tests at room temperature and 1 ml liquid OF_2 for liquid phase tests at -196°C. No pressure changes were detected at either temperature after a two-week exposure. At the termination of the tests, most of the specimens were found to be coated with what was assumed to be a fluoride film; pitting was observed on some specimens stored in the liquid phase.

Even though the discussion above indicates that the possibility is negligible of measurable increase in pressure in compatibility specimen containers, various methods for measuring the pressure in the containers were considered for possible incorporation into the compatibility plan. Pressure in the test containers can possibly be measured by 1) Bourdon gauges attached to the container, 2) pressure transducer attached to the container, 3) "spoon" gauges, or 4) strain gauges mounted on the outer walls of the container. The first two methods, Bourdon gauges and pressure transducers, can be considered together. These two types of pressure measuring devices are usually attached to a container by means of fittings or welds and they are constructed from a limited variety of materials. If dissimilar materials are to be avoided in order that the results of compatibility tests are not invalidated, these two techniques are not applicable to pressure measurement during the compatibility studies. "Spoon" gauges, which have been used in compatibility studies without introducing new variables, can be considered for use in this plan, but will be costly to use. The "spoon" gauge is a thin walled continuation of the test specimen container necked down to a small tube bent into a "U" shape. As the pressure changes, the arm of the "U" is deflected. This deflection can be measured and the deflection related to the pressure in the specimen container. Not only is cost of fabrication and calibration high, but the set-up of adequate instrumentation to measure deflections in a remote manner at -230°F is very expensive. Both electrical and optical methods have been used for ambient temperature tests, but even at ambient temperature the cost is great. Therefore, from a cost consideration, the "spoon" gauge is not recommended. Strain gauges cannot be utilized on the containers because no method is known for attaching the strain gauges in a reliable manner having effective adhesion at temperatures as low as -230°F.

On the basis of this discussion, it is recommended not to provide pressure monitoring during tests. In addition, on the basis of the discussion presented above concerning the propellant composition and reactions with the materials being tested and the compatibility experiments for OF_2 by Dawson, et al,(20) in glass ampoules, there appears to be a limited probability that the pressure in the test specimen containers will be appreciable.

From the discussion presented on reactions that can take place between the propellants and the materials being tested, it can be concluded that most reaction products are insoluble solids in the propellants at -230°F, exceptions being H_2 in B_2H_6, O_2 and SiF_4 (if glass and HF are present) in OF_2. Because two phases will be present, spectrophotometric techniques for following the course of reaction in specimen containers can be eliminated. TRW developed a method for measuring the formation of precipitates during storage.(13) A light beam from a helium-neon laser was passed through the liquid and the scattered light measured at right angles to the incident beam. The laser viewing assembly was constructed inside a large clear Dewar flask to serve as a cryostat. It contained a laser viewing tube prepared from 1/2-inch O.D. heavy wall Pyrex tubing, having optical flat surface at 90° to each other, one serving as the inlet from the laser source and the other an outlet to the detector for measuring the scattered light. Though the Tyndall effect can be measured in the liquid propellant contained in specimen compatibility containers, it is not recommended that the large number of compatibility tests in this plan be instrumented for the Tyndall effect.

The technique recommended in Section 4.4, "Test Assembly and Installation," cannot be utilized in a safe manner with light pipes to each compatibility test capsule. The requirement that optical flats be used on the compatibility test capsules, will result in capsules that are more subject to pressure failure than the cylindrical capsules recommended. With the light pipes in position, the positioning of metal tubes to prevent one pressure ruptured capsule from breaking an adjacent capsule, cannot be easily positioned. It is recommended that consideration be given using the Tyndall effect as part of an investigation independent of this plan, to study the mechanisms of corrosion for materials that are corroded by propellant when the compatibility test plan is implemented.

On the basis of the discussion presented in this section and the fact that OF_2 (vapor pressure ∿1 atm at -230°F) and B_2H_6 (vapor pressure of ∿0.02 atm at -230°F) can easily be contained in glass containers, glass compatibility test capsules are recommended. An alternative container for metallic specimens, is the use of containers fabricated from metal stock having the same composition as the test specimen. These metal containers requiring 1 to 2 hours to manufacture are more costly than the glass containers that require only 20 minutes to prepare. An additional disadvantage of the metal containers is that dissimilar materials are introduced in order to effect closure; valves, welds, or Teflon tape in threads. Glass containers offer the advantage that they are easy to prepare and are inert to the propellants OF_2 and B_2H_6 at -230°F, except that in the case of OF_2, any hydrogen fluoride impurity will react with the glass to form SiF_4 and frozen water. Post reaction of water "snow" with OF_2 would result in oxygen gas and regeneration of HF. Consequently, it is recommended to remove any HF fluoride impurities from the OF_2 by scrubbing with sodium fluoride immediately prior to filling the test capsule with propellant.

For the metallic specimens there is no ready means for generation of hydrogen fluoride during the test, consequently, it is not expected that significant quantities of water could form. For non-metallic specimens hydrogen fluoride could form however, in this case, the effect of water on specimen corrosion is not nearly as pronounced; the major concern would be in weakening the glass container strength. It must be remembered that hydrogen fluoride only has a solubility of <-0.02-percent in oxygen difluoride and any reaction with silica is significantly retarded at -230°F. The measurement of the generated silicon tetrafluoride and oxygen provides an excellent technique for post test determination of the amount of any hydrogen fluoride that might be formed during the test.

The glass container approach discussed above appears to be a viable alternative to the high cost of metal test containers. The only concern that one may have is that use of sodium fluoride scrubbed oxygen difluoride is not the same as "propellant grade" oxygen difluoride. However, in practice, all oxygen difluoride is scrubbed during preparation and only the 0.02-percent soluble HF that may be introduced during propellant handling could cause uncontrolled effects.

Consequently, it is planned to conduct a few selected tests with "propellant grade" oxygen difluoride to determine the magnitude of any HF impurity-cause affects. Irrespective of any SiO_2-HF initiated reaction, the HF itself could initiate long term incompatibility. If this is verified, a routine procedure of scrubbing the oxygen difluoride as part of the overall propellant loading operation could be readily implemented to assure long term compatibility.

The recommended glass compatibility test capsule is illustrated in Figure 5. For reliability the test containers are designed by use of the nomogram in Figure 6(21) to withstand 400 psig internal pressure at 77°F and will be tested at 200 psig internal pressure before propellant is charged into the test container. Prior to placing the test specimen in the bottom of the container, both the bottom and reducer will be annealed. After the test specimen has been placed in the container, the bottom and the glass reducer will be fused together.

4.4 TEST ASSEMBLY AND INSTALLATION

The test specimen containers can be loaded with propellant by two methods; 1) by adding liquid propellant directly into the container, or, 2) by vacuum transferring the propellant into the container. Because vacuum transferring of measured previously condensed liquid propellant is easily accomplished in a safe manner, the vacuum transferring technique will be used. This technique involves the steps as follows:

- The test container shown in Figure 5 is connected to a vacuum manifold by means of a Swagelok fitting with Teflon ferrules.
- The test container containing the specimen is evacuated.

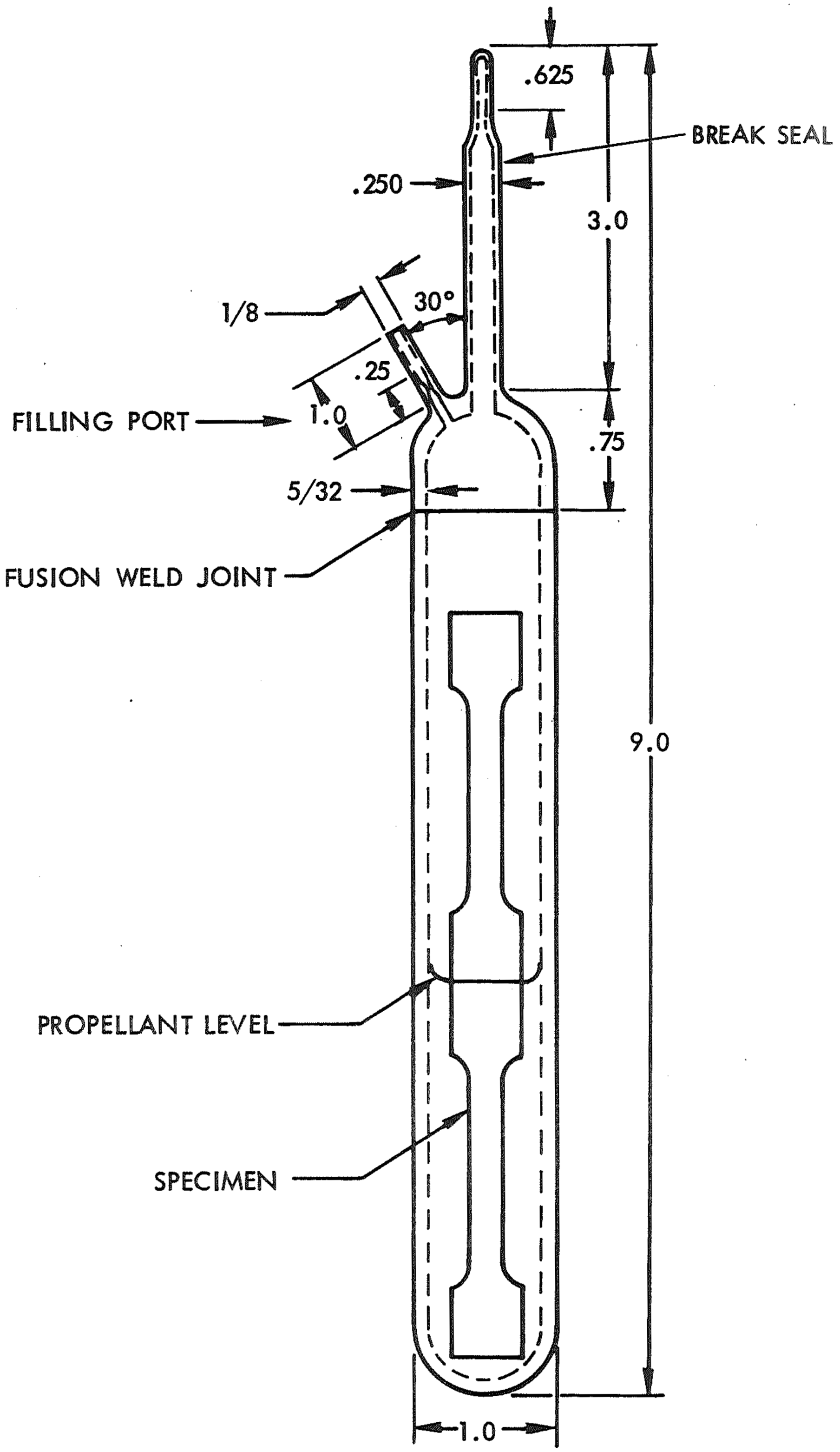


Figure 5. Sealed Compatibility Test Capsule

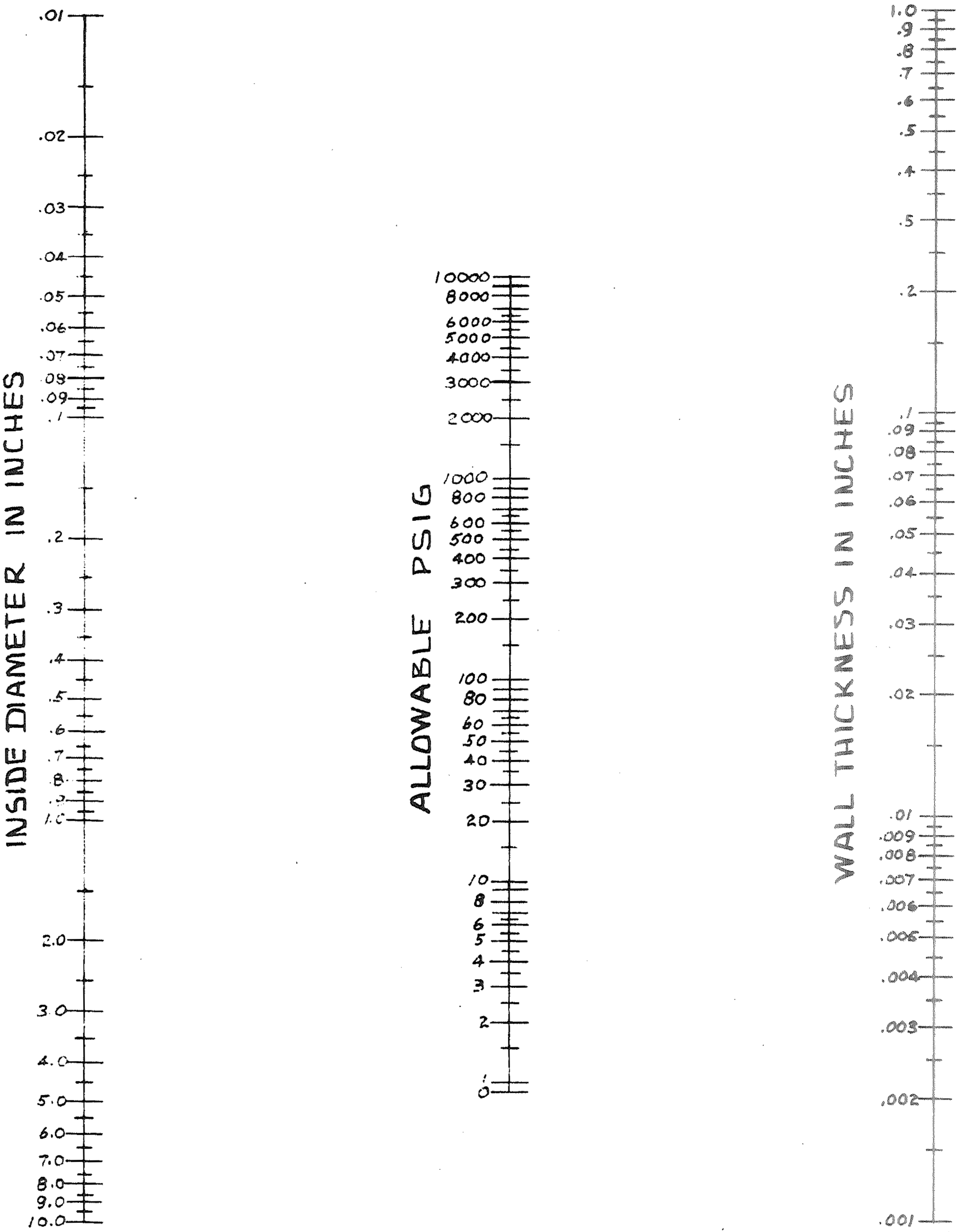


Figure 6. Nomogram of Allowable Pressures for Borosilicate Glass Tubes

- Propellant (approximately 10 ml) is condensed at liquid nitrogen temperature into a calibrated tube fabricated from quartz. Before condensing of OF_2, the propellant is passed through a sodium fluoride scrubber to remove traces of HF. Ten (10) ml of propellant is sufficient to cover one-half the unstressed test specimen (one dog-bone), when two glass rods (0.3-inch in diameter) are added to displace some propellant.

- The test container is cooled to liquid nitrogen temperature, the propellant in the quartz tube allowed to warm, and valves between the test container and the quartz tube are opened, allowing the propellant to distill into the sample container.

- The sample container is then sealed and maintained at liquid nitrogen temperature until being placed into the temperature conditioning chamber.

After the test specimen and propellant has been loaded into a sealed test container, an economical and reliable method must be employed for storing the test containers up to two years at temperatures of -230°F ±30°F. The method selected for temperature control will have a far reaching effect on the overall cost of any immersion tests performed. Mechanical refrigeration cannot normally maintain storage cabinets at -230°F. Methods that can maintain test specimens at -230°F include:

- Maintenance of dry ice at 0.14 torr pressure.

- Tetrafluoromethane (Freon 14) bath with liquid nitrogen cooling coils.

- Mechanically controlled cooling with liquid nitrogen refrigerant.

Dry ice maintained at 0.14 torr in a cryogen flask is a convenient and economical means of maintaining a storage temperature of -230°F. However, dry ice must be recharged into the cryogen flask every two weeks. Because a fatal accident(22) occurred during the addition of dry ice to the Dewar flask containing a OF_2 compatibility experiment, the use of this method for maintaining a temperature of -230°F has been eliminated from further consideration.

A Freon-14 bath(23) has been successfully used to maintain temperatures between -180°F and -284°F. Basically, the temperature control system consists of a Dewar flask that serves as a liquid bath of Freon-14 in which cooling coils circulating liquid nitrogen are inserted. In operation, a pressure controller compares the Freon-14 tank ullage pressure with the desired set point pressure (4.4 psia for -230°F), and opens or closes the liquid nitrogen supply valve to the refrigerating coil in the Freon-14 tank as required to maintain the set vapor pressure. At -230°F, the saturation temperature change is 5.8°F per pound vapor change, allowing a probable temperature control accuracy of ±3°F.

The use of a secondary refrigerant system rather than direct liquid nitrogen cooling, offers several advantages as indicated below:

- It provides a more accurate temperature control than is usually possible with liquid nitrogen expansion.
- It provides a liquid transfer medium at all times.
- It provides a refrigeration reservoir in event of loss of liquid nitrogen supply.

The use of the secondary refrigerant system has the disadvantages listed below:

- It requires that the Freon-14 bath be maintained at a 4.4 psia pressure which does not allow the use of low cost commercially available Dewars.
- The use of a cooling coil for heat transfer will result in some loss in liquid nitrogen cooling efficiency.

The secondary refrigerant system using the Freon-14 bath is obviously more expensive than a direct liquid nitrogen cooling system. Because only a ±15°F control of the temperature is required and a ±10°F control is easily obtained at less cost, the secondary refrigerant system has been eliminated from the plan.

A simple temperature control chamber has been used in OF_2 compatibility testing.(13) This chamber utilized liquid nitrogen expansion as the refrigerant. Basically, it consisted of a temperature probe mounted in the refrigerated chamber and a temperature control box connected directly to a liquid nitrogen supply line. When the temperature of the chamber changes from the desired temperature, the signal generated in the probe operates a solenoid valve. This in turn admits nitrogen into the chamber through a spray heater, and brings the temperature back to the desired point. This type of temperature control chamber, capable of controlling to ±6°F, is commercially available for about $3,800 from Bemco Inc., Pacoima, California. The estimated consumption for temperature control of liquid nitrogen is about five pounds per day which is $20 per month for a conditioning box if the liquid nitrogen is obtained from a bulk storage tank. Since 12 conditioning chambers are required by the plan and boil-off losses are considerable, the cost of liquid nitrogen would be approximately $400 per month.

Fortunately, a low cost ($375) commercially available cryogenic flask, manufactured by Minnesota Valley Engineering Company is ideally designed for storing the test specimen containers previously described and has a considerably lower liquid nitrogen requirement. The Model A-1500 Liquid Nitrogen CRYO-FLASK was designed to maintain biological samples at low temperatures in glass specimen containers. The specimen containers are placed in nine specimen canisters, 2-13/16-inch inside diameter by 10-5/8-inch high. Each canister can hold four specimen containers which allows 36 specimens to be stored in each flask. The canisters have handles that fit over the lip of the flask for easy removal of the canisters. The estimated liquid nitrogen consumption is one pound per day or about 1/6 of that required by the Bemco chambers. The temperature control will be maintained to ±10°F in the same manner as that discussed for the liquid nitrogen cooled chamber. A Model 123-000 cryogenic temperature controller ($285) manufactured by Cryogenics Controls Company will be used to energize a liquid nitrogen solenoid valve when the temperature rises above that set on the controller. Because the liquid nitrogen cooled CRYO-FLASK can maintain specimens at the desired temperature for less than 1/3 the cost of the Bemco Chamber and considerably less than the Freon-14 bath, the CRYO-FLASK has been selected as the temperature control chamber.

4.5 TRANSPORTATION OF SPECIMENS AND PROPELLANTS

Two approaches were considered for transportation of test specimens and propellant. One system consists of enclosing the test specimens in their containers in a clean room, capping the specimen container, and then transporting the specimen container to the test facility where it is loaded with propellant to initiate the tests. Alternatively, the propellants are transferred into the test specimen containers at the point of specimen enclosure and then the propellant-filled containers are transported to the test facility.

Because glass has been selected for construction of the specimen containers, safety considerations make it undesirable to transport propellant loaded specimen containers a long distance to a test site. Consequently, the recommended procedure consists of enclosing specimens in their containers in a clean room many miles from the test site. At a test site designed for propellant handling, the propellant will be transferred into the test specimen containers, the containers sealed while in liquid nitrogen, placed in storage canisters, and then the propellant and specimen loaded containers transported short distances on carts. While being transported the specimen containers must be submerged in liquid nitrogen. After the canisters are placed in the controlled temperature flasks, the specimens will then be allowed to warm to the storage temperature of -230°F.

Safe removal of the propellant loaded specimen containers will be accomplished by lowering the temperature conditioning chamber temperature to -320°F with liquid nitrogen, removing the canisters, and quickly placing the canisters in liquid nitrogen filled Dewars. The canisters will be transported on carts to the propellant handling facility for removal of propellant. Care must be exercised at this time because the pressure in the specimen containers is unknown, but the pressure is less after cooling to -320°F than it was while the specimens were stored in the temperature conditioning flask.

The transporting of test specimens, non-volatile residue formed during storage, and propellant aliquots for laboratory analysis creates special handling problems. It is obvious for safety reasons, that the propellant must be removed from the specimen container before being transported over open access roads.

After the specimen container is attached to a manifold and opened, the pressure in a known volume will be measured to determine if non-condensable gases are present. If non-condensable gases are present, a sample of these gases will be taken by means of an evacuated glass sample container. The low pressure in this chamber will not present a transportation problem. The liquid propellant will then be removed by vacuum transfer after the break seal on the specimen container is opened. The entire volume of propellant is condensed in a quartz graduated flask and a 0.5-ml to 1.0-ml liquid aliquot transferred by helium pressure into a high pressure sample vessel. This sample vessel is then transported in dry ice to a distant laboratory. After the propellant is removed, the sealed specimen container containing the specimen can be transported by conventional means to a distant laboratory.

An alternate procedure, though not recommended because it does not provide a completely representative sample, is to expand the entire propellant sample into a large volume, and then remove an aliquot under low pressure. The transporting of liquid B_2H_6 samples is possible under ICC Task No. 19, Department of Transportation Regulation MIL-C-43063B, and OF_2 can be transported under Tariff No. 15-ICC7 (with a white label), "Regulations for Transportation of Explosives and Other Dangerous Articles."

4.6 TEST INITIATION AND TERMINATION CRITERIA

With cost considerations in mind, the initiation of all immersion tests will not be started at the same time. The storage periods of 0.1, 0.5, 1.0 and 2.0 years will be staged so that only the specimens for two storage times will be in progress at one time. The 0.1, and 2.0 year storage periods will be initiated at the beginning of the study. After the 0.1 year storage period has terminated, the 0.5 year storage period will be initiated thus permitting the re-use of B_2H_6 and OF_2 constant temperature storage flasks. In the event that results obtained from the specimens stored 0.1 year indicate for particular material(s) the formation of significant quantities of compounds that have an appreciable vapor pressure at -230°F, the questionable materials can be removed from the longer term exposure.

The possibility that the tests must be terminated because of equipment failure has been virtually eliminated by proper planning. Redundant temperature control is planned. The primary controller will be set at -230°F to energize a normally closed solenoid valve, which will control the introduction of liquid nitrogen refrigerant from a large storage tank into the constant temperature storage flask. The backup controller will be set at -180°F to energize in the closed position a normally open solenoid valve that is connected to a 110-liter liquid nitrogen supply tank. In the event of a power failure, the backup controller will not control and the cryogenic storage flask will be flooded with liquid nitrogen. After all equipment is placed in satisfactory service, the storage tests can be reinitiated. The cryogenic flask can be warmed to -230°F by discharging ambient temperature nitrogen into the cryogenic flask. Using the redundant controllers, the cost of elaborate and expensive alarm systems and methods for aborting the tests are eliminated.

Methods for terminating tests at the completion of a storage period were carefully considered because the method selected will affect costs and safety. The specimen containers must be opened and propellant removed at the storage location (in the cryogenic flask) or at a nearby location. If the storage containers are to be opened while in the cryogenic flask, expensive handling equipment and numerous valves are required. However, opening the sample containers and removing the propellant while the containers are attached to a general purpose manifold, reduces the equipment cost.

A low cost method was decided upon for termination of tests which consisted of the following steps:

- Cooling the storage flask to liquid nitrogen temperature by means of the primary controller.
- Removal of one canister (four specimen containers) and placing the canister in a liquid nitrogen filled Dewar that is behind a shield on a cart used to transport the canister to the general purpose manifold for opening.

5. TASK IV - TEST FACILITY REQUIREMENTS

Detailed requirements for the test facility are given in the following paragraphs. Included are layouts of the facility and engineering information of necessary equipment in sufficient detail to permit preparation of plans by an architectural and engineering organization selected by JPL. The specific steps required to meet the requirements of the test program are identified on the flow charts shown in Figures 7-11. For convenience, each step is numbered and the facilities required to accomplish the step are described unless the facilities are common to most aerospace laboratories. That is, machine shops, cleaning facilities and normal instrumentation are not described.

Detailed procedures for performing the various operations, a list of equipment and a test plan are given in appendices to this report.

5.1 SPECIMEN PREPARATION AND ENCAPSULATION

The preparation, cleaning and packing of metallic specimens (Steps 1-12) are performed in facilities common to most aerospace laboratories. Each metallic specimen will be fabricated to the specified dimensions and tolerances shown in Figures 1 and 2. The preparation, cleaning and packaging of non-metallic specimens (Steps 13-19) can also be accomplished without special facilities.

Glass capsules and reducers can be manufactured according to the specified dimensions and tolerances shown in Figure 5 (Steps 20 and 21), by the use of an ordinary glass-blowers lathe. The capsule design permits the use of the opening device described in Section 5.4. The capsules and reducers are then annealed (Step 22) in a furnace that will be found in most well-equipped glass-blower shops. The furnace must be capable of heating the glass parts to 575°C and holding the glass parts to 575°C and maintaining this temperature for one hour. The furnace can be cooled at a cooling rate normal to the furnace. Additional unusual facilities are not

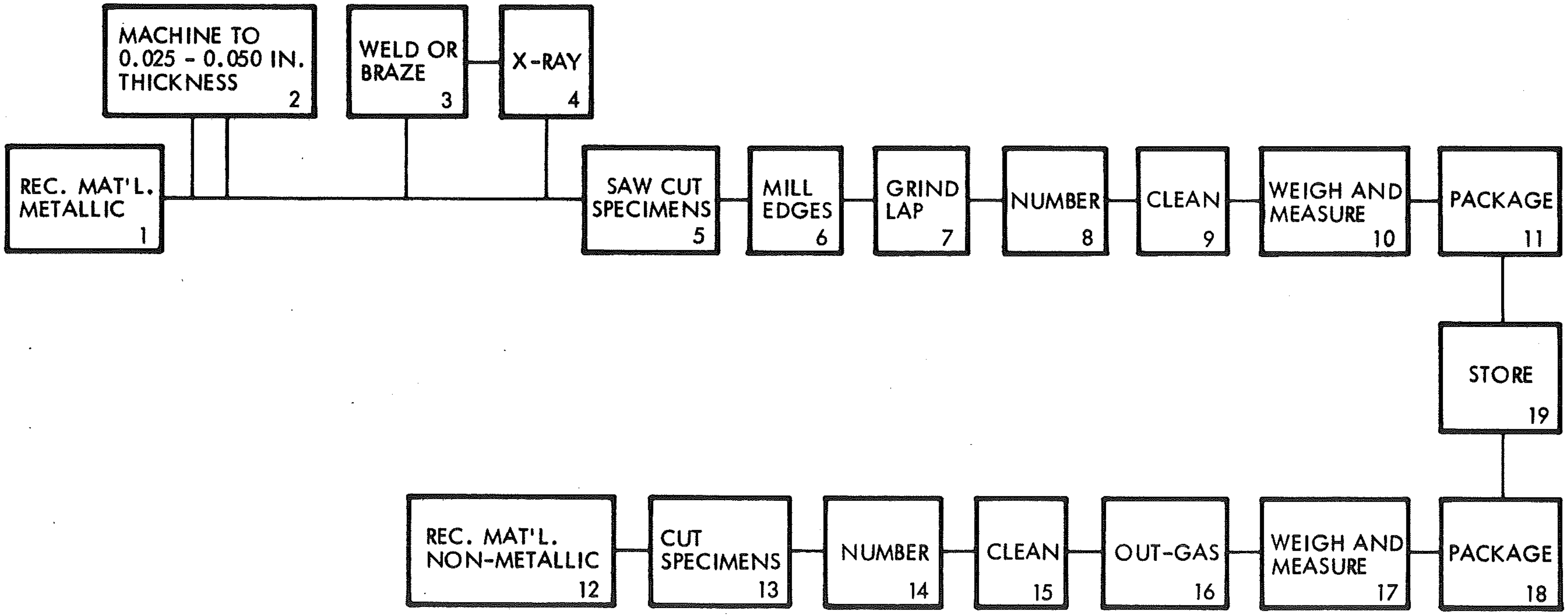


Figure 7. Preparation of Specimens

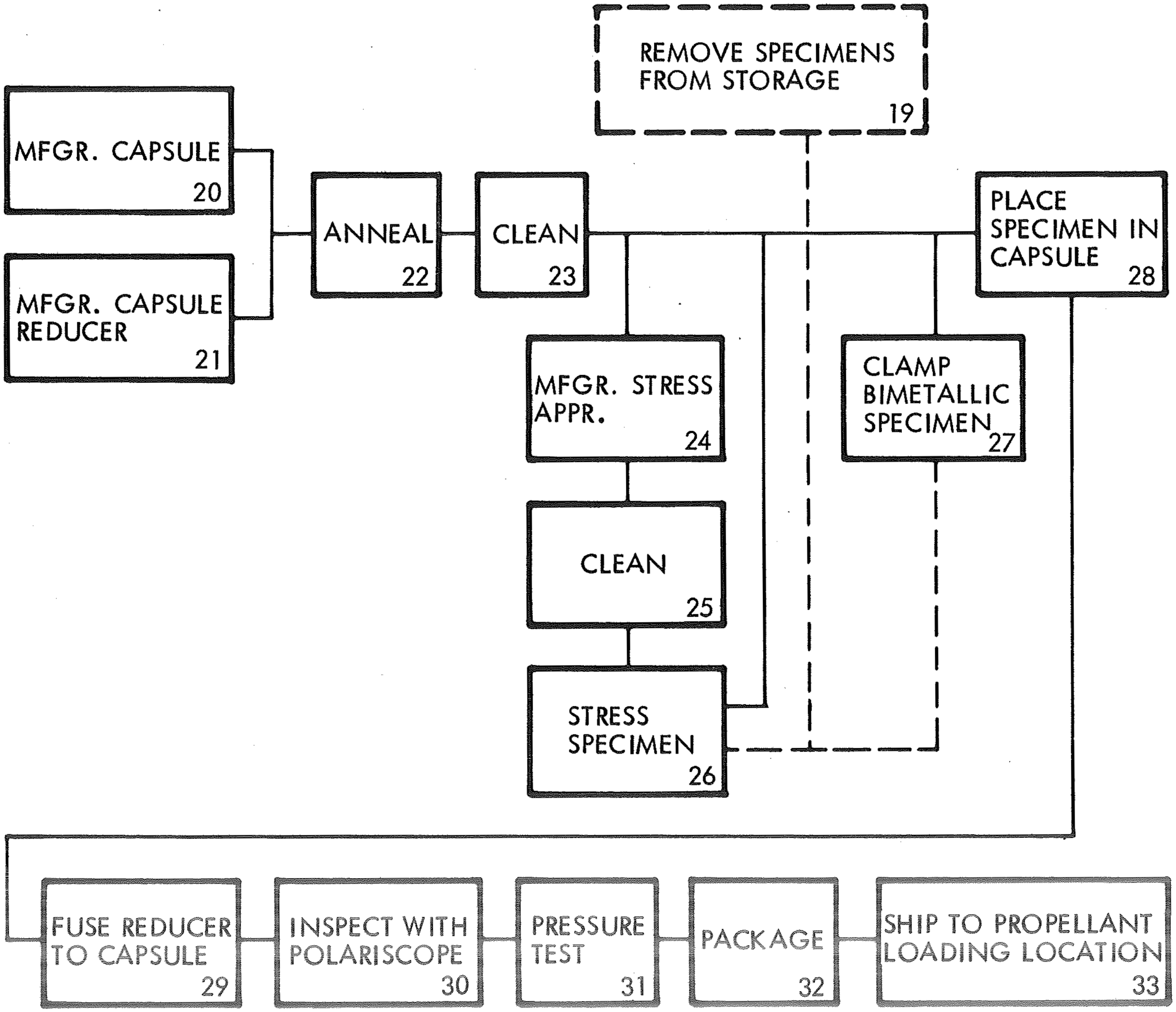


Figure 8. Encapsulation of Specimens

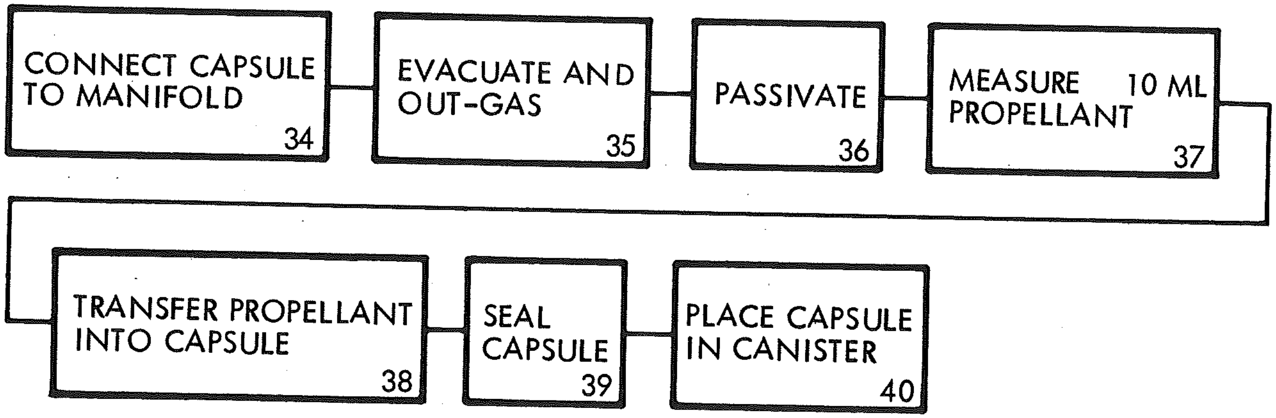


Figure 9. Propellant Loading of Capsules

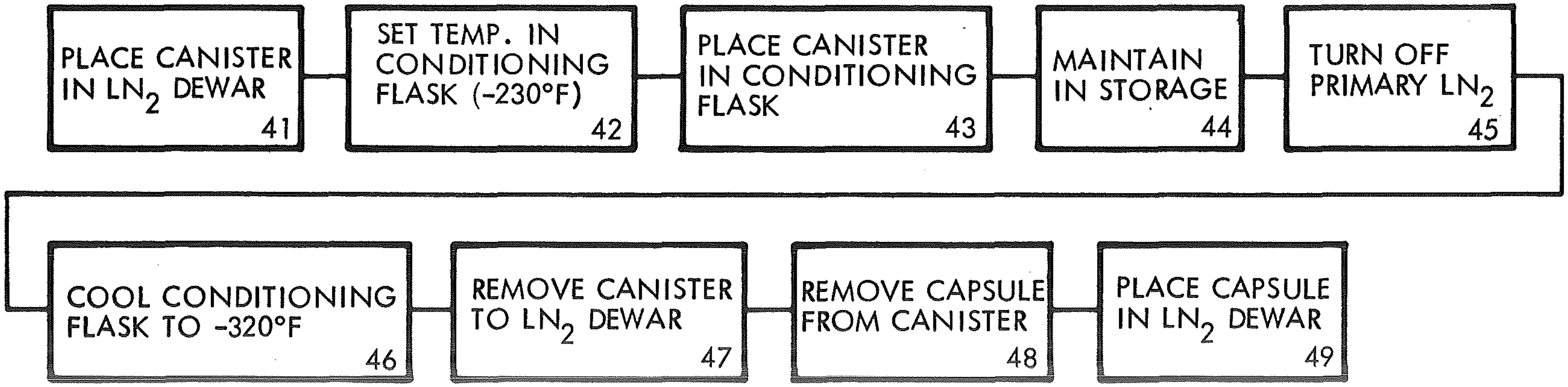


Figure 10. Specimen Storage

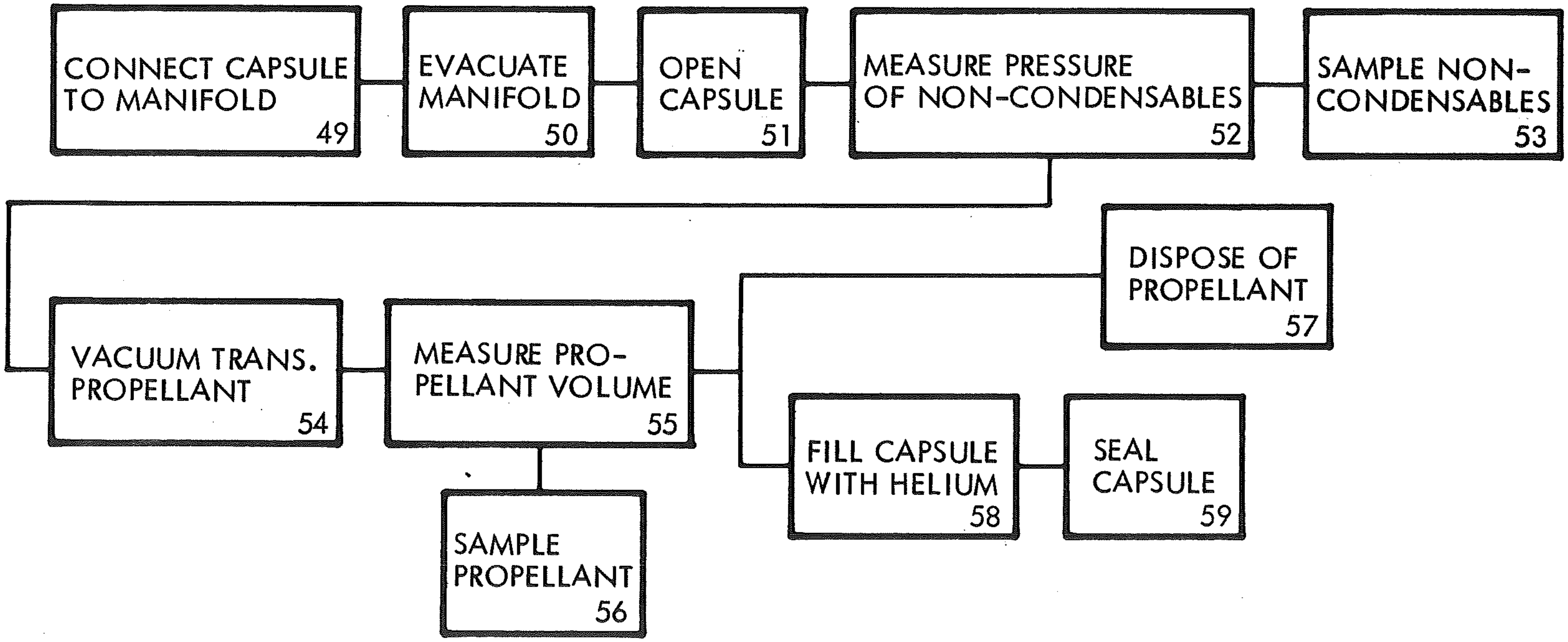


Figure 11. Termination of Tests

required to clean the capsules, stress samples, make bimetallic couples, encapsulate specimens and transport encapsulated specimens (Steps 23-33).

5.2 LOADING OF PROPELLANT

The loading of propellant into the capsule and the sealing of the capsule is accomplished (Steps 34-39) by use of the manifold shown in Figure 12 with a list of materials and equipment listed in Table IX. The manifolds for loading OF_2 and B_2H_6 are similar and only one drawing is used to describe both manifolds. The differences in the two manifolds are described below:

- Only the OF_2 manifold has a hydrogen fluoride trap.
- The B_2H_6 manifold has a propane burner for the destruction of B_2H_6.
- The OF_2 manifold has a heated charcoal burner for the destruction of OF_2. Traps after the charcoal burner are for trapping tetrafluoromethane.

The manifold is connected by means of 0.25-inch stainless steel line to a propellant tank behind a barricade.

When OF_2 is used, the OF_2 supply tank at ambient temperature must be opened behind a barricade to protect the operator from any metal ignition which conceivably could occur. Remote valve controls are available from The Matheson Company. The automatic pressure regulator is used to reduce cylinder pressure to a safe value, consistent with the system design. The control pressure may be varied from 5 to 50 psig. Commercially available OF_2 may contain up to 0.2% hydrogen fluoride and the hydrogen fluoride must be reduced to a negligible amount in order that glass capsules are not attacked. The hydrogen fluoride is removed by passing the OF_2 through a sodium fluoride trap.

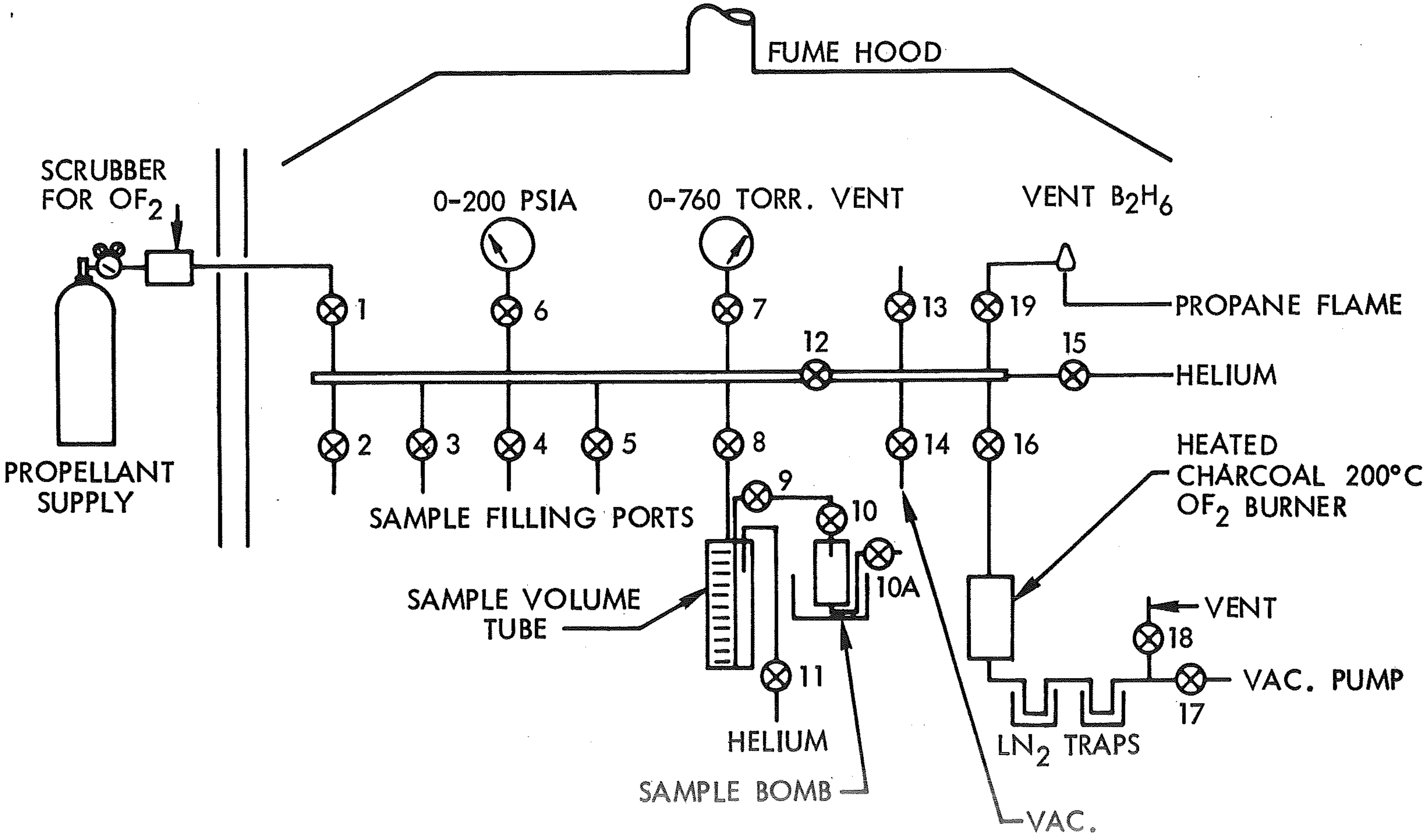


Figure 12. Propellant Handling Manifold

TABLE IX

LIST OF MATERIALS FOR MANIFOLDS

Item	Supplier	Cost Each	No.
Regulator No. 15F-670 (1)	Matheson Co.	$150.00	1
Valves, Model 4251N6Y (2)	Hoke, Castle Controls	43.30	38
Gauge, 0-800 torr, Model FA-145	Wallace & Tiernan	280.00	2
Gauge, low cost, 0-300 psia			2
Valve modified for sample opening (see Fig. 16) SV-11 #11C19L4-2	Valcor, Castle Controls	27.00	2

(1) Regulator required for OF_2 manifold only.

(2) Valves are welded to 1/4-inch stainless steel tubing.

When B_2H_6 is used, the supply tank must be retained in a dry ice storage chest. By means of stainless steel lines, the B_2H_6 is then connected to the manifold.

Before loading capsules with either OF_2 or B_2H_6, the 0.125-inch O.D. side arms on four capsules are attached by means of Swagelok fittings with Teflon ferrules to 0.125-inch O.D. lines connected to Valves 1-4 (Figure 12), (Step 34). To remove absorbed gases and moisture from the samples and capsules, the manifold is evacuated and the entire system held at less than 0.01 torr for one hour (Step 35). Before filling, the capsules and samples are passivated with 1 atmosphere of propellant for 0.25 hours (Step 36). The propellant used for passivation is removed by vacuum transfer. Although B_2H_6 is usually not used to passivate equipment, B_2H_6 is added first as a gas to react with any moisture or other reactive material that may be present in the capsule. Then, approximately 10 ml of liquid propellant is condensed by means of liquid nitrogen cooling, into a heavy wall graduated glass tube with Valves 9 and 11 closed (Step 37). The propellant is then transferred by vacuum handling methods into each of the capsules attached to the manifold (Step 38).

For safety considerations, the sealing of the capsule (Step 39) requires use of a propane-oxygen torch modified with a three-foot extension to allow the operator to maintain a safety shield between his hand and the propellant during the sealing operation.

The four sealed capsules are removed from the manifold and placed into a canister (Step 40). The canisters to be used are those supplied with CRYO-FLASK Model A-1500, but these canisters must be modified as indicated in Figures 13 and 14. The bottom plate of the capsule is removed and a removable capsule holder is fabricated for insertion into the canister. A 0.125-inch rod that extends above the top of the canisters is fastened to the center of the removable capsule holder. This rod is to be used for lifting the capsules.

5.3 STORAGE OF SPECIMENS

After the sealed capsules are in the canister, the canister is placed in a Dewar flask filled with liquid nitrogen (Step 41). The Dewar is clamped to a metal laboratory cart equipped with safety shields. Before placing the canisters in the conditioning flasks (Figure 15), the flasks are brought to liquid nitrogen temperature by partially filling with liquid nitrogen (Step 42). The conditioning flask and controls to be used are listed in Table X and shown in their operational configuration for one conditioning flask set-up in Figure 15. Basically, the controls consist

TABLE X

EQUIPMENT FOR CONDITIONING FLASK AND CONTROLS

Item	Supplier	Cost Each	No.
CRYO-FLASK, Model A-1500	MVE Cryogenics	$375.00	12
Solenoid Valve	General Controls	21.90	24
Temp. Controller, Model 123-000	Cryogenic Controls	285.00	24
Recorder, eight point	Any	Usually available	
Canisters, Model A-1500	MVE Cryogenics	5.00	108

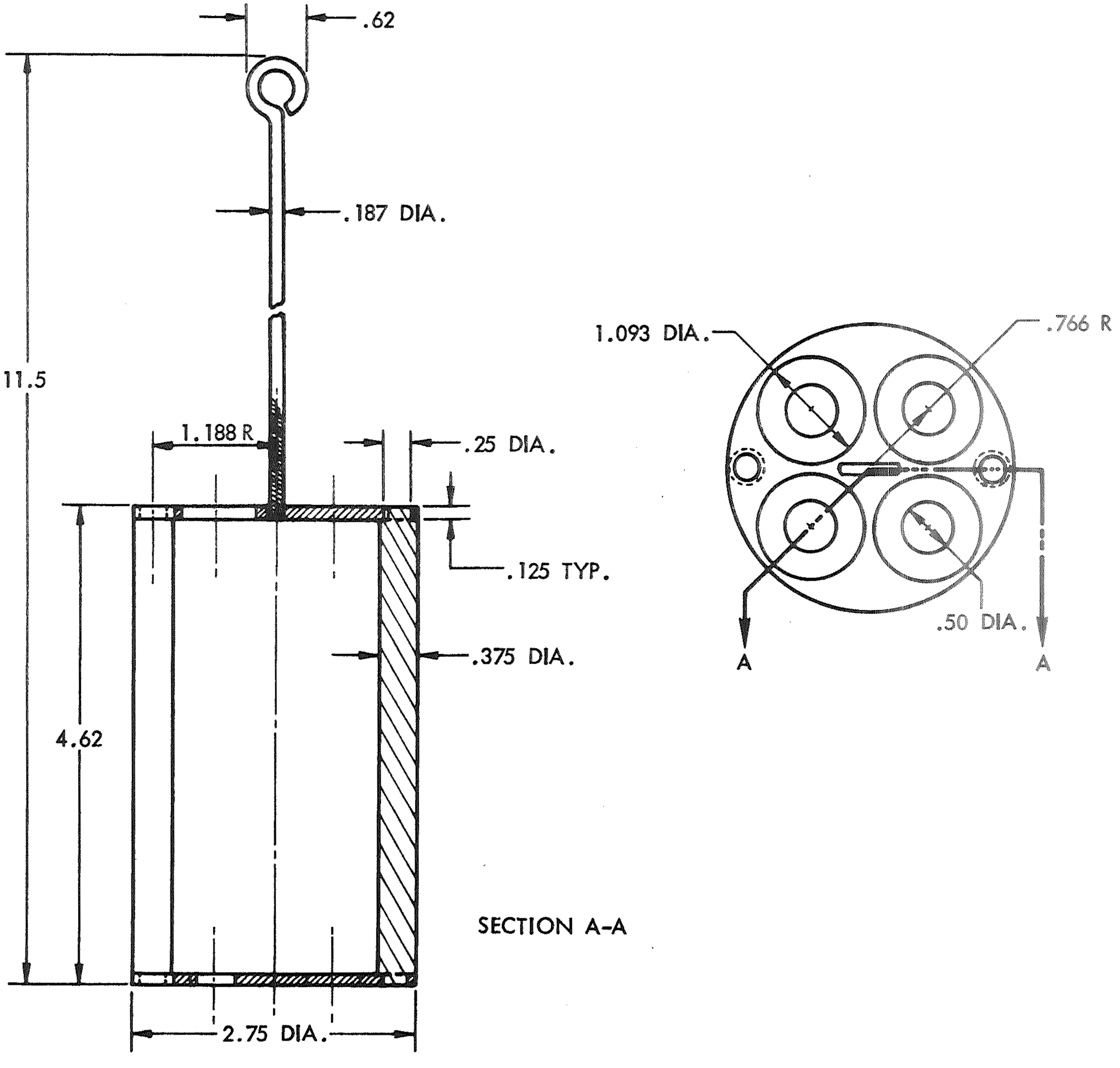


Figure 13. Canister Modification

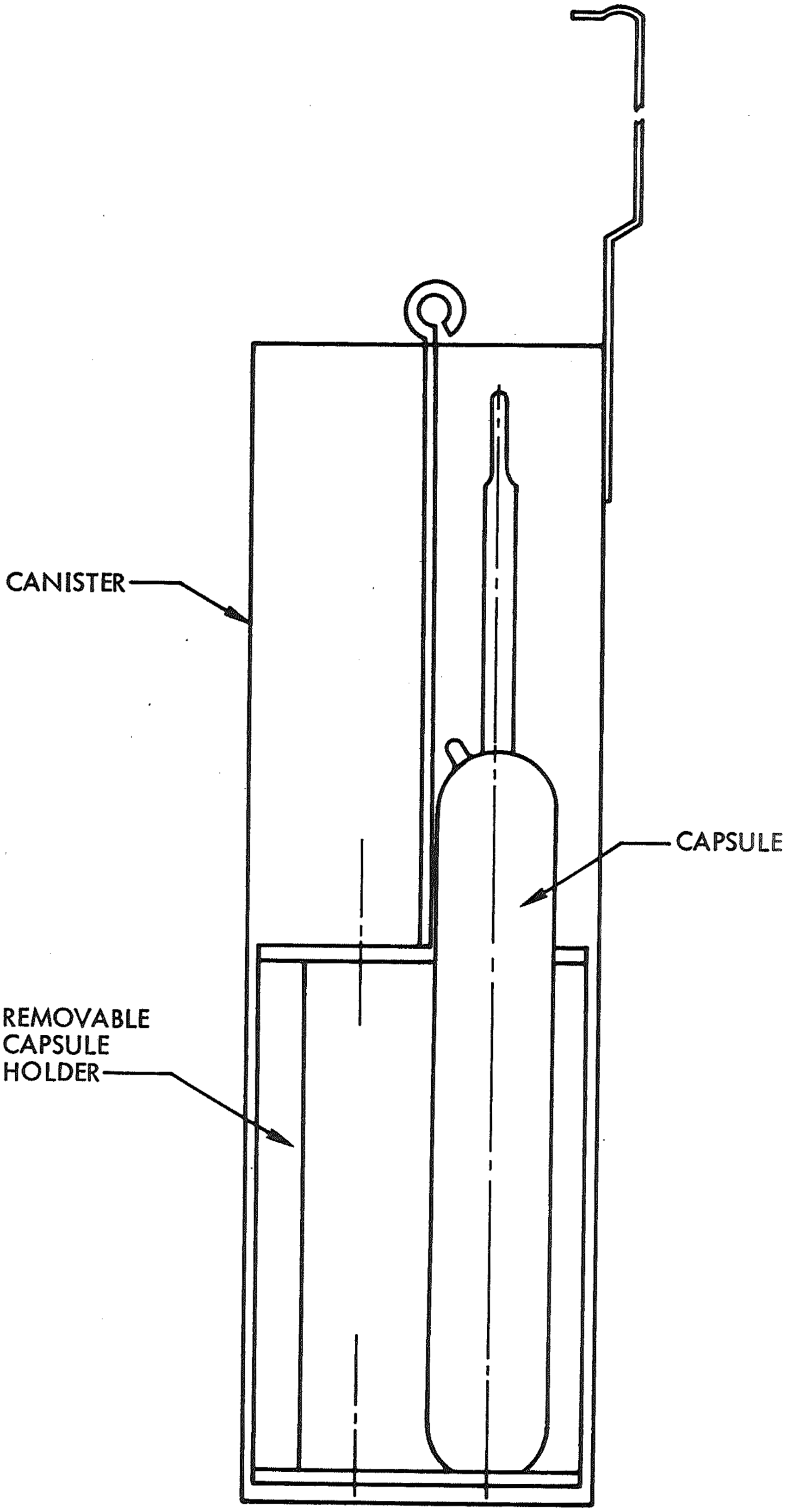


Figure 14. Capsule Situated in Canister

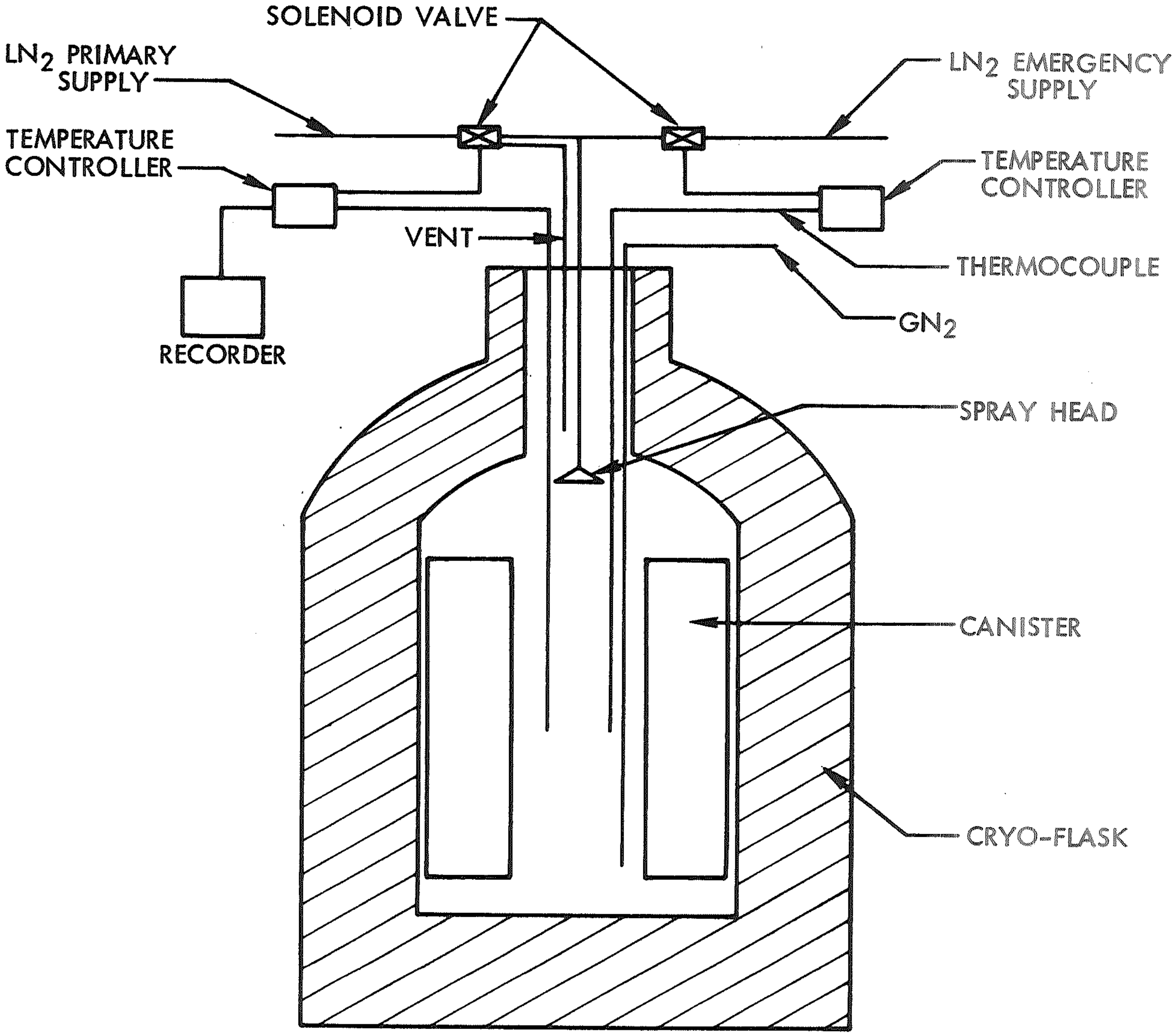


Figure 15. Conditioning Flask and Controls

of a temperature probe mounted in the refrigerated chamber and a control box connected directly to a nitrogen supply line. When the temperature of the chamber changes from the desired -230°F, the signal generated by the controller operates a normally closed solenoid valve that is cooled by a vent tube from the flask. Redundant temperature control is provided by a backup temperature controller and probe set at -180°F to energize in the closed position a normally-open solenoid valve that is connected to a 110-liter emergency liquid nitrogen supply tank. An ambient gaseous nitrogen supply line is also provided to permit warming the cryogenic flask to -230°F after cooling to -320°F (LN_2). In order to provide a record of the temperature in the storage flask, a recorder is attached to one of the temperature probes.

The placing of the canister in the storage flask and temperature conditioning for the storage period (Steps 43 and 44) are accomplished in the facilities shown in Figure 16. The canisters are removed from the storage facilities and returned to the propellant handling manifold (Steps 45-48) by reversing the sequence of procedures for placing the canisters in the storage flask.

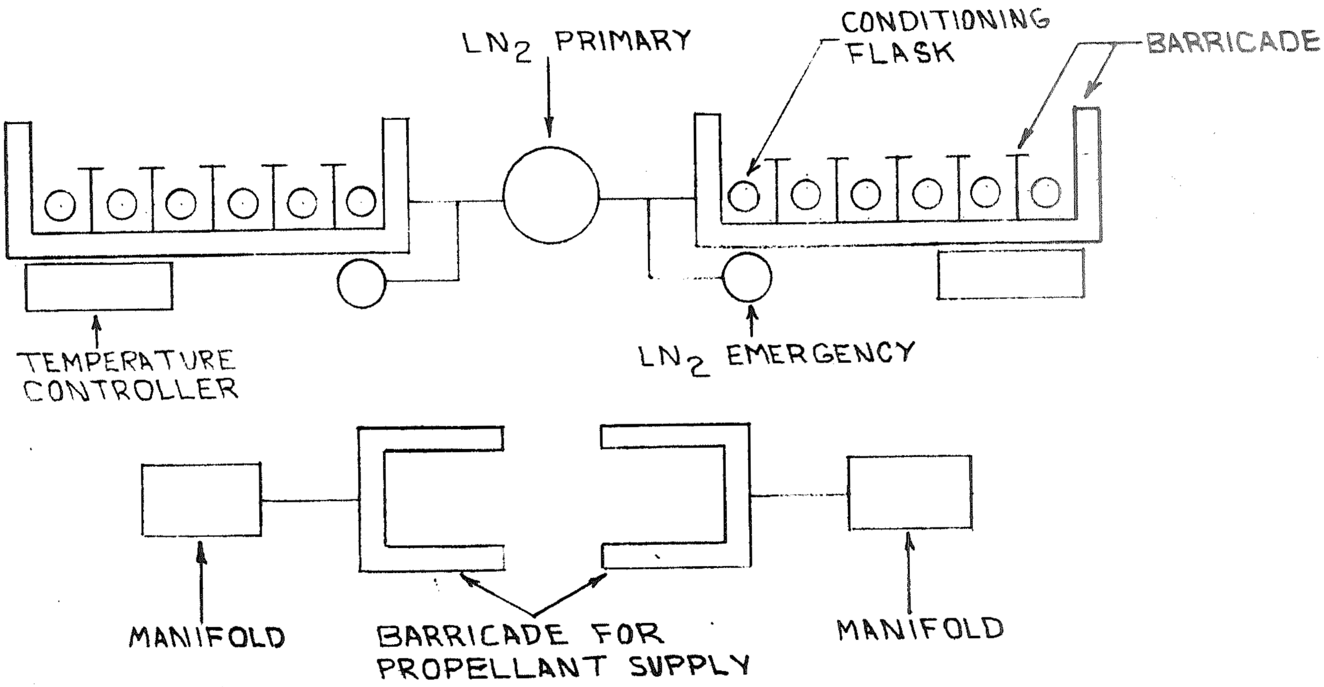


Figure 16. Specimen Storage Facilities

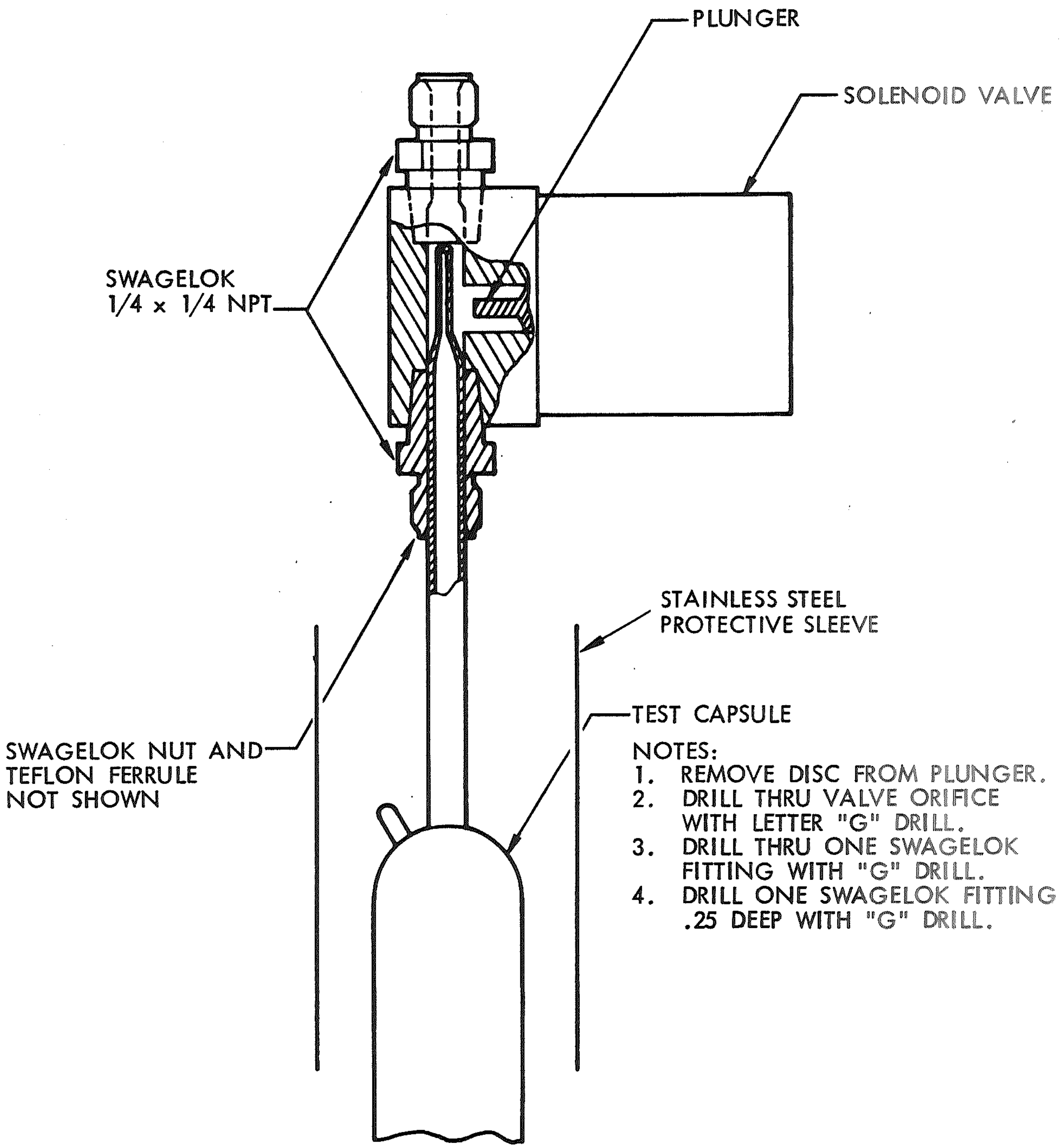
5.4 TEST TERMINATION

The termination of the storage test requires the use of carefully designed facilities because of potential safety hazards. First, the plate at the bottom of the canister is elevated by lifting the 0.125-inch rod attached to the capsule holder with long arm tongs. Then one of the four capsules is removed with tongs and the capsule immediately transferred to a liquid filled Dewar flask. While immersed in liquid nitrogen, the capsule is manipulated by means of a laboratory jack and tongs into position for connection (Step 49) to the opening device shown in Figure 17.

The opening device is attached to the manifold at any one of the four sample filling ports. After evacuation of the manifold (Step 50), the capsule is opened by energizing the coil on the opening device (Step 51). While the capsule is held at liquid nitrogen temperature, the non-condensables are estimated by measuring the pressure in a volume calibrated portion of the manifold (Step 52). If non-condensables are present, they are sampled with an evacuated sample bomb attached to a second filling port (Step 53). The non-condensables that are sampled may be identified by means of mass spectrometry.

The propellant in the capsule is then transferred by a vacuum handling technique, into the calibrated one-inch heavy wall glass tube previously described (Step 55). While the propellant is in a liquid nitrogen bath, a 0.5 to 1.0 ml sample of propellant is removed (Step 56) by applying 2 atm of helium to the propellant and allowing the propellant to flow into a 1 ml sampling bomb (Figure 18). The propellant sample can be transported while packed in dry ice to an analtjcal laboratory for gas-liquid partition chromatography in the case of OF_2 and mass spectrometry in the case of B_2H_6. The propellant can be removed from the calibrated glass tube by simply allowing it to warm to room temperature and venting into the disposal apparatus (Step 57). Diborane is burned in the propane torch and OF_2 is burned in the charcoal burner shown in Figure 12.

After the propellant is removed and the capsule evacuated, the capsule is filled with one atmosphere of helium (Step 58). The capsule is then immediately disconnected from the opening apparatus and sealed with a torch



NOTES:
1. REMOVE DISC FROM PLUNGER.
2. DRILL THRU VALVE ORIFICE WITH LETTER "G" DRILL.
3. DRILL THRU ONE SWAGELOK FITTING WITH "G" DRILL.
4. DRILL ONE SWAGELOK FITTING .25 DEEP WITH "G" DRILL.

Figure 17. Capsule Opening Device

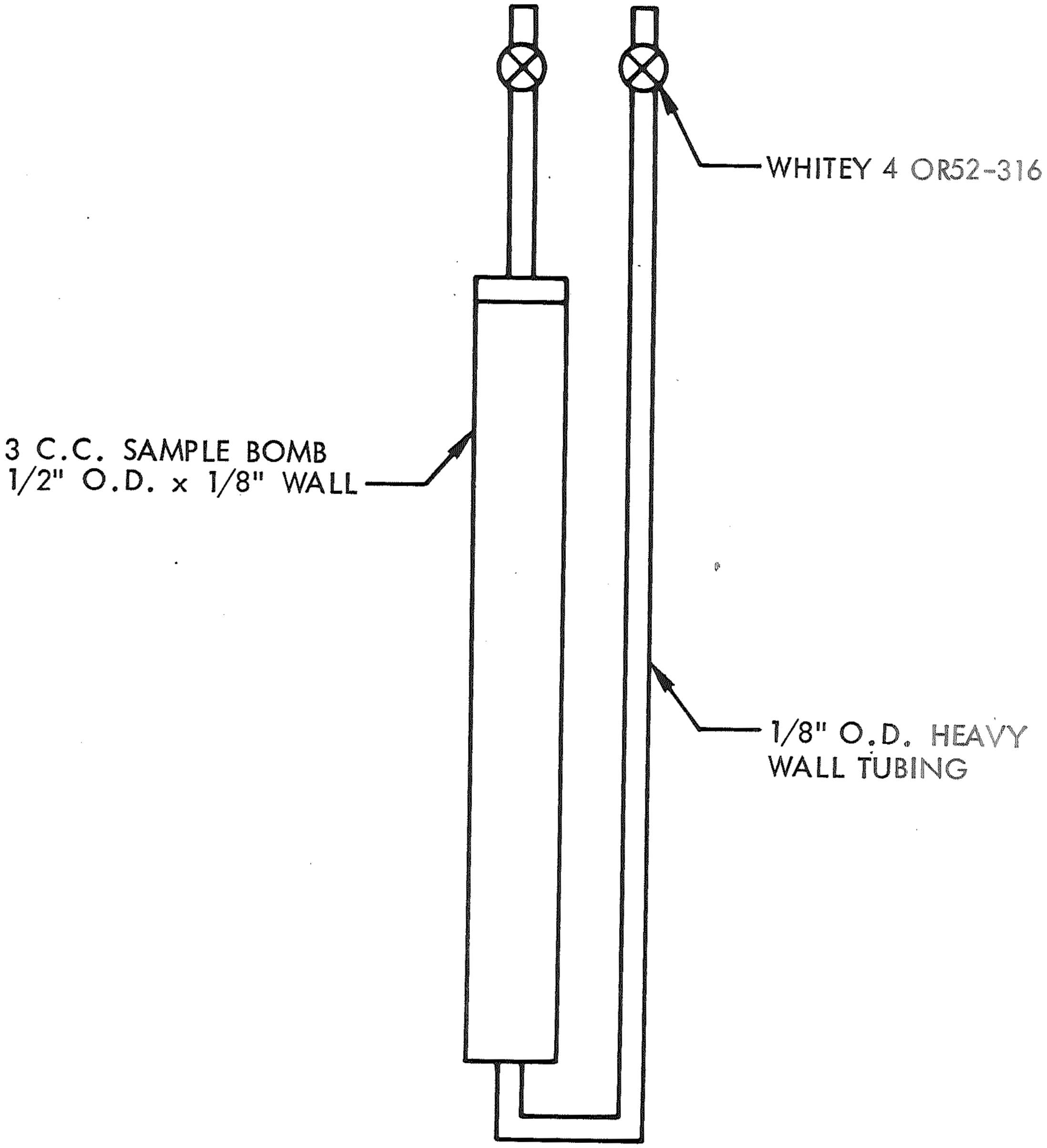


Figure 18. Propellant Sampling Bomb

(Step 59). The specimen in the sealed capsule can be transported to the laboratory for examination. Any non-volatile residues found in the capsules can be identified by suitable analytical techniques, such as the X-ray spectrograph.

6. TASK V - ESTABLISH DATA METHODOLOGY

A procedure was established that will allow an option utilization of computer technology for acquiring and retrieval of data. This procedure provides for recording data on forms that can be used for direct input to a computer for storage and correlation of data. The forms for recording data are based on the reporting format recommended by the Fluids and Materials Compatibility Committee of the JANNAF Working Group on Propellant Characterization and are provided as part of the detailed procedure for implementation and accomplishment of the test plan. The features of the computer data handling technique are outlined below.

6.1 TEST DATA BASE DEVELOPMENT

The objectives of the test data base development are as follows:

- To ensure data completeness - all required data is gathered for each test specimen and supporting facts explaining any deviations.
- To ensure data consistency - through long term storage programs same test procedures must be rigorously adhered to and measurement units consistent throughout program.
- Minimize data transcription - every time data is transcribed from one base to another a potential source of error is introduced plus the additional costs of transcribing to the project.
- To ensure data compatibility with data analysis procedure - data should be gathered in the Fluids and Materials Compatibility Committee format which is suitable for direct incorporation into any automated data processing equipment considered for implementing the data analysis task or suitable for direct input to manual analysis procedures.

6.2 DATA REQUIREMENTS

Data requirements for the compatibility test are those identified in the recommended format for reports of compatibility measurements as generated by the Fluids and Materials Compatibility Committee of the JANNAF Working Group on propellant characterization. A copy of the data requirements of the recommended reporting format is shown as Appendix A.

6.3 DATA ACQUISITION FORMS

Multifunctional data acquisition forms have been designed to encompass the following objectives:

- Laboratory work sheet for original data recording,
- Storage media for film storage and hard copy storage,

or

- Automated data processing input sheet for computer storage,
- Automated data processing input sheet for data analysis,
- Complete test sample traceability,
- Laboratory testing status and schedule determination.

Specimens are to be carefully controlled to ensure traceability and a data package maintained for each test specimen. For metallic specimens the material name, alloy designation, specification number, producer, chemical composition, lot number, metallurgical state, and processing history are to be recorded. For non-metallic specimens similar data is to be recorded. All metallic specimens are to be vibraetched. Nonmetallic specimens are not to be marked with a marking material that may invalidate the tests, but sample identify will be assured by identifying all packages and container into which the specimens are placed. Before placing specimens in the test capsules, all physical dimensions, weight and surface finish will be measured and recorded in the data package on the forms shown in Figure 19. The results of propellant analyses before initiation and after termination of compatibility test will be recorded on a form shown in Figure 20. On this form will also be recorded the quantity of propellant added to the test capsule, the quantity removed after completion of the test, the quantity and identity of volatile material formed during the test, and the quantity and identity of non-volatile residue remaining in the capsule after completion of the tests.

The temperature of each test chamber will be continually recorded and any deviations from the required -230°F ± 30° will be noted in the data sheet for each specimen that was stored in that test chamber.

			73–80
SAMPLE ID NO.	10–20		
SAMPLE TYPE	21–40		
MATERIAL CODE	41–45		
MATERIAL LOG NO.	46–65		
CAPSULE NO.	66–72		A01
TEST NO.	10–20		
TEST DATE	21–30		
TEST PLAN NO.	31–40		
CAPSULE LOADING DATE (SPECIMEN)	41–48		
CAPSULE FILLING DATE (PROPELLANT)	49–56		
CAPSULE UNLOADING DATE (SPECIMEN)	57–64		
CAPSULE EMPTYING DATE (PROPELLANT)	65–72		A02

	SAMPLE A	SAMPLE B	73–80
INITIAL SAMPLE WEIGHT	10–15	16–20	
INITIAL SAMPLE LENGTH	21–25	26–30	
INITIAL SAMPLE THICKNESS	31–35	36–40	
INITIAL SAMPLE WIDTH (GAGE)	41–45	46–50	
INITIAL SAMPLE WIDTH (GRIP)	51–55	56–60	A03
SURFACE FINISH	10–20	21–30	
SHORE HARDNESS	31–40	41–50	A04
AVERAGE STORAGE TEMPERATURE	10–15		
STORAGE DURATION	16–20		A05
REMARKS	10–72		A06
REMARKS	10–72		A07

	SAMPLE A	SAMPLE B	73–80
FINAL SAMPLE WEIGHT	10–15	16–20	
FINAL SAMPLE LENGTH	21–25	26–30	
FINAL SAMPLE THICKNESS	31–35	36–40	
FINAL SAMPLE WIDTH (GAGE)	41–45	46–50	
FINAL SAMPLE WIDTH (GRIP)	51–55	56–60	A08
SURFACE FINISH	10–20	21–30	
SHORE HARDNESS	31–40	41–50	
PROPELLANT ANALYSIS CROSS REFERENCE	51–72		A09

Figure 19. Test Data Sheet

73 80

TEST NUMBER ________ 10 20

TEST DATE ________ 21 30

SAMPLE CROSS REFERENCE ________ 31 72 B01

PROPELLANT TYPE LIQUID DIBORANE 10 30 B02

	INITIAL	FINAL	% CHANGE	
PERCENT HYDROGEN	10 15	16 20	21 25	
PERCENT B_2H_6	26 30	31 35	36 40	
PERCENT IMPURITIES	41 45	46 50	51 55	B03

PROPELLANT TYPE OXYGEN DIFLUORIDE 10 30 B04

	INITIAL	FINAL	% CHANGE	
PERCENT CARBON DIOXIDE	10 15	16 20	21 25	
PERCENT HYDROGEN FLUORIDE	26 30	31 35	36 40	
PERCENT OXYGEN	41 45	46 50	51 55	B05
PERCENT SILICON TETRAFLUORIDE	10 15	16 20	21 25	
PERCENT IMPURITIES	26 30	31 35	36 40	B06

NON CONDENSIBLE GASES FORMED DURING STORAGE:

NAMES ________ 10 72 B07

AMOUNTS ________ 10 72 B08

RESIDUE WEIGHT ________ 10 72 B09

RESIDUE COMPOSITION ________ 10 72 B10

Figure 20. Propellant Analysis Data Sheet

6.4 DATA STORAGE

The data storage media is a function of data volume, budget, and available systems and procedures.

- Small data banks are best left in hand copy form with an extensive cross index of major data categories.
- Intermediate data banks might consider microfilm aperture cards as a storage media.
- Large data bank should utilize computer storage and retrieval techniques.

The storage of data banks on microfilm aperture cards is recommended for this program because of the quantity of data to be collected.

6.5 DATA ANALYSIS

The mathematical analysis effort for treatment of the test data from the program will require capability to perform the following calculations:

- Simple statistical dispersion calculations including mean, range, standard deviation, median, and mode.
- Linear regressions with transforms including X vs. Y, Log (X) vs. Y, X vs. Log (Y), and Log (X) US Log (Y).
- "t" value of linear regressions.
- Correlation coefficients of linear regressions.
- Standard deviation about regressions.

7. TASK VI - DETAILED TEST PLAN DOCUMENTATION

Pertinent documentation required to accomplish the immersion test program was generated and is presented in Appendices A-H. Procedures cover all aspects of the program such as processing, cleaning, encapsulation, installation and post test handling and testing.

8. CONCLUSIONS

Summarized below are the conclusions reached during the development of the plan for a material compatibility program for oxygen difluoride and diborane liquid propellants.

1. Insufficient information is available to determine whether acceptably inert (short term) materials can have high performance and reliability after periods up to two years storage under mission environments while in contact with liquid OF_2 and B_2H_6 at a temperature of -230°F.
2. A double dog-bone test specimen configuration was recommended for compatibility testing with OF_2 and B_2H_6 based on maximizing the test information yet permitting minimum propellant required for test (for safety and propellant test economical reasons).
3. Glass test containers have been selected for use in the compatibility test based on detailed consideration of 1) potential chemical reactions that might occur during the compatibility test and 2) minimization of test container costs. Furthermore, this assessment of these potential chemical reactions and the desire to maintain a totally inert capsule material necessitated the elimination of pressure monitoring during testing. With the exception of hydrogen from B_2H_6 and O_2 and SiF_4 from OF_2 tests all potential reaction products have negligible vapor pressure at the -230°F test temperature; consequently, incompatibility cannot be readily monitored by pressure measurement. Candidate materials have been selected based on short term compatibility and, hence, severe failure over long term storage is improbable.

4. The glass test container permits assembly and installation by common laboratory manometric techniques thereby enhancing safety and economy.

5. Detailed assessment of available cryogenic refrigeration techniques to maintain the -230°F for long periods of time has resulted in the selection of a commercially available cryogenic flask for housing the test containers during storage. The selection of this device minimizes the cost of cryogens during long term testing.

6. It is concluded that the use of the recommended format for reports of compatibility measurements (JANNAF 725.0, Feb. 1971, CPIA/PCWG) would provide sufficient data to permit meaningful assessment of the compatibility of candidate materials with oxygen difluoride and diborane at the test temperatures.

9. RECOMMENDATIONS

Based on the findings and the plan generated during this program it is recommended that detailed materials compatibility experimental program be undertaken. It is believed the approach planned for the recommended program will provide reliable information that can be used to understand in not only gross but also the subtle implications of extended storage periods of 2, 5 and 10 years such as those associated with the advanced missions to outer planets and to generate data shown which to base flight commitments.

Prior to committing the detailed testing program, it is recommended that two simple experiments should be performed; 1) a few tests should be performed with propellant-grade OF_2, that contains traces of HF, in glass capsules containing specimens of several of the candidate metals to determine the magnitude of any HF impurity caused effects. If HF appears to present a problem, the HF should be removed as recommended in the plan, and 2) the temperature conditions design using the CRYO-FLASK is believed to be satisfactory for the planned compatibility studies, but without circulation by means of a rotating fan blade in the flask, liquid nitrogen could collect in the bottom of the flask. If a problem exists, a small fan blade can be rotated in the flask by attaching the blade to a shaft running through the top of the CRYO-FLASK.

When these two remaining questions have been answered, it is appropriate to initiate the detailed program outlined in this report.

10. NEW TECHNOLOGY

During the performance of Contract 952964, no new technology was developed.

11. REFERENCES

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APPENDIX A

COMPATIBILITY TESTING DATA REQUIREMENTS

A.1 FLUID CHARACTERIZATION

A.1.1 Pretest

A.1.1.1 Identity and Source - Provide the following: manufacture and/or supplier, specification number used in the procurement, chemical name, chemical formula, trivial and/or code names, date of purchase and/or preparation, type of transporter and container material.

A.1.1.2 Chemical Analysis - Provide the following: major and minor components as provided by the manufacturer and/or determined by the user (report in weight percent), analytical method used by manufacturer and/or user, number of analysis replicates.

A.1.1.3 Impurity Analysis - Provide the following: soluble and insoluble components including particle size (report in weight percent). For cryogenic fluids, differentiate between particles which are solid at ambient conditions and those which melt or vaporize at ambient.

A.1.1.4 Storage History and Reanalysis - If a significant time has elapsed between fluid analysis as conducted under A.1.1.2 and A.1.1.3 and fluid use in testing, provide the following: storage history of the fluid and reanalysis as detailed under A.1.1.2 and A.1.1.3.

A.1.2 Post Test

A.1.2.1 Chemical Analysis - Provide the following: major and minor components (report in weight percent), analytical method used, indicate changes if any, from A.1.1.2 (report in weight percent), number of analysis replicates.

A.1.2.2 Impurity Analysis - Provide the following: soluble and insoluble components including particle size (report in weight percent), indicate changes, if any, from A.1.1.3 (report in weight percent).

A.1.2.3 Material-Fluid Interaction Products - Provide the following: identify the soluble and insoluble gas, liquid and/or solid constituents which may have been formed during the test (report in weight percent). If possible, report the rates of formation of these constituents.

A.1.3 Control Test for Fluid

A.1.3.1 Chemical Analysis - Provide the following: data as in A.1.2 for fluid exposed to same chemical, thermal and pressure environment or cycles as that for test but in the absence of material, number of analysis replicates.

A.1.3.2 Impurity Analysis - Provide the following: data as in A.1.2.2 for fluid as tested in A.1.3.1.

A.1.3.3 Decomposition Products - Provide the following: data as in A.1.2 3 for fluid as tested in A.1.3.1.

A.2 MATERIAL CHARACTERIZATION

A.2.1 Pretest

A.2.1.1 Identity and Source - Provide the following for either a metal or non-metallic material: manufacturer (including heat or batch, processing method (forging, plate extrusion, casting, molding, etc.) and mill (surface) finish, manufacturer's specification, MIL or AMS specification, trade name, chemical name, and chemical analysis (major and minor components).

A.2.1.2 Specific Processing - Provide the following: cleaning prior to preparation of specimen (including materials used), welded or unwelded (if welded, specify whether chill bars where used (include type of bar), type of welding (EB, TIG, MIG, etc.), and weld filler material used), heat treatment (i.e., stress relief prior to welding, after welding and, if not welded prior to test, any thermal processing), specimen configuration and orientation (transverse or longitudinal), cleaning after preparation (specify materials used and whether passivated, abrasive, etc.), surface finish and lay, and applied stresses or unstressed (if stressed, specify procedure, loads and specimen configuration).

A.2.1.3 Properties - Provide the following: surface area exposed in test, mechanical properties (i.e., tensile, ultimate, % elongation, etc.), metallographic properties, visual and magnified surface examination (specify magnification), map or record defect locations, and specimen weight.

A.2.2 Post Test

A.2.2.1 Visual Examination of Specimen - Provide the following: appearance, magnification, and time elapsed after test to examination with description of exposure environment.

A.2.2.2 Chemical Analysis of Surface Films - Describe corrosion products, etc., and specify type of analysis used.

A.2.2.3 Sample Weight - Provide the following: weight before surface films, corrosion products, etc., were removed and weight after removal of surface films, etc., (specify how surface films, etc., were removed).

A.2.2.4 Metallographic Examination - Provide the following: surface finish, cross section, and photographs of typical sections including magnification (including a standard scale in all original photographs), and photograph of views from a scanning electron microscope.

A.2.2.5 Mechanical Properties - Provide tensile, ultimate, % elongation, etc.

A.2.3 Control Test for Material

A.2.3.1 Inert Atmosphere Storage Without Stress - Specimen qualified under A.2.1 but stored in an inert atmosphere during compatibility test. Processed as in A.2.2 after test completion.

A.2.3.2 Inert Atmosphere Storage with Stress - Specimen qualified under A.2.1 and exposed to the same thermal and pressure environment or cycle in an inert atmosphere but in absence of fluid. Processed as in A.2.2 after test completion.

A.3 TEST PROCEDURES

A.3.1 Test Description

Provide a complete, detailed description of test method used. Refer to number and name of related standard test procedure.

A.3.2 Test Precautions

Provide a complete, detailed description of the precautions exercised to eliminate spurious test results.

A.3.3 Temperature and Thermal Cycle

Provide data in English and System Internationale (Metric) system units.

A.3.4 Pressure

Provide data in English and S.I. (Metric) system units.

A.3.5 Exposure Duration

A.3.6 Stress Level

Provide data on stress level (at test temperature) and method used for its measurement. Report any changes during the test period.

A.3.7 Geometry

Provide surface to volume ratio and other geometric effects.

A.3.8 Flow Rate

Provide data in English and S.I. (Metric) system units.

A.3.9 Instrumentation

Provide information on the instrumentation used and data as to its accuracy and precision.

A.3.10 Ullage Volume

Provide data in absolute and relative volumes.

APPENDIX B
TEST PLAN

B.1 SCOPE

This test plan identifies the recommended specimens to be manufactured, tested, compatibility and examined after testing.

B.2 PURPOSE

The purpose of this test plan is to identify the specimens to be tested, and conditions of storage, i.e., stressed and unstressed, storage times, and pre and post test examination.

B.3 SPECIMEN MANUFACTURE AND PRETESTING

B.3.1 Specimen Manufacture

In accordance with Procedure for Preparation of Test Specimens, Appendix C, the double "dog-bone" specimens indicated in Table B.1 and four stress specimens 5-inch long from the materials tested in Table B.II. After the specimen length for each material to be tested in a stressed condition has been determined, prepare 33 specimens for each of the materials listed in Table B.II to the required length. From raw-stock having the same composition as metals to be stressed prepare 30 stress fixtures for each material. Prepare 33 welded double "dog-bone" specimens for the materials listed in Table B.III.

B.3.2 Pre-Testing

Determine by ASTM Method E8-57T the physical properties (yield strength, ultimate tensile strength and percent elongation) for three specimens of each of the materials listed in Tables B.I - B.III. Clean and weigh all specimens not tested at this time. Then package the specimens according to Appendix C.

B.4 STORAGE OF SPECIMENS

To minimize storage facility cost store through specimens in OF_2 and B_2H_6 for each of materials listed in Tables B.I - B.III for each of the time periods according to the storage schedule shown in Table B.IV.

TABLE B.I
DOUBLE DOG-BONE SPECIMENS

Material	No. of Specimens
A-286 Steel	33
347 CRES	63
17-4 PH CRES (H-900 min)	33
1100 Aluminum	63
6061 Aluminum	33
Alumina	33
6Al-4V Titanium	63
Inconel-718	93
Beryllium Copper (Brush 190)	63
303 CRES	33
Inconel-X(X-750)	33
301 CRES	33
321 CRES	93
Super-Pure Teflon	33
Teflon-Aluminum Laminate	33
Monel 400	33
316L CRES	33
Rene 41/CMR	33
	834

TABLE B.II
STRESS SPECIMENS MATERIALS

A-286 Steel	321 CRES
A-1100 Aluminum	Welded 321 CRES
6Al-4V Titanium	A-1100 Al
Inconel-718	Inconel-718
Beryllium Copper (Brush 190)	

TABLE B.III

WELDED DOUBLE DOG-BONE SPECIMENS MATERIALS

6Al-4V Titanium
321 CRES

TABLE B.IV
STORAGE SCHEDULE

Days	Facility 1	Facility 2
30	24	1*
60	24	3
90	24	3
120	24	3
150	24	6
180	24	6
210	24	6
240	24	6
270	24	6
300	24	6
330	24	12
360	24	12
390	24	12
420	24	12
450	24	12
480	24	12
510	24	12
540	24	12
570	24	12
600	24	12
630	24	12
660	24	12
690	24	
710	24	

*Months of Storage

APPENDIX C

PROCEDURE FOR PREPARATION OF TEST SPECIMENS

C.1 SCOPE

This procedure describes the preparation of test specimens; both metallic and non-metallic.

C.2 PURPOSE

The purpose of this procedure is to provide sufficient information in order that test specimens can be manufactured by shop personnel.

C.3 METALLIC SPECIMENS

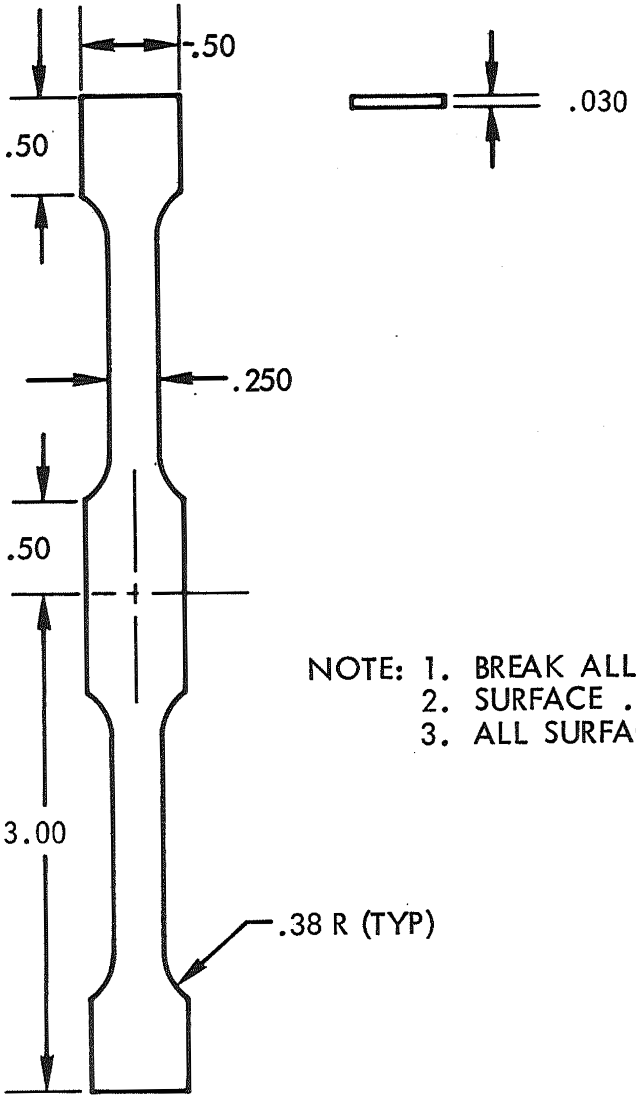
C.3.1 Double Dog-Bone Specimens

C.3.1.1 Weld or Brazed Specimens

Obtain sheet stock between 0.025-inch and 0.040-inch thick. Weld or braze 1.3-inch wide strips of the two sheet stocks, making the joint traverse to the rolling direction. Cut (as described in Paragraph B.3.1.2) the jointed materials in such a manner that the joint traverses the guage section. X-ray welds or brazed section of specimens and retain X-ray with Test Data Sheet.

C.3.1.2 Standard Specimen

Cut a slightly oversized specimen (Figure C.1) with a band saw, using sheet material that is 0.046-inch thick. Mill width and length dimensions to those shown in Figure C.1. Rough grind and then lap thickness to the requirements of Figure C.1. To eliminate contamination during grinding, dress grinding wheels, completely clean machines and use new coolant. Use masks thinner than the specimen to hold the specimen in place. Dimensionally inspect specimens for compliance with the drawing (Figure C.1). Vibra etch serial number on each specimen using four digit numbers. Initiate a Test Data Sheet for each specimen. Designate the material and a lot or heat numbers on the Test Data Sheet. Degrease the specimen with acetone (do not use halogenated solvents). In a clean-room, wash the specimens in 4.0%



NOTE: 1. BREAK ALL EDGES .005
2. SURFACE .0025 FLAT/IN. TYP.
3. ALL SURFACE 16 - 8

Figure C.1. Double Dogbone Test Specimen solution of liquid detergent ("Joy"), at 180+ - 30°F for five (5) minutes. Then rinse thoroughly with distilled water. Dry the specimen with dry filtered nitrogen. Weigh specimen and record weight on Test Data Sheet. Place the specimen in clear clean plastic bags. Care must be taken to avoid hand contact after the cleaning operation.

C.3.2 Non-Metallic Specimens

Prepare a die for cutting non-metallic specimens to the dimensions shown in Figure C.1. Cut molded sheets of the non-metallic specimens. The thickness of the sheets should be about 0.12-inch. Degrease the specimens with acetone. Then in a clean-room wash the specimens in a 4.0% of liquid detergent ("Joy"), at 180 ± 30°F for five (5) minutes. Then rinse thoroughly with distilled water. The pH of the run-off water must be equal to that of the initial distilled water.

C.3.3 Stressed Specimens

Calculate the required length of the stressed specimens using data collected from measured physical properties determined for Standard Test Specimens and the procedure described in Section 4.1 of the Final Report. Then cut with a band saw, a blank size of 0.062-inch x 0.625-inch and the calculated length + 0.19-inch. Mill length and width to the dimensions shown in Figure C.2. Dimensionally inspect specimens for compliance with the drawing. Initiate a Test Data Sheet for each specimen. Designate the material and lot or heat numbers on the Test Data Sheet. Degrease the specimens with acetone (do not use halogenated solvents). Dry the specimen with dry filtered nitrogen. Weigh specimen and record weight on Test Data Sheet. Prepare a stress apparatus from the same material as the specimen to be stressed. The stress apparatus is to be manufactured according to Figure C.3. Degrease the stress apparatus with acetone. Then place the specimen to be stressed in the apparatus as shown in Figure C.3, being careful not to over stress the specimen while placing it in the stress apparatus.

In a clean-room, wash the specimen and stress apparatus before stressing the specimen in 4.0% solution of liquid detergent ("Joy"), at 180 ± 30°F for five (5) minutes. Then rinse the assemblies thoroughly with distilled

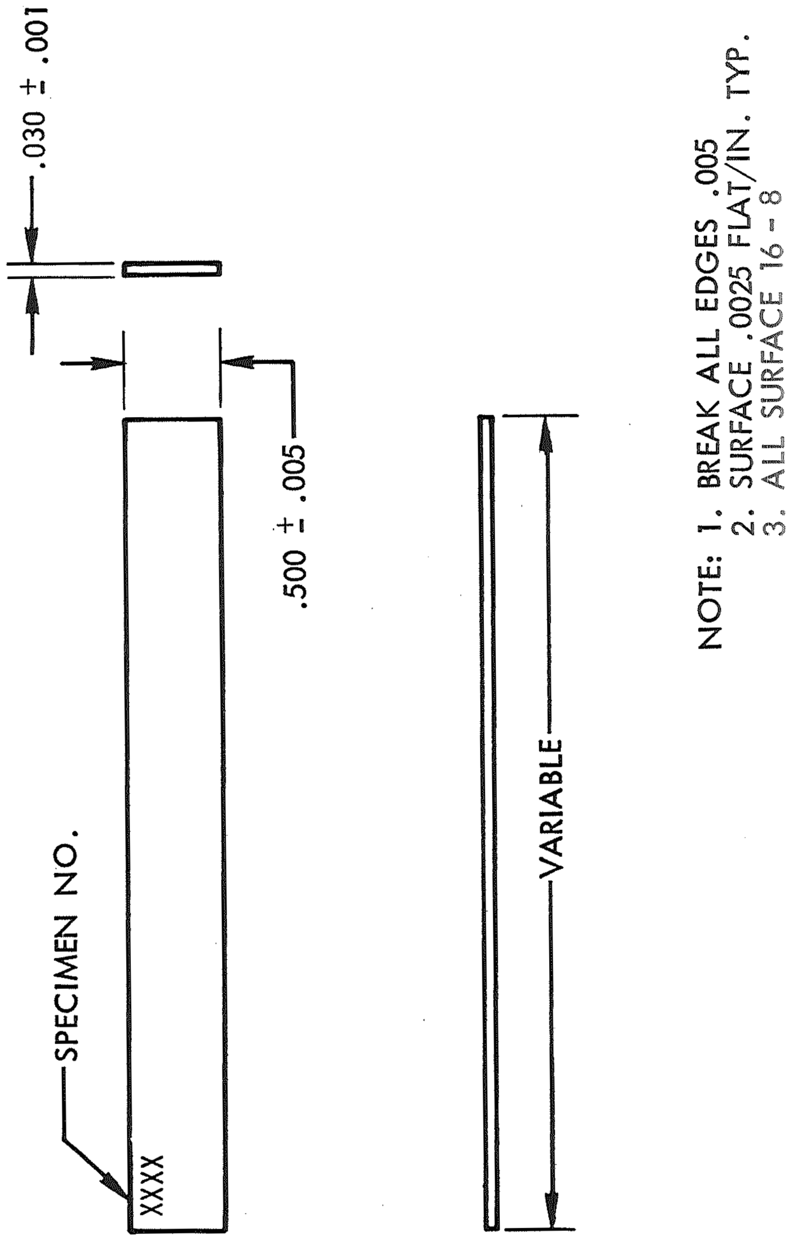


Figure C.2. Stressed Test Specimen

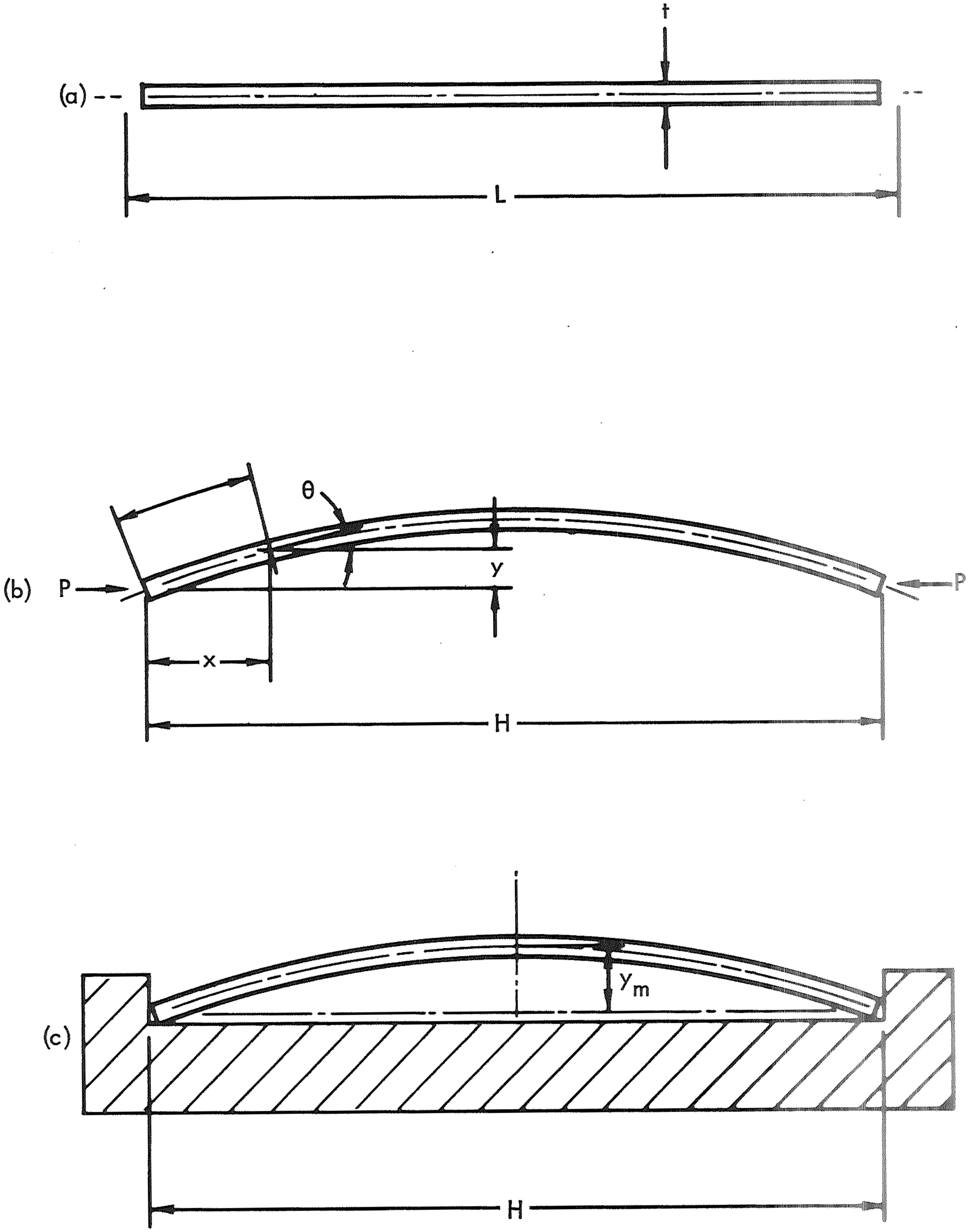


Figure C.3. Stressing of Bent-Beam Stress Corrosion Specimen water until the pH of run-off water is equal to that of the initial distilled water. Dry the specimen with dry filtered nitrogen gas. Place the specimen and stress apparatus in a clear clean plastic bag marked with the serial number of the specimen. Care must be taken to avoid hand contact after the cleaning operation. White gloves should be used to handle specimens.

APPENDIX D

PROCEDURE FOR MANUFACTURING OF TEST CAPSULES

D.1 SCOPE

The scope of this procedure includes methods used for test capsule manufacture, annealing, special cleaning, inserting specimens, glass fusing and packaging.

D.2 PURPOSE

The purpose of this procedure is to document the methods used to manufacture test capsules and to seal test specimens in the capsules.

D.3 CAPSULE MANUFACTURE

D.3.1 Capsule Section

Use a hydrogen-oxygen flame to perform all glass-blowing operations. This is to avoid leaving any carbon particles on or in the glass.

Prepare the capsule section (bottom section) to the dimensions shown in Figure D.1.

Prepare two glass rods, 0.3-inch in diameter by 2.5-inch long; for each capsule section (bottom section), except for those to contain stressed specimens.

D.3.2 Reducer Section

Using the procedure outlined in Paragraph D.3.1, prepare the reducer section to the dimensions shown in Figure D.1.

D.3.3 Anneal Test Capsules

Anneal test capsules (capsule and reducer section are separate units) in lots consisting of 250 units or less. Heat to 575°C (1067°F) and hold at this temperature for one hour. Heating rate is not critical. Cool from 575°C (1067°F) to ambient temperature at the normal furnace cooling rate. Records of temperature profiles during all annealing cycles shall be maintained.

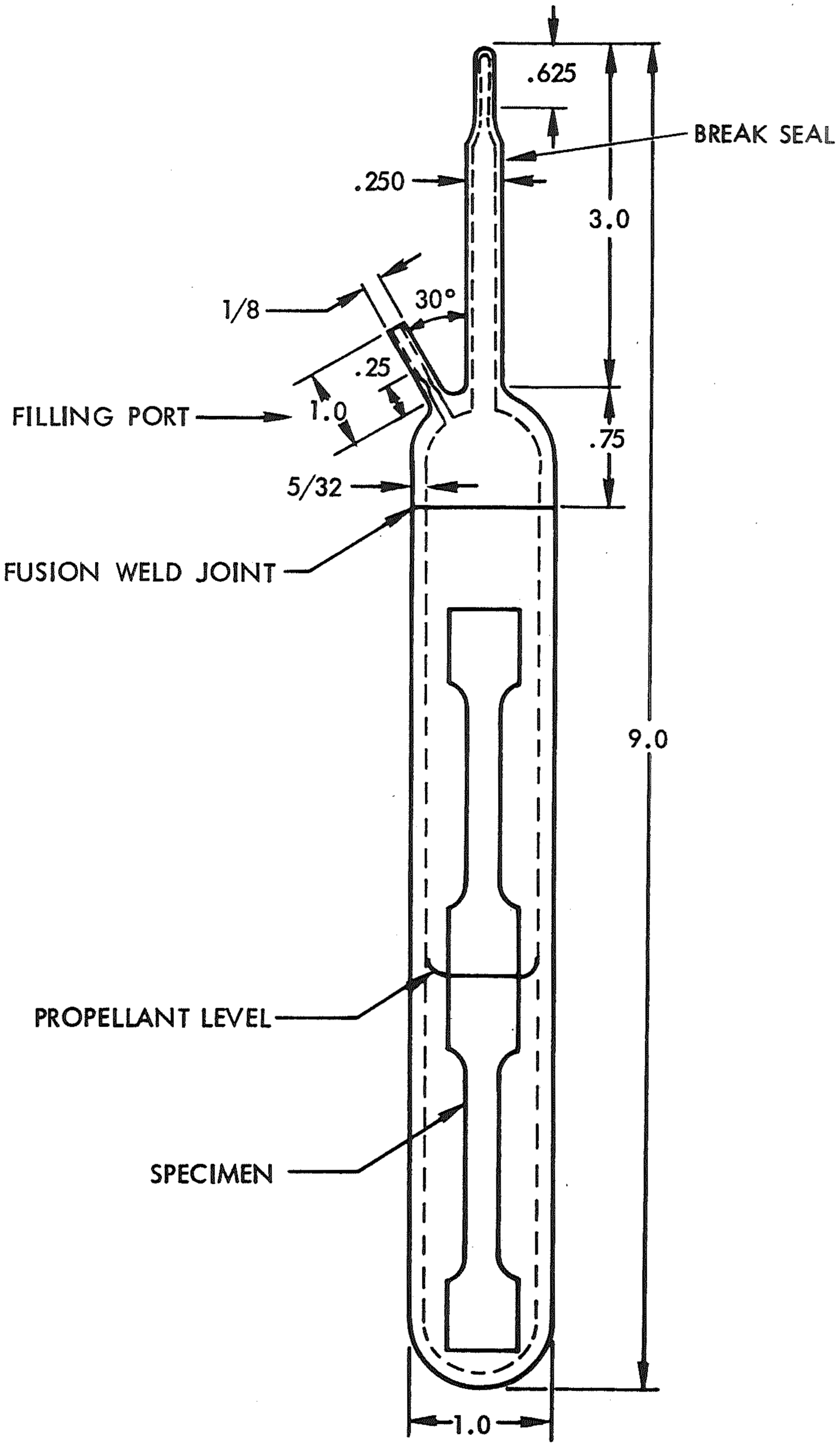


Figure D.1. Sealed Compatibility Test Capsule

D.3.4 Dissimilar Metal Specimens

For each set of dissimilar metal specimens, prepare from glass rods six "C" clamps that will hold the specimens snugly together.

D.3.5 Specimen Insertion

Thoroughly clean in a certified clean-room the capsule and reducer sections, glass rods and "C" clamps, using a 4.0% solution of liquid detergent ("Joy" or equivalent) in water at 82 ± 17°C (180 ± 30°F) for a minimum of five minutes. By use of a jet wash, thoroughly wash the break seal portion of the reducer. Thoroughly rinse all glass surfaces using a distilled water-jet spray applied directly to all portions of the surfaces prior to measuring the run-off water pH. Check the pH of the run-off water and compare this pH with the pH of distilled water. Continue rinsing until the pH of the run-off water differs by less than ±0.5 units from the distilled water. Blow dry with oil-free filtered nitrogen.

Using white lint-free gloves to hold all external glass surfaces and with forceps having TEFLON coated tips, place a specimen in a capsule bottom. There are four different types of specimens: (1) Double "dog-bone", (2) welded or brazed double "dog-bone", (3) dissimilar metals, and (4) stressed. Place the double "dog-bone" and welded or brazed specimens into the specimen capsule bottom while using lint-free gloves to hold all external glass surfaces and TEFLON coated tipped forceps to place the specimens in the capsule bottom. Then place two glass rods, 0.3-inch in diameter and 2.5-inch long, on either side of the test specimen. Clamp the dissimilar metal specimens to gether with six glass "C" clamps and insert in the capsule bottom in the manner described above. Place the stress specimen and stress apparatus in the capsule bottom in the same manner as the other specimens, except do not add glass rods because there will not be sufficient room.

While working in the clean-room, fuse the reducer to the bottom of the test capsule as shown in Figure D.1. While fusing the reducer to the bottom, purge the capsule with dry filtered argon to avoid moisture condensation in the capsule. For the fusing operation use a hydrogen-oxygen flame. Constrict the 0.125-inch O.D. tube to be used as a filling port as an aid in completing the test capsule hermetical seal. Inspect the test capsule for glass strains with a polariscope. All strains from the reducer installation should be concentrated in the test capsule neck.

By means of the filling port tube, connect the capsule to a gauge and a source of oil-free filtered nitrogen. Pressurize the capsule to 200 psig. Capsules failing to pass this test must be reconstructed being careful to re-clean specimens. Bleed the nitrogen pressure down to one atmosphere and disconnect the capsule from the nitrogen source.

By means of a rubber band, place a plastic bag over the filling port. Tag the capsule by placing over the break-seal tube a stainless steel tag scribed with the sample number. The capsule is now ready for transporting to the test site.

APPENDIX E

PROCEDURE FOR PROPELLANT FILLING OF CAPSULES

E.1 SCOPE

This procedure describes the propellant loading of specimen capsules, sealing of capsules, and the placing of capsules in storage canisters for transporting to -230°F conditioning flasks.

E.2 PURPOSE

The purpose of this procedure is to provide sufficient detail for the safe filling of propellant into specimen capsules.

E.3 FILLING CAPSULES

E.3.1 Preparing Capsules for Loading

Connect 0.125-inch stainless steel tubing to valves 1-5 shown on the Propellant Handling Manifold drawing (Figure E.1). By means of a Swagelok fitting with Teflon ferrules, connect four filling ports on four compatibility test capsules. By means of a vacuum pump attached at valve 14, with valve 9, 11, 13, 14, 15, 16, and 19 closed, evacuate the manifold and specimen capsules for one hour. With safety shield in place, close valve 14 and introduce approximately 1.1 atmospheres of propellant from propellant supply tank. (The following section describes the introduction and removal of the pre-treatment of passivation propellant.) Allow the propellant to remain in the system for 0.5 hours and then evacuate the system.

E.3.2 Introduction and Removal of Pre-Treatment Propellant

(The introduction and removal of OF_2 and B_2H_6 is similar, but discussed separately to avoid confusion. Nearly identical manifolds are used for handling both propellants.)

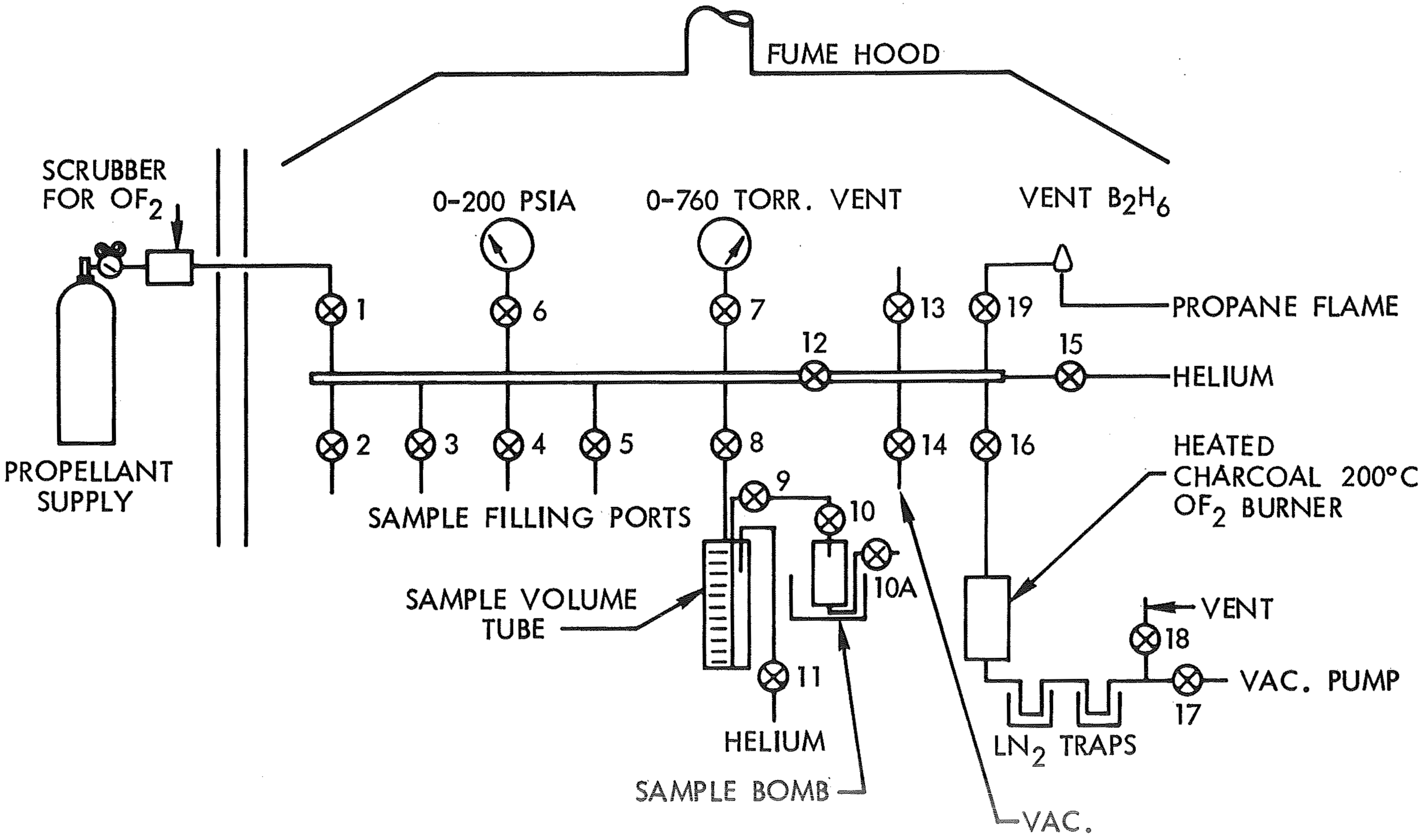


Figure E.1. Propellant Handling Manifold

By means of the line attached to valve 1, OF_2 is introduced to the system. Connect the supply tank to a fluorine pressure reducing regulator, designated as No. B-15F-F70M by the Matheson Company. Connect this valve to a rod extending through a barricade that is to be used for setting the regulator at 10 psig. Connect the OF_2 cylinder to a manually actuated gear box that can be operated by an extension handle passing through a barricade. Connect the gas regulator with 0.25-inch stainless steel tubing to a sodium fluoride-hydrogen fluoride packed trap available from the Matheson Company. Then by means of 0.25-inch stainless steel tubing, connect the hydrogen fluoride trap to the manifold.

With valve 1 closed, open the OF_2 supply cylinder and adjust the regulator to 10 psig. Introduce by valve 1 about 1.1 atmosphere of OF_2 into the system. After 0.5 hours, remove the propellant by means of a vacuum pump attached to valve 17 with valve 18 closed. Allow the propellant to pass over a 200°C charcoal burner by opening valve 16. Condense the CF_4 formed by the charcoal burner in liquid nitrogen cooled metal traps. At the end of each day, discharge through a vent tube into a hood or high vent line the CF_4 in the traps by closing valves 16 and 17, opening valve 18 and allowing the traps to warm.

By means of valve 1 on a manifold similar to the one used for OF_2 handling, B_2H_6 is introduced into the system. Connect the gas supply outlet of the B_2H_6 tank to valve 1 by means of 0.25-inch stainless steel tubing. While the B_2H_6 cylinder is in a dry-ice packed container and the line between valve 1 and the B_2H_6 supply tank is evacuated, open the gas supply valve on the B_2H_6 tank. By means of valve 1, introduce 1.1 atmospheres of B_2H_6 into the propellant handling manifold and the attached specimen capsules. Allow the B_2H_6 to remain in the system for 0.5 hours. Then remove the B_2H_6 by pumping through a vacuum pump attached to valve 14. (Small quantities of gaseous B_2H_6 can be pumped through a vacuum pump contained in a fume hood, but larger quantities, especially condensed liquid, must be burned in the propane flame.)

E.3.3 Loading of Propellant into Capsules

Place a clear liquid nitrogen filled Dewar around the graduated quartz sample volume tube. Be sure the entire manifold and sample capsules are evacuated (valves 2, 3, 4, 5, 6, 7, 8, and 12 are opened; valves 1, 9, 11, 13, 14, 15, 16, and 19 are closed). Then by means of valve 1, slowly allow propellant to enter manifold and 10 ml of liquid to condense in the sample volume tube. Do not allow the pressure in the manifold to exceed 1 atm. If any non-condensables, such as hydrogen in B_2H_6, can be detected on the 0.760 torr gage, remove the non-condensables in the manner described for removing the Pre-Treatment Propellant (Section E.3.2). Non-condensables should not be present in OF_2. Close valves 3, 4, and 5. Place a clear liquid nitrogen filled Dewar under each of the sample capsules. By means of a laboratory jack, raise the Dewar to submerge a 4-inch length of the sample capsule in liquid nitrogen. Remove the Dewar from the sample volume tube and allow the propellant to transfer to the sample capsule attached to valve 2. Determine that the propellant submerges one-half of the test specimen. Add, if required, additional propellant to submerge one-half of the test specimen by the procedure described above.

By means of a four-foot extension on a hydrogen-oxygen torch, seal the filling port on the sample capsule. (This operation should be performed using all safety precautions because it is the most hazardous operation in the entire plan.) While the first sample capsule is cooled in liquid nitrogen, fill the other three capsules in an identical manner. Plac e a canister (Figure E.2) into a liquid filled Dewar that is attached to a cart with safety shield mounted. Then by means of tongs place the four sample capsules in the canister. Transfer the loaded canisters to the conditioning flasks. The above operation can be repeated until all the sample capsules are loaded.

E.4 PROPELLANT SAMPLING

Collect a liquid sample of both propellants according to Appendix F, "Procedure for Collecting Propellant Samples."

SAFETY NOTES: Anyone working with OF_2 or B_2H_6 should be familiar with all safety precautions recommended by the suppliers. Protective clothing, neoprene gloves and face shields should be worn at all times. Safety shields should be between the operator and all equipment containing the propellants.

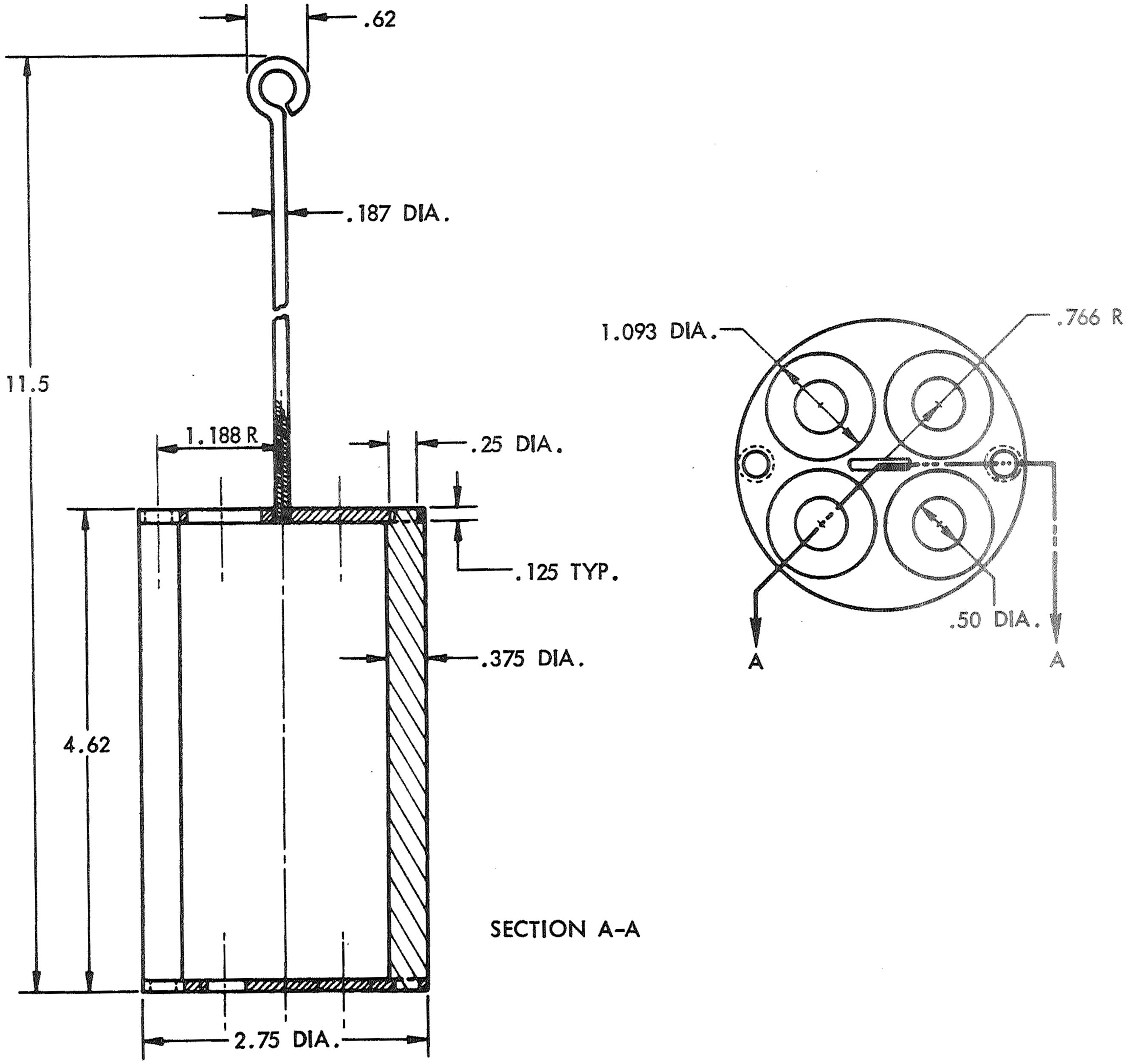


Figure E.2. Canister Modification

APPENDIX F

PROCEDURE FOR COLLECTING PROPELLANT SAMPLES

F.1 SCOPE

This procedure describes the collecting of gaseous and liquid propellant samples.

F.2 PURPOSE

The purpose of this procedure is to provide details for the collecting gaseous and liquid propellant samples for analysis. Samples are to be taken of the initial propellant and the propellant removed at the completion of compatibility tests.

F.3 SAMPLE COLLECTION

F.3.1 Initial Propellant Samples

Evacuate the propellant handling manifold through Valve 14 for B_2H_6 and Valve 16 for OF_2, with Valves 1, 2, 3, 4, 5, 11, 13, 15, 18 and 19 closed. (See Figure F.1). The sample bomb connected to Valve 10 is a heavy walled stainless steel tube, 1/4-inch i.d. x 4-inch long. (See Figure F.2). Place the evacuated sample bomb in a liquid nitrogen filled Dewar. Then place 3 ml of liquid propellant into the sample volume tube in the manner described in Appendix 4, "Procedure for Propellant Loading of Capsules," Section 2.3, "Loading of Propellant into Capsules." With 50 psig of helium supplied to Valve 11, carefully supply helium pressure to transfer 1 ml of liquid propellant into the sample bomb. Close Valve 10. Remove the liquid nitrogen Dewar from the sample volume tube and dispose of the propellant in the same volume tube. If B_2H_6 is the propellant, allow the propellant to escape through Valve 19 to the propane flame until all the liquid in the sample volume tube is gone. When the pressure in the manifold drops to 1.5 atm, close Valve 19 and pump with a vacuum pump in a fume hood the remaining propellant through Valve 14. If OF_2 is the propellant, pump the propellant through the 200°C charcoal burner. The traps in Figure F.1 are liquid nitrogen cooled to collect CF_4. At the end of each day, allow the trap to warm and vent the contents through Valve 18.

With the valves on the sample bomb closed, disconnect the sample bomb and immediately pack in dry ice. While still packed in dry ice, the liquid

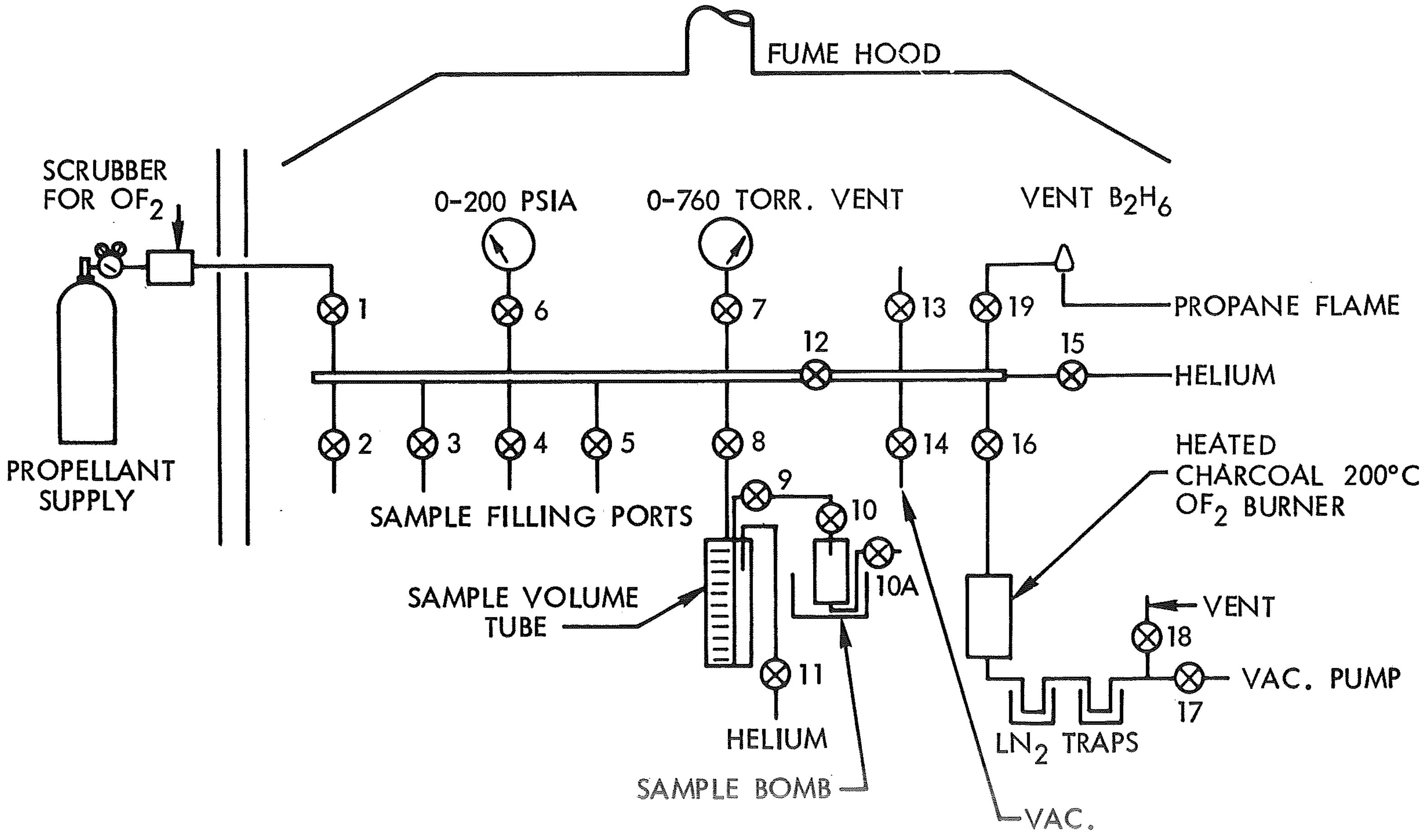
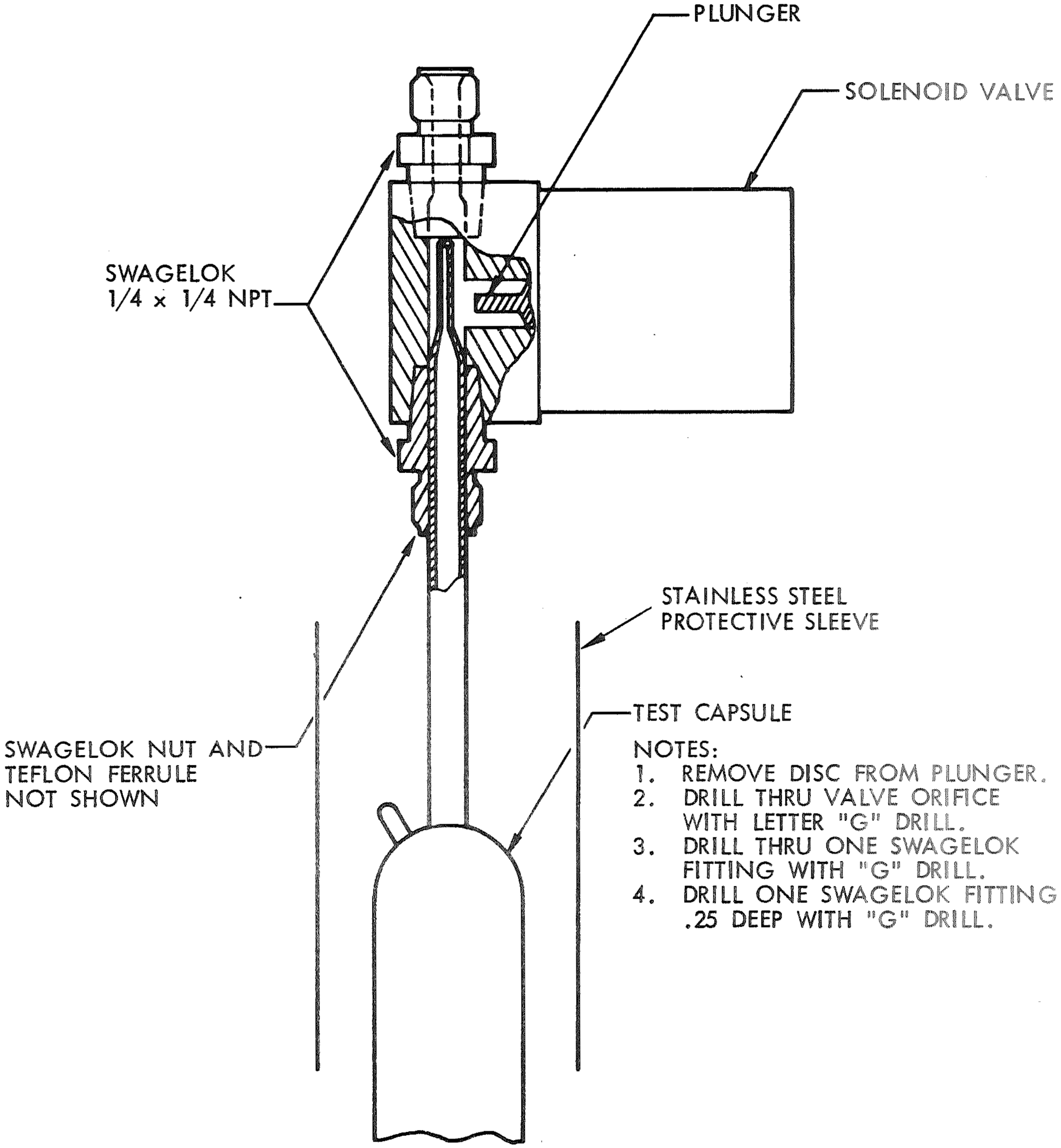


Figure F.1. Propellant Handling Manifold



NOTES:

1. REMOVE DISC FROM PLUNGER.
2. DRILL THRU VALVE ORIFICE WITH LETTER "G" DRILL.
3. DRILL THRU ONE SWAGELOK FITTING WITH "G" DRILL.
4. DRILL ONE SWAGELOK FITTING .25 DEEP WITH "G" DRILL.

Figure F.2. Propellant Sampling Bomb

propellant in this bomb can be connected to a mass spectrometer for B_2H_6 analysis and to a gas chromatograph for OF_2 analysis.

At the completion of compatibility testing, non-condensable propellant (not a liquid at liquid nitrogen temperature) are collected in the same sampling bomb used for liquid propellant sampling. The condensing of liquid in the sample volume tube and the helium pressure transfer will not be involved. Condensable liquid propellant samples are taken at the completion of compatibility testing. Collect a 1 ml liquid sample as described above after the volume is measured as described in Appendix H, Section H.3.2 "Opening of Specimen Capsule."

After sampling operations, evacuate and then fill the propellant handling manifold with slightly over 1 atmosphere of helium to prevent moisture from entering the manifold.

APPENDIX G

PROCEDURE FOR STORAGE OF SPECIMENS

G.1 SCOPE

This procedure describes the placing of canisters loaded with specimen capsules into the temperature conditioning flasks, the storage of specimens, and the removal of canisters from the temperature conditioning flasks.

G.2 PURPOSE

The purpose of this procedure is to provide sufficient information for the safe loading, storage, and unloading canisters from the temperature conditioning flasks and a description of how the controls are to be operated for delivering liquid nitrogen into the conditioning flasks.

G.3 SPECIMEN STORAGE

G.3.1 Loading of Canisters into Conditioning Flasks

Set the controller for the primary liquid nitrogen (LN_2) supply at -230°F (see Figure G.1). Set the controller for the emergency LN_2 supply at -180°F. Then with the primary LN_2 supply turned off, cool the flask to -180°F with the emergency supply controller. Connect the thermocouples (there are two in the flask) to a multipoint recorder and plot the temperature for 24 hours. Then with the primary LN_2 supply controller turned on, allow the flask to reach -230°F. Again, plot the temperature as measured by both thermocouples for 24 hours. After the controllers have been demonstrated to control the temperature, turn the controller on the primary LN_2 supply to -320°F and allow the conditioning flask to fill about half full of LN_2. When the thermocouple attached to the controller continuously reads -320°F, the flask should be half full. Turn off the LN_2 supply and visually determine the level of LN_2 in the flask. Leave the primary controller set at -230°F. Connect the thermocouples as shown in Figure G.1.

Transport one canister loaded, as described in Appendix E, to the temperature conditioning flask. The canister is in LN_2 on a cart with a safety shield. Then place the canister into the conditioning flask, and hook the handle into the slot provided at the mouth of the flask. Repeat this procedure until the flask is loaded with nine canisters. Maintain the flask at -320°F until all adjacent flasks are loaded. After the flasks

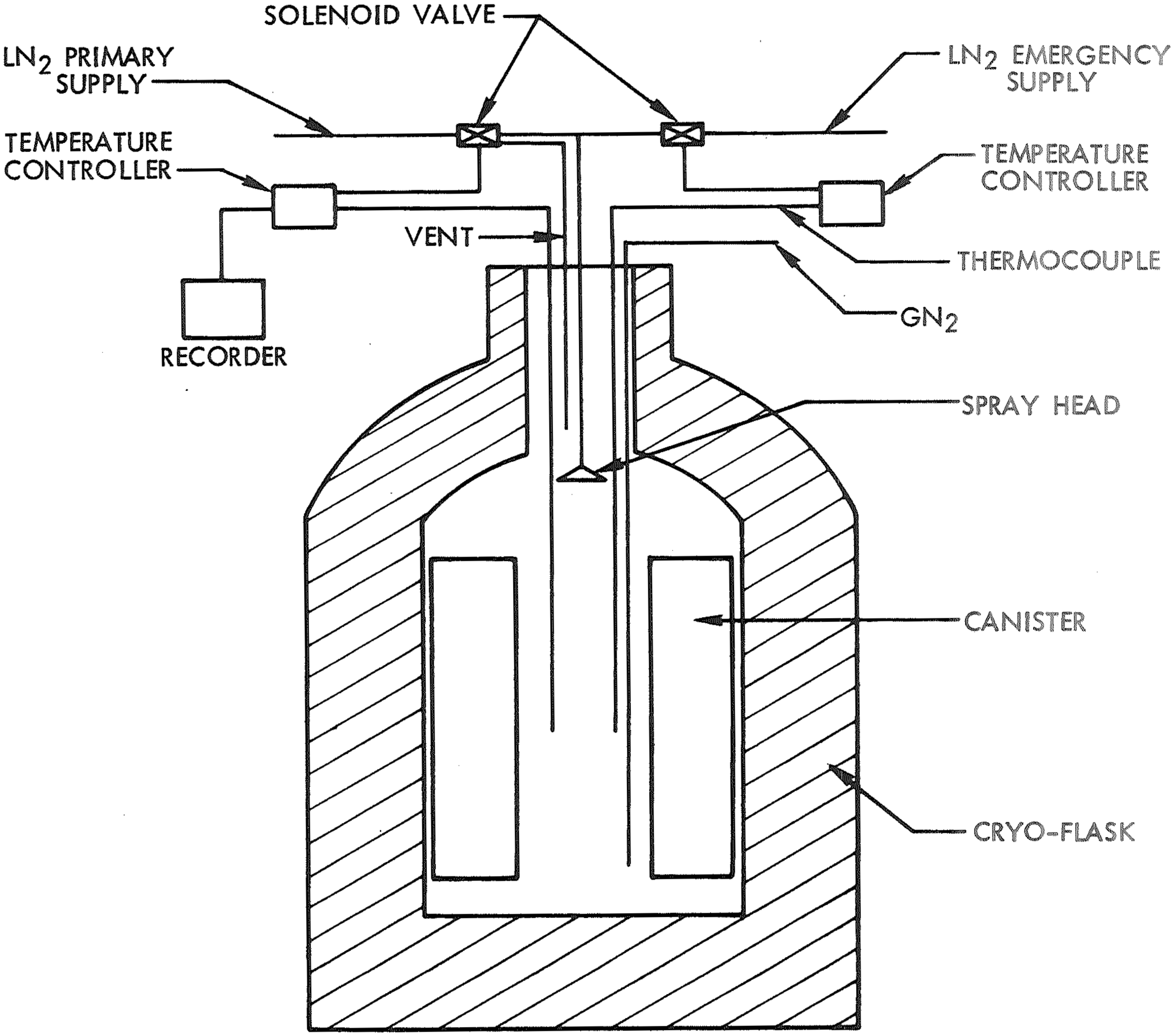


Figure G.1. Conditioning Flasks and Controls have been loaded, adjust the primary LN_2 controller to -230°F. Warm the flask to -230°F by slowly flowing gaseous nitrogen into the flask using a 0.25-inch tube inserted in the bottom of the flask.

G.3.2 Storage of Specimen

Record the temperature in the flasks by means of a multipoint recorder. Determine daily that LN_2 controllers are functioning properly and that the LN_2 supply tanks contain adequate supplies of LN_2. If a malfunction develops, fill the storage flask with LN_2 by adjusting either the primary or emergency controller to -320°F. If the electrical power service is interrupted, the normally open solenoid valve on the emergency LN_2 supply line will open and fill the flask with LN_2. After electrical power is restored, bring the temperature in theflask back up to -230°F by flowing gaseous nitrogen into the flask.

G.3.3 Unloading of Canisters from Temperature Conditioning Flasks

Care must be exercised when unloading the temperature conditioning flasks because the pressure in the specimen containers is unknown, but the pressure is less after cooling to -320°F than it was at -230°F; thus, permitting safe removal of the canisters.

Fill the conditioning flask half full of LN_2 in the same manner used in loading the flasks. Remove one canister at a time from the conditioning flask and place the canister in a LN_2 cooled Dewar mounted to a cart equipped with safety shields. Push the cart to the handling manifold for opening the specimen capsules.

APPENDIX H

PROCEDURE FOR REMOVING PROPELLANT FROM SPECIMEN CAPSULES

H.1 SCOPE

This procedure describes the removal of propellant from the specimen capsule.

H.2 PURPOSE

The purpose of this procedure is to describe the safe unloading of propellant from the specimen capsule.

H.3 OPENING CAPSULE

H.3.1 Connecting Capsule to Propellant Handling Manifold

While the canister is in the LN_2 filled Dewar, raise the bottom plate of the canister (Figure H.1) by lifting with tongs the 0.125-inch rod attached to the bottom plate of the canister. Remove with tongs the metal protective tube from one of the capsules and by means of tongs remove the specimen capsule from the canister. Immediately place the specimen capsule in a LN_2 filled Dewar flask. While immersed in LN_2, manipulate the specimen capsule into position for connection to the opening device (Figure H.2) attached to the manifold at Valve 2 (Figure H.3), by means of a laboratory jack and tongs. Connect the specimen capsule to the opening device using a Swagelok nut and Teflon ferrules as indicated in Figure H.2. While the manifold is evacuated, open Valve 2 and allow the tip of the specimen capsule to remain in a vacuum for 15 minutes to remove any moisture on the surface of the capsule tip.

H.3.2 Opening of Specimen Capsule

With Valves 1, 3, 4, 5, 11, and 12 and Valve 10A closed, use a 28-volt power supply to actuate the solenoid of the opening device which will crush the tip of the specimen capsule. Observe if the pressure in the system increases by observing the 0-760 torr gage on the propellant handling manifold. If pressure increases, note the pressure on the Test Specimen Data Sheet for the specimen in the capsule. Calculate the quantity of noncondensable gas as follows:

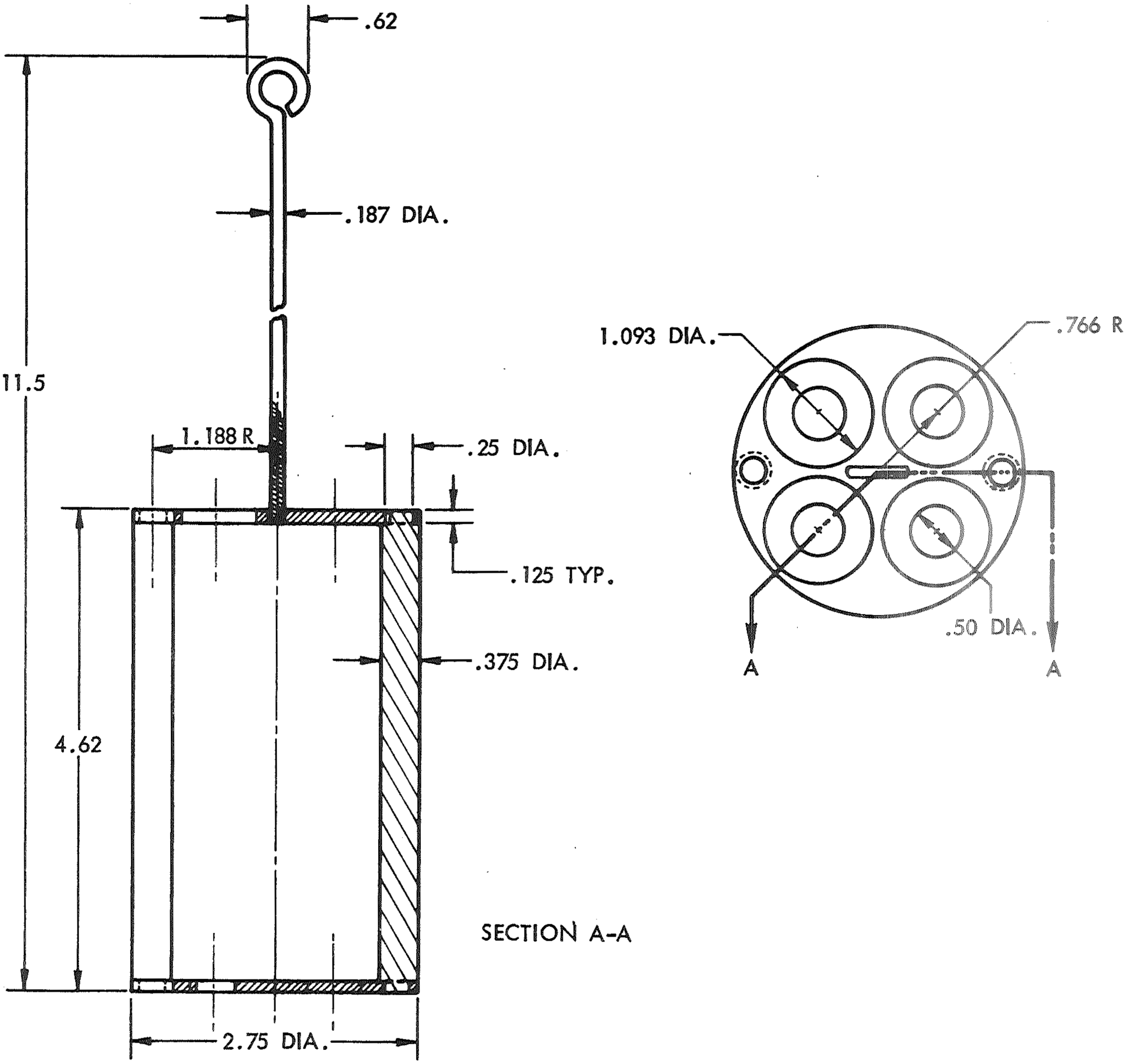
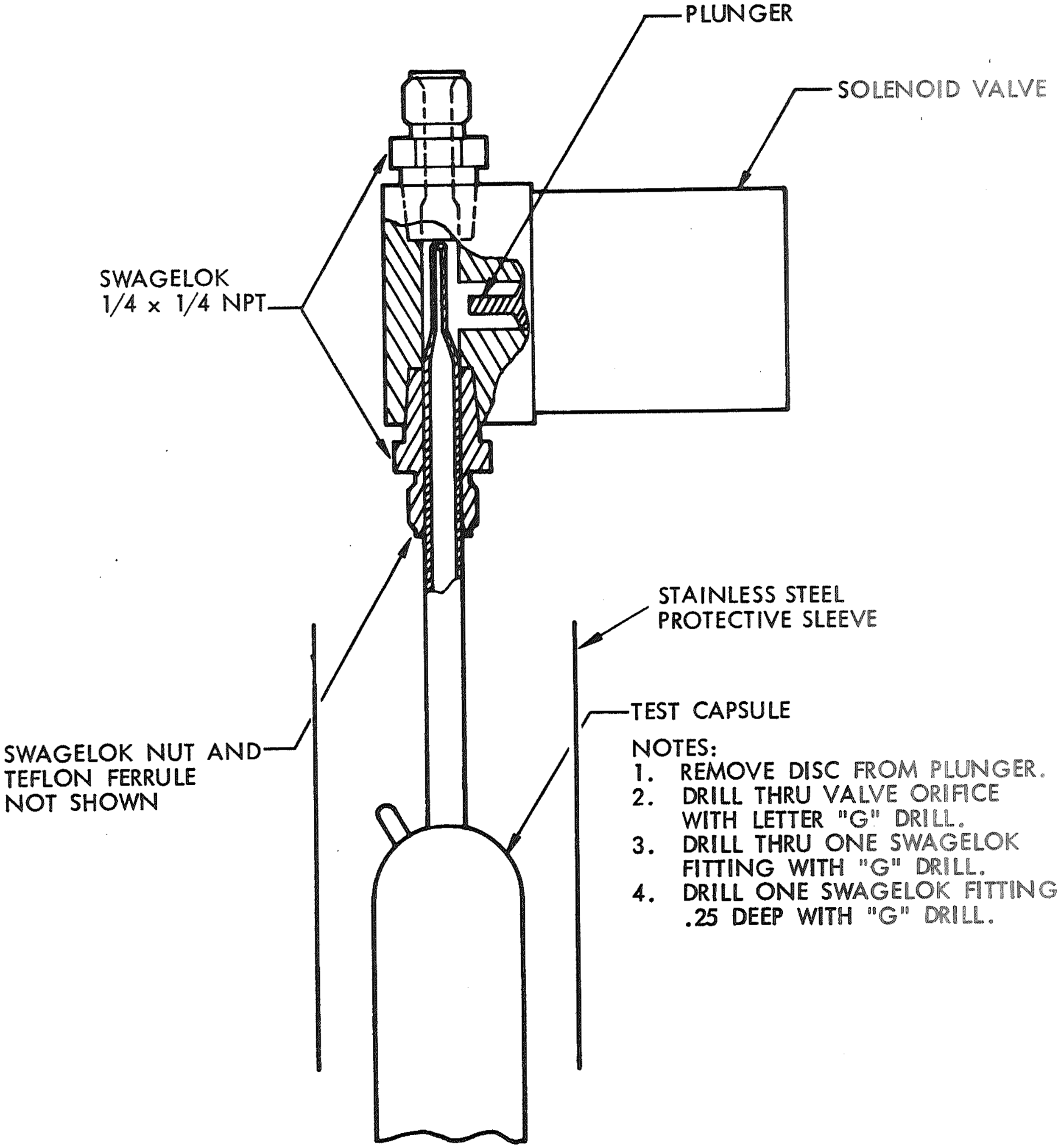


Figure H.1. Canister Modification



NOTES:
1. REMOVE DISC FROM PLUNGER.
2. DRILL THRU VALVE ORIFICE WITH LETTER "G" DRILL.
3. DRILL THRU ONE SWAGELOK FITTING WITH "G" DRILL.
4. DRILL ONE SWAGELOK FITTING .25 DEEP WITH "G" DRILL.

Figure H.2. Capsule Opening Device

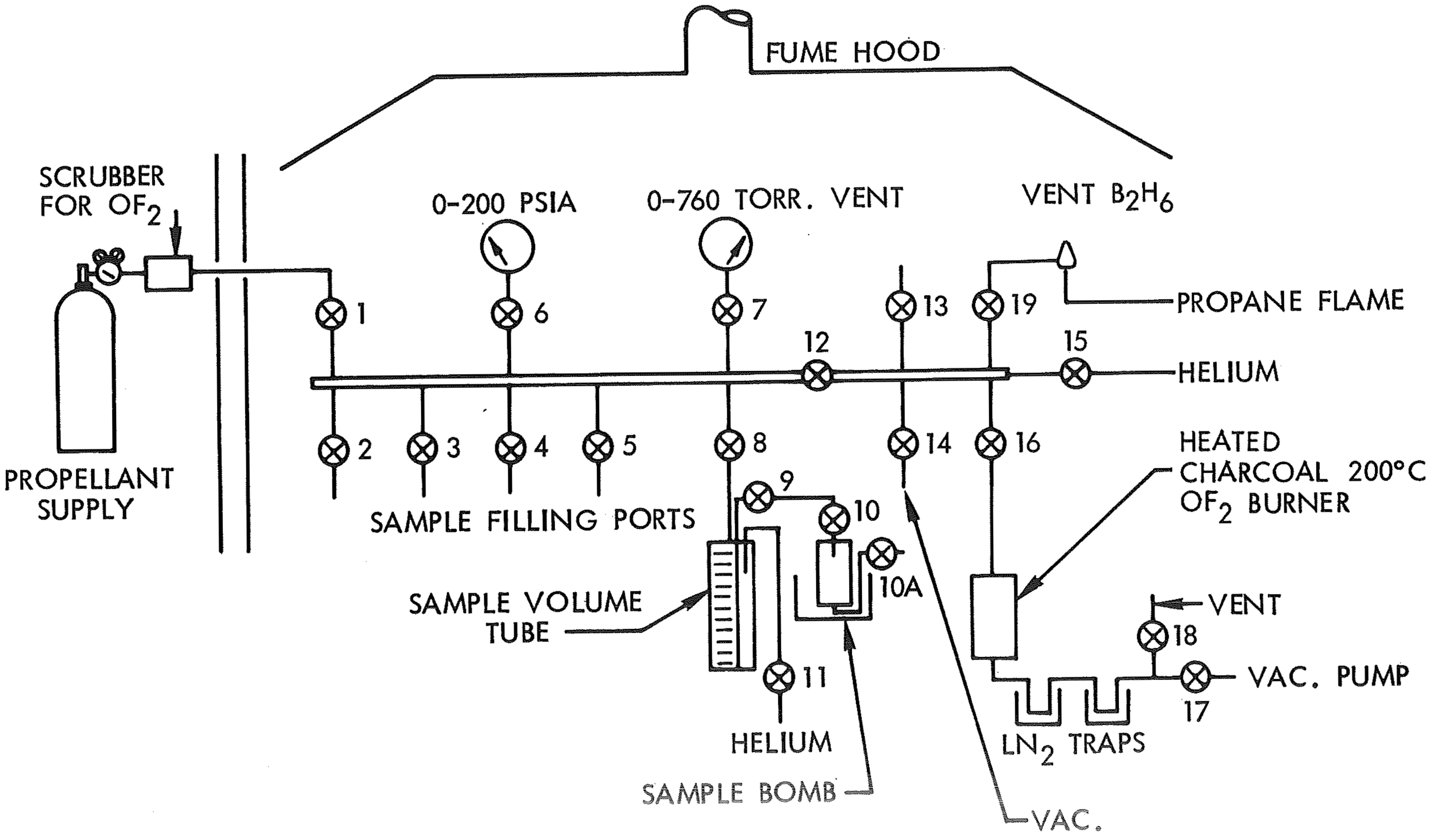


Figure H.3. Propellant Handling Manifold

$$\text{cc STP} = \frac{273\ PV}{760T}$$

where: P = pressure in manifold, torr
V = volume of manifold and sample bomb open, cc (must be calibrated)
T = temperature of manifold, °K

If any non-condensable gas is detected, collect a sample by closing Valve 10. Then close Valve 9 and disconnect the sample bomb. Submit the sample to mass spectrometer analysis.

With a sample bomb connected at Valve 9 and Valves 9 and 10 open, place the sample volume tube in a clear Dewar flask filled with LN_2. Remove the LN_2 filled Dewar flask from the specimen capsule and allow the propellant to vacuum transfer to the sample volume tube. Measure the propellant volume and record on the Test Specimen Data Sheet. Remove a one ml liquid sample according to the procedure in Appendix F.

H.3.3 Disposal of B_2H_6

After the valves on the sample bomb are closed, open Valve 12 with Valves 7, 13, 14, 15, 16, and 19 closed. Light the propane burner. Remove the LN_2 from the sample volume tube. When the pressure in the manifold exceeds 1.5 atmospheres, open Valve 19 slowly and leave open until the pressure in the manifold drops below that pressure. Repeat the bleeding of B_2H_6 vapors into the propane flame until all the liquid B_2H_6 is removed from the sample volume tube. With Valve 19 closed, open Valve 7 and pump the remaining B_2H_6 through the vacuum pump attached to Valve 14. With the specimen capsule attached to the manifold, fill the manifold to atmosphere with helium.

H.3.4 Disposal of OF_2

Dispose of liquid OF_2 in a similar manner to that described above for disposal of B_2H_6, with the exceptions described below. After removal of the LN_2 filled Dewar flask from the sample volume tube and the pressure in the manifold exceeds 1.5 atmosphere, instead of through Valve 19, slowly bleed the OF_2 through Valve 16 to the charcoal burner with the vacuum pump attached at Valve 17 and Valve 18 closed. At the end of each day, close

Valves 16 and 17, remove LN_2 from the metal traps, and vent the trapped CF_4 through Valve 18.

H.3.5 Closing of Specimen Capsules

By means of a hydrogen-oxygen torch seal the tip of the specimen capsule. The capsule is filled with 1.0 atmosphere of helium at this time. By ordinary handling techniques the specimen capsules are shipped to a metallurgical laboratory for examination.

APPENDIX I

PROCEDURE FOR POST TEST EXAMINATION

I.1 SCOPE

This procedure describes the post test examination of non-condensable gases, propellant and specimens.

I.2 PURPOSE

The purpose of this procedure is to describe the techniques that are recommended for post test examination of non-condensable gases, propellant and specimens.

I.3 EXAMINATION OF NON-CONDENSABLE GASES

Submit the contents of the sample bomb (see Appendix H. Section H.3.2) containing non-condensable gases to mass spectrometric analysis. This sample bomb should contain no corrosive material from either the OF_2 or B_2H_6 compatibility studies.

I.4 EXAMINATION OF LIQUID PROPELLANTS

Submit liquid samples collected (see Appendix H. Section H.3.2) to the following analyses:

Propellant	Method of Analysis
B_2H_6	Mass Spectrometer
OF_2	Gas-Liquid Partition Chromatography

I.5 EXAMINATION OF TEST SPECIMENS

Pack in a box to protect from breakage. Capsules sealed according to the procedure in Appendix H, Section H.3.5. Transport the sealed capsules to a clean room for opening. By means of diamond tool scratch a line around the capsule and open by placing a heated rod against the scratch on the capsule. The final opening operation may be performed in a dry box if this appears desirable. Collect any residue in the bottom of the capsule, weigh residue and then submit it to identification analysis. (The method of analysis must be selected at this time, but X-ray diffraction is recommended.) Weigh the specimen and carefully remove any adhering salts with a Teflon coated tool. Weigh the adhering salts and submit them to the same analysis as the residue found in the capsule. Examine the specimen by means of a microscope. If any changes are noted at the propellant-vapor interface line, cut this section from the specimen for metallurgical examination. If no changes are noted at the interface line, cut the two dog-bones apart and submit both specimens to tensile testing in accordance with ASTM Method E8-57T. Record all results on the forms shown in Figures 16-18 of the final report. If corrosion is detected by visual and microscope inspection or by tensile testing, perform a detailed metallographic examination on corroded materials.