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STUDY TO DETERMINE AN IMPROVED METHOD FOR APOLLO PROPELLANT SYSTEM DECONTAMINATION AND PROPELLANT TANK DRYING

FINAL REPORT

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I. INTRODUCTION

This report describes the work accomplished in Phase I and Phase II and is submitted in partial fulfillment of NAS 9-4605 contract, "A Study to Determine An Improved Method for Apollo Propulsion System Decontamination."

Effective decontamination of the Apollo propulsion system containing N_2O_4 as the oxidizer and 50% UDMH/50% hydrazine as the fuel is necessary to eliminate the possibility of personnel exposure to toxic vapors when a system or components are being disassembled for inspection or maintenance. Thorough decontamination is required, also, when a system is to be stored for an indefinite period of time.

Numerous methods have been used to decontaminate assembled systems and components. However, a completely satisfactory procedure has not been established for the Apollo propulsion systems. The "Tri-Flush" method of decontamination has some undesirable characteristics, respecting (1) possible formation of salts in crevices from reaction of the neutralizer with the propellant, (2) the requirement of large quantities of three flushing fluids in the launch area, (3) the questionable effectiveness of this method unless extensive flushings have been made, and (4) possible formation of nitric acid.

About the time The Dow Chemical Company was awarded this contract, the "Tri-Flush" cleaning method was abandoned in favor of the "Single-Flush" method which did not have the above objectionable features. The "Single-Flush" method uses methanol for the fuel side and Freon® MF for the oxidizer side as the flushing solvents at ambient temperature. The procedure is to fill the systems with the respective solvents, drain, and dry with GN_2.

It is also necessary to insure that the propellant tanks are completely free of all propellant, including referee or substitute propellants, and/or moisture before leak tests are conducted using helium; otherwise, the trapped residual propellant and/or moisture will act as a barrier and prevent an accurate determination of helium leakage rates.

II. OBJECTIVE

The objective of this study is a decontamination method which does not involve long time periods or large quantities of materials. It must be a reliable procedure and include appropriate means of measuring or detecting trace quantities of contaminants. Additional restrictions limit the choice of solvents. The use of water or aqueous-based solvents is undesirable because of the drying problems which would lengthen the procedure time. Also, high localized concentrations of nitric acid could be formed in crevices and capillaries of the oxidizer system. The solvents used should be adequately inert toward the propellants and materials of construction, have acceptable toxicity properties, be economical, and be sufficiently volatile to be easily removed.

III. SUMMARY

The experimental work in Phase I was done in laboratory bench-scale apparatus and includes studies of (1) compatibility of solvent with propellant and components, (2) method of decontamination, (3) efficiency of solvents, (4) temperature effects, (5) diffusion rates of propellants from the elastomers, (6) removal of propellants from flushing solvents, and (7) a survey of the published literature, proprietary information, and private correspondence on the technology of the decontamination of rocket propulsion systems.

The work in Phase II includes design, construction, and operation of a test unit which consisted of a test vessel, pumps, solvent storage tanks, heat exchangers, a vent gas scrubber, a filter, adsorption and drying columns, instruments, and the necessary piping and control valves. The titanium test vessel was cylindrical with hemispherical heads and was approximately 1/20th the size of an Apollo service module propellant tank. Tests were made in this unit that compared single-flush cleaning (present method) with vapor-phase cleaning (proposed method) and pressure cycle vapor-phase cleaning. The costs of the two methods were estimated and compared.

IV. CONCLUSIONS

1. The propellants, Aerozine-50 and N_2O_4, are not appreciably adsorbed on the metal walls of the propellant system.

2. The elastomers contain most of the residual contaminant after the system has been flushed with a solvent.

3. The rate at which the contaminant is released from the elastomer is independent of the environment at a given temperature. No detectable difference was noted in the efficiencies of the various solvents tested in removing contaminants from the elastomers.

4. Temperature is the major factor determining the rate of release of contaminants from the elastomers. The rate of release was found to double for every 15° C increase in temperature.

5. Heat may be introduced into the system by the vapors of a boiling solvent. Methanol is satisfactory for use in Aerozine-50 decontamination and Freon® MF is satisfactory for use in N_2O_4 decontamination.

6. Vapor-phase cleaning is feasible and has advantages over liquid flushing as follows:

   a. Latent heat of vaporization of solvent is available to heat the system uniformly throughout.

   b. Flowing film of condensed solvent vapor is effective in removing solid, as well as liquid contaminants.

   c. All surfaces within the system are bathed by the flowing condensate film.

   d. Vapor-phase flushing reduces contamination to a lower level than obtained by liquid flushing.

   e. Vapor-phase flushing requires less time by a factor of five to reach a given level of contamination.

   f. The solvent required is reduced by a factor of at least two, maybe five.

   g. The volume of purge gas required for drying the system is reduced by a factor of five.

   h. The associated equipment to decontaminate the service module of the Apollo would not be complex if the vapor-phase flushing was accepted.

7. Substantial improvement in effectiveness of vapor-phase cleaning is obtained by several cycles of raising and lowering of the pressure in the system being cleaned.

8. The results of tests indicate that the flushing solvents can tolerate several hundred parts per million of the contaminant and still effectively extract the contaminant from the elastomer.

9. Aerozine-50 is efficiently removed from methanol and Freon® 113 by cation exchange resin (Dowex® 50W-X8, 50-100 mesh, H^+).

10. Silica gel, water-swollen and containing dissolved sodium hydroxide, is a satisfactory method for removing N_2O_4 from the flushing solvent.

11. Cleaning an Apollo service module propellant system is estimated to require one full day and to cost well over $11,000 when accomplished by the single-flush procedure. This is compared with a time requirement of less than one-half day at a cost of about $600 if decontamination is accomplished by the proposed pressure-cycle vapor-phase cleaning procedure.

V. RECOMMENDATIONS

1. Continued use of methanol and of Freon® MF as the cleaning solvents in decontamination of the Apollo service module.

2. Operate the test unit to obtain design data for full-scale equipment.

3. Design, construct, and place in service a mobile unit with equipment having the capabilities for pressure-cycled, vapor-phase cleaning of the Apollo service module and for solvent reclamation.

VI. UNIT 1 - SOLVENT SCREENING

A. Summary

1. The detonation tests with Aerozine-50 and the candidate solvents were inconclusive since there was no discernable difference in the order of magnitude of the explosion with or without the solvent.

2. The results of the detonation tests show fourteen solvents or solvent mixtures were compatible with N_2O_4. No explosions occurred when the solvents were added to N_2O_4 and the mixture shocked with a blasting cap.

3. Correlating the results of the thermodynamic calculations with the knowledge of compatibility gained from the detonation tests, the following generalizations appear valid:

   a. Solvent-N_2O_4 systems having a ΔF value less than 2 Kcal/gram N_2O_4 are not detonatable regardless of the size of the triggering charge. These solvents are compatible with N_2O_4.

   b. Solvent-N_2O_4 systems showing a ΔF value greater than 2 Kcal/gram N_2O_4 can be detonated if given sufficient shock. These solvents are not compatible with N_2O_4.

4. The results of the compatibility study of elastomers with candidate solvents are given below:

   a. Teflon® TFE and FEP are compatible with the propellant and all solvents.

   b. Kel-F No. 300 was not compatible with the propellant. Failure occurred within one week in the N_2O_4 test and within three weeks in the Aerozine-50 test.

   c. Kynar was found to be compatible with propellant and solvents.

   d. Stillman SR634-70 rubber was not compatible with Aerozine-50. Failure occurred within five weeks. By comparison, B. F. Goodrich' IIR-50 butyl rubber showed a gain in tensile strength.

   e. Rulon was found to be compatible with propellant and solvents.

5. The elastomers absorb a substantial quantity of propellant. The results show that the amount of contaminant diffused from the elastomer per unit of time is proportional to the amount present at that time; therefore, the rate the contaminant diffuses from the elastomer can be expressed mathematically by this equation:

$$K = \frac{2.303}{t_2 - t_1} \cdot \log \frac{c_1}{c_2}$$

where: c_1 = the initial concentration
c_2 = the final concentration of contaminant in the elastomer
t_1 = the initial time
t_2 = the final time

The constant (K) is the specific rate constant or velocity constant for a first order reaction.

a. The specific rate (K) for the diffusion of N_2O_4 from Teflon® FEP at ambient temperature shows values of 1.4×10^{-3}, 1.5×10^{-3}, and 1.8×10^{-3} in environments of GN_2, Freon® TF, and CCl_4. These results show the diffusion rate to be independent of environment.

b. The diffusion of A-50 from Stillman rubber at ambient conditions in environments of GN_2 and methanol shows a (K) value of 3.06×10^{-4} for both environments.

c. The results of N_2O_4 diffusion from Teflon® FEP tests made at 25°, 65°, and 100° C using GN_2 purge show (K) values of 1.4×10^{-3}, 3.4×10^{-3}, and 1.1×10^{-2}. This implies that the diffusion rate is temperature dependent. Plotting these points on semilog paper shows a reasonable fit; therefore, the diffusion rate increases exponentially as the temperature is increased.

6. The results of tests show that the flushing solvents can tolerate several hundred parts per million of the contaminants and still effectively extract the contaminant from the elastomer.

B. Solvent Selection

1. Candidate Solvent Listing

A list of candidate solvents (over 200) was compiled. No consideration was given in this compilation to availability or cost. This master list was reviewed and solvents were selected as promising candidates. These solvents are shown in Table 1-I. Each of these solvents was subjected to at least one test of some type.

2. Detonation Tests

The indiscriminate mixing of solvents with the propellants, especially N_2O_4, is likely to result in an explosive mixture. As a first precaution in the screening of solvents, a testing program was initiated which involved mixing various solvents

with N_2O_4 on Aerozine-50 and shocking or igniting the mixture with a blasting cap to determine if the mixture is explosive. These tests were carried out in an isolated area.

The procedure and equipment used were as follows:

Ignition Source - E-83 electric blasting cap
Sample Holder - 32-ounce paper Dixie cup
Volume of nitrogen tetroxide - same volume as test solvent
Volume of test solvent - as shown in Table 1-II

A paper Dixie cup containing the indicated volume of test solvent was placed on the sand. An equal volume of nitrogen tetroxide was poured remotely into the test solvent. An E-83 electric blasting cap was then detonated, by means of a six-volt battery, in the liquid mixture. The procedure used for the A-50 detonation tests was essentially the same as given above except the initial tests were carried out in vapor phase, and 100 ml of A-50 and solvent were used in all tests. Test results show that placing the blasting cap in the liquid gave a more sensitive and reproducible test. Therefore, the latter A-50 detonation tests and all of the N_2O_4 tests were carried out with the blasting cap in the liquid. The detonation tests were empirical and the explosibility was estimated by concussion, audible, and visual observations. Usually, a crater of some dimension was made in the sand after the tests in which an explosion occurred. The size of the crater was proportional to the charge and intensity of the explosion.

The results of the solvent-N_2O_4 detonation tests are given in Table 1-II. The tests were carried out in triplicate and shown only once unless there was a discrepancy in the results. Dibromochloromethane gave inconsistent results, and analysis of the sample by vapor phase chromatography revealed nothing that would account for this discrepancy. Trichloroethylene, which was known to be not compatible with N_2O_4, was included in the tests to serve as a control since a high order explosion occurred when detonated with N_2O_4. A few low-boiling solvents such as Freon® C-318, $(CF_2)_4$, and dibromodifluoromethane was included, but it was necessary to pack the cup in dry ice to prevent evaporation.

The results of the A-50-solvent detonation tests are shown in Table 1-III. The initial tests were carried out in the vapors above the solution. This resulted in burning the materials, and no explosion occurred. Placing the detonator (blasting cap) in the A-50 solution, with no solvent present, resulted in a low order explosion. When a solvent was added and the test was carried out in the same manner, a low order explosion again occurred. There was no discernible difference in the order of magnitude of the explosion with or without the solvent; therefore, the A-50 detonation tests were discontinued.

3. Thermodynamic Calculations

Some thermodynamic calculations for the reactions of nitrogen tetroxide with various solvents were made to determine if a correlation could be drawn between the energy change and compatibility. The heat of reaction ΔH_{300^oK} and the change in free energy ΔF_{300^oK} were determined according to the following equations:

$$\Delta H = (H_F\ N_2O_4 + H_F\ \text{Solvent}) - (H_F\ \text{Products})$$

$$\Delta F = (F_{N_2O_4} + F_{\text{Solvent}}) - (F\text{Products})$$

The results are given in Table 1-IV, which lists the assumed or possible reaction of solvent and oxidizer together with the calculated heat of reaction and free energy change.

In considering the equilibria involved in the assumed reaction, the further assumption was made that the reaction would ultimately go to completion, bearing in mind the possibility of stepwise and side reactions. The heat of reaction and free energy changes in each case were negative indicating heat would be evolved and the reaction would proceed.

Correlating the results of these calculations with the knowledge of compatibility gained from the empirical detonation tests, the following generalizations would appear valid: (1) Solvent-N_2O_4 systems showing a ΔF value less than 2 Kcal/gram N_2O_4 are not likely to be detonated regardless of the size of the triggering charge. (2) Solvent-N_2O_4 systems showing a ΔF value greater than 2 Kcal/gram N_2O_4 can probably be detonated given sufficient shock.

These considerations point out that compatibility of solvents with N_2O_4 covers a broad spectrum of values relating to the initiating charge required for detonation. There are presently no standard requirements or standardized testing procedures.

All results which are currently available are based upon arbitrary conditions of charge, placement of charge, and concentration.

4. Compatibility Tests

Compatibility tests were made to determine the effect of propellant and various solvents on the soft parts. The test procedure used was ASTM Designation D543-60T, "Resistance of Plastics to Chemical Reagents." This method includes procedures for measuring changes in weight, dimensions, appearance and strength properties. The materials

used in this study are the elastomers and solvents shown in Table 1-V. The results are also given in this table. The elastomer was considered not compatible with the solvent if the elastomer showed a loss of 25% in tensile strength.

C. Fundamental Study of Degassing of the Contaminants From Elastomers

The elastomers contain the residual-propellant contaminants that remain after the Apollo tanks have been flushed with a solvent. Previous work indicated that the contaminants are absorbed in the capillaries of the elastomers and, consequently, the source of contamination. Therefore, a study was initiated to determine the rate at which the contaminants are removed or degassed from the elastomers.

1. Procedure

The procedure used in carrying out these tests at ambient conditions is as follows. Sample specimens of the elastomer were immersed in the contaminant (N_2O_4 or A-50) for several days, and the weight gain was recorded. After determining the contaminant content of each specimen, they were placed individually in 50 milliliters of the solvent under test. The samples were removed from the solvent at specified time intervals and weighed, and the contaminant content of the solvent was determined.

The tests made at elevated temperatures were carried out in this manner. The solvent was placed in a round-bottomed flask which was provided with a heating mantle. Heat was applied, and the temperature of the solvent was increased to boiling. The vapors from the boiling solvent were introduced into the top of a metal test chamber. Specimens of the elastomer containing the contaminant were positioned in the chamber between wire screens. The rate at which the solvent was boiled off was sufficient to maintain vapors in the chamber after the chamber reached the boiling temperature of the solvent. The exit vapors passed through a condenser and the condensate collected in a graduate. The amount collected in a specified time interval was noted, and the contaminant in the condensate determined. The test using steam was essentially carried out in the same manner as the solvent test except that the steam was received from a low pressure steam line. Approximately 13 psig steam pressure was maintained by snubbing the valve in the line of the test chamber. Other test procedures used will be described when the specific test is discussed.

2. Degassing of N_2O_4 From the Elastomers

The first objective was the screening of selected solvents to determine if one was more effective than the others in the removal of N_2O_4 from the elastomers. The solvents used were Freon® MF, Freon® TF, carbon tetrachloride, and

GN_2. The elastomers used were Teflon® FEP, Teflon®, TFE, Rulon, and Kynar. The procedure, described above, was used in carrying out the tests. The results are given in Tables 1-VI through 1-XI. These tables show the elastomer, solvent, the time in minutes that the elastomer was immersed in the solvent, the N_2O_4 absorbed in the elastomer expressed in milligrams per square centimeter, and the percent of N_2O_4 retained in the elastomers.

The results show, at ambient temperature, that all of the solvents and GN_2 have about the same N_2O_4 removal rate. An increase in the temperature shows a definite increase in the amount of N_2O_4 removed in a given period of time. Rulon and Kynar absorbed more N_2O_4 than did the Teflons®.

3. Removal of Aerozine-50 From Stillman SR634-70 Rubber

Stillman SR634-70 Rubber was the elastomer of primary concern in the fuel side since the other elastomers did not absorb an appreciable amount of A-50. A series of tests were made to determine the removal rate of A-50 from the Stillman rubber at ambient temperatures using methanol, water, acetone, iso-octane, benzene, and formamide. The procedure was the same as described previously which consisted of immersing the contaminated specimens in solvent for specified time intervals. The results of these tests are given in Tables 1-XII and 1-XIII. The only significant difference shown by the results was that benzene and iso-octane appear to be superior solvents, but these solvents caused considerable distortion (swelling and elongation) of the specimens. These solvents are not compatible with the rubber.

The rate at which A-50 was removed from Stillman rubber using a gaseous nitrogen purge was investigated at 25° C and 90° C. The apparatus used for the 25° C test consisted of a 200-milliliter, stainless steel test chamber. The specimens were sandwiched between stainless steel wire screens and placed in the chamber. A fixed rate of nitrogen gas was introduced into the top of the chamber, and the exit gas was scrubbed with water to catch the A-50. The water trap was changed at specified time intervals and A-50 determined. A Cenco moisture balance purged with GN_2 was used in carrying out the 90° C test. The balance was equipped with an infrared lamp to supply the heat, and a galvanometer was used to measure the temperature. The weight loss was determined directly from a rotating scale. The results of these tests are given in Table 1-XIV. The results shown in this table indicate that, after 240 minutes, 93.1 percent of the A-50 was retained at ambient temperature and, after 80 minutes at 90°, only 13.6 percent was retained.

The removal of A-50 from Stillman rubber at 65° C and 100° C was determined using methanol and isobutanol vapors using the procedure described previously. The results are given in Table 1-XV and are consistent with the previous results in that the A-50 degassing rate is increased at the higher temperature. Table 1-XVI shows the removal of A-50 from the rubber using 13 psig steam (119° C). The results show that approximately 97.5 percent of the A-50 was removed in 168 minutes.

D. Discussion of Results

The degassing of the elastomers expressed in milligrams per square centimeter given in Tables 1-VI through 1-XVI is shown graphically in Figures 1-1 through 1-13. The figures show a plot on semi-log paper of the contaminants remaining in the sample (mg/cm^2) versus time.

A straight line was obtained for each test, indicating that the amount of materials degassed from the elastomers per unit of time is proportional to the amount present at that time. The fact that this rate of decrease is proportional to the amount of materials present can be expressed mathematically by the equation:

$$-\frac{dcA}{dt} = K_{cA} \qquad (1)$$

where:
- c = the concentration of degassing material (A)
- K = a proportionality factor
- t = time
- $-dc/dt$ = the rate the concentration in the elastomer decreases

Integrating Equation (1) between the limits of concentration (c_1), at time (t_1), and (c_2) at a later time (t_2) is shown below:

$$\int_{c_1}^{c_2} \frac{dc}{c} = K \int_{t_1}^{t_2} dt =$$

$$-\ln c_2 - (-\ln c_1) = K(t_2 - t_1)$$

$$K = \frac{2.303}{t_2 - t_1} \cdot \log \frac{c_1}{c_2} \qquad (2)$$

This is the equation usually given for a first order reaction.

The constant (K) is called the specific rate constant or the velocity constant, and for a first order reaction, it is a

number per unit of time. It is evident from Equation (2) that a straight line is produced when the logarithm of the concentration is plotted against time. The rate constant (K) can be calculated in Figures 1-1 through 1-13 by multiplying the slope of the line by -2.3 as follows:

$$K = -2.3 \text{ (slope)} \qquad (3)$$

The specific degassing rate constants (K) were determined by Equation (3).

Inspection of the figures shows that, in most cases, the degassing of N_2O_4 from the elastomer shows the curves have two slopes which means there is a change in the degassing rate. The break in the curve usually occurred in about two hours, and evaluating (K) shows the degassing rate was considerably reduced after this time. The degassing rate constants (K) are summarized in Tables 1-XVII and 1-XVIII for N_2O_4 and A-50, respectively.

It was anticipated that the specific degassing rate constant would be an excellent way to compare solvents. The order of magnitude of the specific rate constants was found to be about the same for all solvents and also for GN_2 at the same conditions. This means that the rate that contaminants come out of the elastomers is independent of the environment at room temperature. Since this phenomenon was observed, other variables that might affect the rate constant were considered. The variable that was most obvious was temperature since a slight change (increase) can sometimes double the rate of a reaction. Therefore, one test was made at 65° C to determine if this affected the degassing rate of N_2O_4 from Teflon® FEP. The results show that the specific degassing rate (K) was 2.3 times faster at the higher temperature.

The degassing rate constant (K) also provides a means of estimating the contaminant concentration at any time if the area of the exposed elastomers is known. This can be done by multiplying (K) by the concentration at time (t) and this value is multiplied by the area of exposed elastomers. The concentration at time (t) is obtained from the figures. The value from the above calculations would be divided by the weight of the nitrogen in the system to estimate the concentration of contaminant in the entire system which could be stated in parts per million.

The degassing rate from the elastomers was described by numerical values of K. It may also be described by giving the period of half life, that is, the time necessary for half of the contaminant to diffuse from the elastomer. This will give an indication of the time required for decontamination. The half-life equation is derived by substituting 1/2 into (2) as follows:

$$K = \frac{2.303}{t_{\frac{1}{2}}} \log \frac{1}{\frac{1}{2}} = \frac{0.693}{t_{\frac{1}{2}}}$$

Rearranging the above equation, the half life in a first-order equation is then:

$$t_{\frac{1}{2}} = \frac{0.693}{K} \qquad (4)$$

The half-life determination provides a way to estimate the time required to reduce the concentration of the contaminants in the elastomers to an acceptable level. The half-life time values do not imply that all of the contaminants would be removed by doubling the time. The first-order equation shows that the amount of degassing is proportional to the amount present. To use an example, if the initial concentration was 4.0 mg/cm^2 and the half life was 60 minutes, in an hour the concentration would be 2.0 mg/cm^2; and, at the end of the second hour, the concentration would be reduced to 1.0 mg/cm^2.

1. Environmental and Temperature Effect

The results show that the rate the contaminants degas from the elastomers is independent of its environment at the same conditions. The degassing rate constants (K), which are shown in Table 1-XVII, show, for the initial degassing of N_2O_4 from Teflon® FEP, values of 1.4×10^{-3} 1.5×10^{-3}, and 1.8×10^{-3} in environments of GN_2, Freon® TF, and carbon tetrachloride. There is no significant difference in the above values. The degassing of Aerozine-50 from Stillman rubber at ambient conditions in environments of GN_2 and methanol shows the rates were approximately identical. The (K) value shown in Table 1-XVIII is 3.06×10^{-4} for both the GN_2 and methanol.

The rate at which the contaminants degas is temperature-dependent. An increase in temperature significantly increases the degassing rate. The degassing of N_2O_4 from Teflon® FEP shows K values of 1.4×10^{-3}, 3.4×10^{-3}, and 1.1×10^{-2} obtained from the tests using GN_2 purge made at temperatures of 25°, 65°, and 100° C were plotted on a semi-log graph and gave a reasonable fit. This means that as the temperature is increased, the degassing rate is increased exponentially. This is illustrated in Figure 1-14.

Using Equation (4), the half life was determined for the degassing of N_2O_4 from Teflon® FEP at temperatures of 25° C, 65° C, and 100° C. The above equation was also used for determining the half life for the degassing of Aerozine-50 from Stillman rubber. The results are shown below:

Temperature °C	Half Life N_2O_4 From Teflon® FEP Minutes	Half Life A-50 From Stillman SR634-70, Minutes
25	490	2,260
65	240	295
90		70
100	63	
119		36

It is obvious from the above results that the degassing rate of the contaminant from the elastomers is temperature dependent.

E. Allowable Concentration of A-50 in Cleaning Solvent

Two tests were made to determine the concentration of A-50 that can be tolerated in the cleaning solvent and still effectively remove the contaminant from the elastomer. The first test was made using an A-50 concentration of approximately 9,000 ppm in methanol, and the concentration of the second test was 90 ppm. The procedure used was as follows: Three 500-ml round-bottomed flasks, equipped with a heating mantle and reflux condenser, were set up. Approximately 250 ml of the 9,000 ppm solution were placed in each flask. Four specimens of Stillman rubber which had been immersed in A-50 for several hours were placed in the first flask. Four specimens of rubber which had not been exposed to A-50 were placed in the second flask. The third flask was used as a control with uncontaminated solvent in it. After placing the specimens in the flasks, heat was applied, and the temperature of the solutions was raised to the boiling point. The solutions were boiled for 16 hours while maintaining total reflux. The specimens were removed from the solutions after this time and weighed. The A-50 content was determined for each flask. The rubber specimens were then placed in the metal test chamber, and steam was passed through the chamber for several hours. The exit steam from the test chamber was discharged into a condenser and the A-50 content of the condensate determined. The specimens previously exposed to the A-50 and the specimens which had not been exposed to the A-50 were steam-treated separately.

The three different solutions (that which contains specimens exposed to A-50, specimens not exposed to A-50, and the control) show practically no difference in the A-50 concentration. This indicates that the rubber is not selective for the fuel and further substantiates the hypothesis that the propellants are absorbed and not chemically adsorbed into the elastomers. Very little A-50 was extracted by the steam treatment--approximately two milligrams from the specimens preexposed to the A-50, and about one milligram from the specimens not exposed to the A-50.

The test using 90 ppm A-50 in the methanol was carried out as described above with the exception that the specimens were not subjected to the steam treatment after they were refluxed. The most significant results shown by this test were that most A-50 contained in the preexposed specimens was extracted during the 16 hours of boiling under reflux.

The major conclusion drawn from these tests is that the solvent can tolerate several hundred parts per million of the contaminant and still effectively extract the contaminant from the elastomer. More work should be done in this area.

TABLE 1-I SOLVENTS USED IN THE SCREENING TESTS

Solvent	Service		Compatibility Test	
	Oxidant	Fuel	Propellant	Elastomer
Tribromofluoromethane	X		Compatible	Failed
Trichlorofluoromethane (Freon® MF)	X	X	Both Compatible	Compatible
Dibromodifluoromethane	X		Compatible	
Difluorotetrachloroethane (Freon® 112) Mixed Isomer	X		Compatible	
1,1-Dichloro-2,2,2-Trifluoroethane (Freon® 123)	X		Compatible	
1,1-Dibromo-2,2,2-Trifluoroethane	X		Compatible	Failed
1,2-Dibromo-1,2,2,-Tetrafluoroethane	X			
1,1,2-Trichloro-1,2,2-Trifluoroethane (Freon® TF)	X	X	Both Compatible	Compatible
Perfluorocyclobutane (Freon® C-318)	X		Compatible	
Perfluorodimethylcyclobutane	X		Compatible	
Freon® E-2	X	X	Compatible	Compatible
Dibromochloromethane	X		Failed	
Methylene Chloride		X	Compatible	
Chloroform	X	X	Both Compatible	
Bromochloromethane	X	X	Failed (ox) Compatible (fuel)	Compatible
Carbon Tetrachloride	X		Compatible	Compatible
Bromodichloromethane	X		Compatible	Failed
1,1,1-Trichloroethane	X		Failed	
Trichloroethylene	X		Failed	
Tetrachloroethylene	X		Failed	
Methylene Bromide	X		Failed	
Formamide		X		
Methanol		X	Compatible	Compatible
Ethanol		X	Compatible	Compatible
Acetone		X	Compatible	Failed
2,2-Dichloro-1,1-Difluoromethyl ethyl ether	X		Failed	Failed
n-Propanol		X		Compatible
Isopropanol		X		Compatible
Isobutanol		X		
Secondary Butanol		X		
1,2-Butylene Oxide		X		
1,4-Dioxane		X		
Pentane				Failed
Benzene				Failed
Cyclohexane				Failed
Hexane				Failed
Iso-octane				Failed
Nitrogen				Compatible
Steam				Compatible

TABLE 1-II

RESULTS OF N_2O_4 DETONATION TEST

Test Solvent	Test Results
1. Trichloroethylene - 200 ml	High order explosion
2. 2,2-Dichloro-1,1-difluoroethyl methyl ether - 100 ml	High order explosion
3. Bromodichloromethane - 100 ml	No explosion
4. Tribromofluoromethane - 50 ml	No explosion
5. Freon® 11 (Fluorotrichloromethane - 100 ml	No explosion
6. Dibromochloromethane - 100 ml	High order explosion
Dibromochloromethane - 100 ml	No explosion
Dibromochloromethane - 100 ml	No explosion
7. 1,1-Dibromo-2,2,2-trifluoroethane - 100 ml	No explosion
8. Freon® 112 (mixed isomers of difluoro-tetrachloroethane) - 100 ml	No explosion
9. Freon® C-318 (Cyclo$(CF_2)_4$ - 50 ml	No explosion
10. Dibromodifluoromethane - 50 ml	No explosion
11. 50 Vol. % Freon® 112 - 100 ml 50 Vol. % Bromochloromethane	No explosion

TABLE 1-III

RESULTS OF AEROZINE-50 DETONATION TEST

Test Mixture	Results
1. Methanol	Ignition. No detonation Sample cup intact
2. Ethanol	Ignition. No detonation Sample cup intact
3. n-Hexane	Ignition. No detonation Sample cup intact
4. Aerozine-50	Ignition. No detonation Sample cup intact
5. Aerozine-50 - Methanol	Ignition. No detonation Sample cup intact
6. Aerozine-50 - Ethanol	Ignition. No detonation Sample cup intact
7. Aerozine-50 - n-Hexane	Ignition. No detonation Sample cup intact
8. Aerozine-50 - Methylene chloride	Ignition. No detonation Sample cup intact
9. Aerozine-50	Ignition. No detonation Sample cup intact
10. Aerozine-50 - Chloroform	Ignition. No detonation Sample cup intact
11. Aerozine-50 - Freon® 11	Ignition. No detonation Sample cup intact
12. Aerozine-50 - Freon® 113	Ignition. No detonation Sample cup intact
13. Aerozine-50 - Bromochloromethane	Ignition. No detonation Sample cup intact

TABLE 1-III (CONTINUED)

Liquid Tested

Same procedure as above except the blasting cap was placed in the liquid portion of the mixture.

Test Mixture	Results
1. Aerozine-50	Low order explosion. No ignition.
2. Aerozine-50 - Freon® 11	Low order explosion. No ignition.
3. Aerozine-50 - Methylene chloride	Low order explosion. No ignition.
4. Aerozine-50 - Bromochloromethane	Low order explosion. No ignition.

TABLE 1-IV THERMODYNAMIC CALCULATION RESULTS

Reaction	ΔH Kcal	ΔH Kcal Per g N_2O_4	ΔH Kcal Per Mol Solvent	ΔF Kcal	ΔF Kcal Per g N_2O_4	ΔF Kcal Per Mol Solvent
$N_2O_4 + 8HCl \rightarrow 4H_2O + N_2 + 4Cl_2$	- 50.6	-0.55	- 6.3	- 61.1	-0.657	- 7.64
$N_2O_4 + 2\ CCl_3F \rightarrow 2CO_2 + F_2 + Cl_2 + N_2$	- 41.4	-0.45	- 20.7	- 88.9	-0.967	- 44.45
$5/4N_2O_4 + 2CHCl_2F \rightarrow 2CO_2 + H_2O + Cl_2 + F_25/4N_2$	-102.1	-1.01	- 51.0	-149.0	-1.62	- 74.6
$N_2O_4 + 2CCl_4 \longrightarrow 2CO_2 + 4Cl_2 + N_2$	-136.0	-1.5	- 63.0	-184.0	-2.0	- 92.0
$5/4N_2O_4 + 2CHCl_3 \longrightarrow 2CO_2 + H_2O + 3O_2 + 5/4N_2$	-191.0	-1.7	- 95.0	-238.0	-2.1	-119.0
$3/4N_2O_4 + CH_2Cl_2 \rightarrow CO_2 + H_2O + Cl_2 + 3/4N_2$	-126.0	-1.8	-126.0	-150.0	-2.3	-151.0
$N_2O_4 + 2N_2H_2 \longrightarrow 4H_2O + 3\ N_2$	-272.0	-3.0	-136.0	-308.0	-3.3	-154.0
$5/4N_2O_4 + 2HCN \longrightarrow 2CO_2 + H_2O + 5/4N_2$	-303.0	-2.6	-152.0	-324.0	-2.8	-162.0
$N_2O_4 + C_2Cl_4 \longrightarrow 2CO_2 + 2Cl_2 + N_2$	-181.0	-2.0	-181.0	-208.0	-2.3	-208.0
$9/4N_2O_4 + 2C_2HCl3 \longrightarrow 4CO2 + H_2O + 3Cl_2 + 9/4N2$	-422.0	-2.0	-211.0	-494.0	-2.4	-247.0
$5/4N_2O_4 + C_2H_2Cl_2 \longrightarrow 2CO_2 + H_2O + Cl_2 + 5/4N_2$	-240.0	-2.1	-240.0	-271.0	-2.4	-271.0

TABLE 1-V

RESULTS OF SOLVENT-ELASTOMER COMPATIBILITY STUDY

Solvents	Elastomers					
	Teflon® TFE	Teflon® FEP	Kel-F No. 300	Kynar	Rulon	Stillman SR634-70 Rubber
Ethanol	10 Wks Compat	8 Wks Compat	10 Wks Compat	No Test	5 Wks Compat	5 Wks Compat
Methanol	10 Wks Compat	8 Wks Compat	10 Wks Compat	5 Wks Compat	5 Wks Compat	5 Wks Compat
Acetone	10 Wks Compat	8 Wks Compat	10 Wks Compat	No Test	No Test	1 Wk Failed
90% Hexane 10% Aerozine-50	9 Wks Compat	No Test	9 Wks Compat	No Test	No Test	No Test
Aerozine-50	9 Wks Compat	8 Wks Compat	3 Wks Failed	5 Wks Compat	5 Wks Compat	5 Wks Failed
Freon® 11	8 Wks Compat	8 Wks Compat	4 Wks Compat	5 Wks Compat	5 Wks Compat	No Test
90% Freon® 11 10% N_2O_4	8 Wks Compat	8 Wks Compat	1 Wk Failed	No Test	No Test	No Test
Freon® 113	8 Wks Compat	8 Wks Compat	8 Wks Failed	No Test	No Test	No Test
90% Freon® 113 10% N_2O_4	8 Wks Compat	8 Wks Compat	1 Wk Failed	No Test	No Test	No Test
Bromo-chloro Methane	8 Wks Compat	8 Wks Compat	8 Wks Compat	No Test	No Test	No Test
90% Bromo-chloro Methane 10% N_2O_4	No Test	8 Wks Compat	No Test	No Test	No Test	No Test
N_2O_4	8 Wks Compat	8 Wks Compat	1 Wk Failed	5 Wks Compat	5 Wks Compat	No Test
Bromo-dichloro Methane	4 Wks Compat	4 Wks Compat	No Test	4 Wks Compat	4 Wks Compat	1 Wk Failed
Tribromo-fluoro Methane	4 Wks Compat	4 Wks Compat	No Test	4 Wks Compat	4 Wks Compat	1 Wk Failed

TABLE 1-V
(CONTINUED)

RESULTS OF SOLVENT-ELASTOMER COMPATIBILITY STUDY

Solvents	Elastomers					
	Teflon® TFE	Teflon® FEP	Kel-F No. 300	Kynar	Rulon	Stillman SR634-70 Rubber
1,1 Dibromo-2,2,2 trifluoro Ethane	4 Wks Compat	4 Wks Compat	No Test	4 Wks Compat	4 Wks Compat	1 Wk Failed
2,2-Dichloro-1,1-difluoro Ethyl Methyl Ether	No Test	No Test	No Test	1 Wk Compat	No Test	1 Wk Failed
Carbon Tetrachloride	No Test	No Test	No Test	No Test	1 Wk Compat	No Test
Isopropyl Alcohol	No Test	No Test	No Test	No Test	No Test	1 Wk Compat
Cyclohexane	No Test	No Test	No Test	No Test	No Test	1 Wk Failed
Iso-Octane	No Test	No Test	No Test	No Test	No Test	1 Wk Failed
Benzene	No Test	No Test	No Test	No Test	No Test	1 Wk Failed

TABLE 1-VI

REMOVAL OF N_2O_4 FROM TEFLON® FEP BY VARIOUS SOLVENTS

Time	Freon® MF		Freon® TF		Carbon Tetrachloride	
	N_2O_4 mg/cm²	% N_2O_4 Retained	N_2O_4 mg/cm²	% N_2O_4 Retained	N_2O_4 mg/cm²	% N_2O_4 Retained
0	0.89	-	2.11	-	2.57	-
15 min.	0.829	93.2	1.967	93.1	2.35	91.4
30 min.	0.828	93.1	1.925	91.2	2.28	88.7
60 min.	0.801	90.0	1.832	86.8	2.145	83.3
120 min.	0.78	87.6	1.74	82.4	2.08	80.5
240 min.	0.721	80.9	1.64	75.7	1.97	76.6
24 hrs.	-	-	1.267	60.0	1.31	51.0

TABLE 1-VII

REMOVAL OF N_2O_4 FROM TEFLON® TFE BY VARIOUS SOLVENTS

Time	Freon® MF		Freon® TF		Carbon Tetrachloride	
	N_2O_4 mg/cm²	% N_2O_4 Retained	N_2O_4 mg/cm²	% N_2O_4 Retained	N_2O_4 mg/cm²	% N_2O_4 Retained
0	2.44	-	1.65	-	2.6	-
15 min.	2.23	91.3	1.45	88.0	2.18	83.9
30 min.	2.18	89.2	1.34	81.0	2.15	83.7
60 min.	2.12	87.0	1.315	79.8	2.01	77.4
120 min.	1.97	80.6	1.26	76.3	1.82	70.0
240 min.	1.81	74.2	1.144	69.3	1.49	57.4
24 hrs.	1.67	68.4	0.895	54.3	1.195	45.8

TABLE 1-VIII

REMOVAL OF N_2O_4 FROM RULON BY VARIOUS SOLVENTS

Time Min.	Carbon Tetrachloride N_2O_4 mg/cm^2	Carbon Tetrachloride % N_2O_4 Retained	Freon® MF N_2O_4 mg/cm^2	Freon® MF % N_2O_4 Retained	Nitrogen Purge Time	Nitrogen Purge N_2O_4 mg/cm^2	Nitrogen Purge % N_2O_4 Retained
0	6.93	-	4.5	-	0	5.07	-
15	5.68	82.8	3.89	86.3	15 min.	4.54	89.7
30	5.48	79.0	3.72	82.6	45 min.	4.22	83.2
60	5.39	77.7	3.39	75.2	75 min.	4.01	79.1
120	5.08	73.2	3.15	70.0	135 min.	3.77	74.4
240	4.48	64.7	2.45	54.4	165 min.	3.59	70.8
					195 min.	3.41	67.2
					28 hrs.	2.05	40.5

TABLE 1-IX

REMOVAL OF N_2O_4 FROM KYNAR BY VARIOUS SOLVENTS

Ambient Temperature

	Freon® MF		Carbon Tetrachloride			Nitrogen Purge	
Time	N_2O_4 mg/cm^2	% N_2O_4 Retained	N_2O_4 mg/cm^2	% N_2O_4 Retained	Time	N_2O_4 mg/cm^2	% N_2O_4 Retained
0	11.2	-	11.06	-	0	5.62	-
15 min.	10.62	94.8	9.41	85.0	30 min.	4.65	82.2
30 min.	10.58	94.5	9.48	85.6	75 min.	4.39	77.1
60 min.	10.18	91.0	8.9	83.8	165 min.	4.07	72.3
120 min.	9.89	88.1	8.5	80.4	380 min.	3.79	67.4
240 min.	9.46	84.4	8.37	75.6			
24 hrs.	8.69	68.7	6.97	63.0	24 hrs.	2.9	51.6

TABLE 1-X

REMOVAL OF N_2O_4 FROM ELASTOMERS, BY GN_2 AT AMBIENT

Time	Teflon® FEP Ambient		Teflon® FEP 65° C		Teflon® TFE 65° C	
	mg/cm^2	% N_2O_4 Retained	mg/cm^2	% N_2O_4 Retained	mg/cm^2	% N_2O_4 Retained
0	2.060		5.345		2.44	
20 min.			4.19	78.4		
30 min.	1.481	70.1			1.467	59.8
40 min.			3.94	73.6		
1.0 hr.			3.61	67.5		
1.33 hrs.	1.385	67.2			1.3	53.2
2.0 hrs.			2.94	55.0		
2.75 hrs.	1.230	59.7			1.04	42.6
6.33 hrs.	1.055	51.2			.743	30.2
19.0 hrs.			.785	14.6		
24.0 hrs.	.710	34.4	.524	9.8	.275	11.3

TABLE 1-XI

REMOVAL OF N_2O_4 FROM TEFLON® TFE AND FEP BY GN_2 AT 100° C

Time Min.	TFE		FEP	
	N_2O_4 mg/cm^2	% N_2O_4 Retained	N_2O_4 mg/cm^2	% N_2O_4 Retained
0	1.77	-	5.39	-
30	0.44	24.8	2.62	48.6
60	0.34	19.2	1.85	34.3
90	0.27	15.2	1.28	23.7

TABLE 1 -XII

REMOVAL OF AEROZINE-50 FROM STILLMAN SR634-70 RUBBER
BY VARIOUS SOLVENTS

Time Min.	Iso-Octane A-50 mg/cm^2	Iso-Octane % A-50 Retained	Benzene A-50 mg/cm^2	Benzene % A-50 Retained	Formamide A-50 mg/cm^2	Formamide % A-50 Retained
0	4.14	-	3.98	-	5.11	-
30	3.98	96.0	2.45	61.4	5.10	99.7
60	3.89	94.0	2.16	54.2	5.09	99.6
120	3.68	88.9	2.1	52.7	5.07	99.3
180	3.35	80.9	2.7	67.8	5.05	98.9

TABLE 1-XIII

REMOVAL OF AEROZINE-50 FROM STILLMAN SR634-70 RUBBER
BY METHANOL AND WATER

Time Min.	Methanol A-50 mg/cm^2	Methanol % A-50 Retained	Water A-50 mg/cm^2	Water % A-50 Retained
0	7.42	-	7.55	-
30	7.3	98.3	7.35	97.4
60	7.23	97.4	7.30	96.7
90	7.16	96.4	7.29	96.5
120	7.10	95.7	7.24	95.9
180	7.01	94.4	7.17	95.0
210	6.95	93.7	7.17	95.0
240			7.17	95.0

TABLE 1-XIV

REMOVAL OF AEROZINE-50 FROM STILLMAN SR634-70 RUBBER BY GN_2 PURGE AT 25° AND 90° C

25° C			90° C		
Time Min.	A-50 mg/cm^2	% A-50 Retained	Time Min.	A-50 mg/cm^2	% A-50 Retained
0	7.21	-	0	6.34	-
30	7.13	98.8	10	3.61	56.9
60	7.04	97.5	20	2.31	36.6
90	6.98	96.8	40	1.28	20.2
120	6.92	95.9	60	1.07	16.9
180	6.82	94.6	80	0.861	13.6
210	6.77	93.9	24 hrs.	0.0	0
240	6.71	93.1			

TABLE 1-XV

REMOVAL OF AEROZINE-50 FROM STILLMAN SR634-70 RUBBER BY METHANOL AND ISOBUTANOL VAPORS AT 65° AND 100° C

	Methanol Vapors		Isobutanol Vapors	
Time Min.	A-50 mg/cm^2	% A-50 Retained	A-50 mg/cm^2	% A-50 Retained
0	7.38	-	7.89	-
30	6.68	90.4	7.24	86.3
60	6.08	82.3	6.17	73.5
90	5.66	76.7	5.34	63.7
120	5.28	72.5	5.14	61.2
150	4.96	67.1	4.52	53.9
180	4.69	63.5	3.84	45.7
210	4.5	60.9	3.58	42.6
240	2.44	60.2	3.48	41.5

TABLE 1-XVI

REMOVAL OF AEROZINE-50 FROM STILLMAN SR634-70 RUBBER
BY 13 PSIG STEAM AT 119° C

Time Min.	A-50 mg/cm^2	% A-50 Retained
0	5.97	-
5.3	5.26	88.0
12.2	4.24	71.3
20.0	3.48	68.2
27.8	2.9	48.5
35.6	2.46	41.1
43.4	2.1	35.1
51.2	1.81	30.3
59.0	1.58	26.4
66.8	1.37	22.9
74.6	1.2	20.1
82.4	1.06	17.7
90.2	0.94	15.7
98.0	0.82	13.7
105.8	0.72	12.1
113.6	0.61	10.3
121.4	0.53	8.9
128.4	0.45	7.5
136.2	0.39	6.5
145.0	0.33	5.5
152.8	0.28	4.7
160.6	0.23	3.8
168.4	0.19	3.2
H_2O Trap		2.5

TABLE 1-XVII

SPECIFIC RATE CONSTANTS (K) FOR THE DECONTAMINATION OF FREON® 11 AND 113 AND N_2O_4 FROM VARIOUS ELASTOMERS

Elastomer		Degassing Rate K = $mg/cm^2/min.$						
		Freon® 11	Freon® 113	N_2O_4	N_2O_4	N_2O_4	N_2O_4	N_2O_4
Condition		GN_2 Purge Ambient	GN_2 Purge Ambient	GN_2 Purge Ambient	GN_2 Purge 65° C	in CCl_3F	in CCl_2F-$CClF_2$	in CCl_4
Teflon® FEP	K_1	8.47×10^{-4}	1.1×10^{-3}	1.44×10^{-3}	3.4×10^{-3}		1.56×10^{-3}	1.83×10^{-3}
	K_2	5.2×10^{-4}	4.6×10^{-4}	3.7×10^{-4}	1.21×10^{-3}	7.32×10^{-4}	7.1×10^{-4}	8.1×10^{-4}
Teflon® TFE	K_1	9.08×10^{-4}	9.08×10^{-4}	2.7×10^{-3}		9.8×10^{-4}	3.24×10^{-4}	2.65×10^{-3}
	K_2	1.0×10^{-4}	1.0×10^{-4}	5.9×10^{-4}				
Rulon	K_1			2.2×10^{-3}		2.8×10^{-3}		1.08×10^{-3}
	K_2			9.5×10^{-4}				3.9×10^{-4}
Kynar	K_1					1.1×10^{-3}	1.4×10^{-3}	1.5×10^{-3}
	K_2					3.2×10^{-4}	2.75×10^{-4}	8.8×10^{-4}

TABLE 1-XVIII

SPECIFIC RATE CONSTANTS (K) FOR AEROZINE-50
FROM STILLMAN SR634-70 RUBBER
AND FOR N_2O_4 FROM TEFLONS® FEP AND TFE

	Stillman SR634-70 Rubber	Teflon® FEP	Teflon® TFE
GN_2 Ambient	3.06×10^{-4}		
Methanol Ambient	3.06×10^{-4}		
Methanol KSI	3.07×10^{-3}		
65° C (Vapor) KSII	2.34×10^{-3}		
Steam KSI	2.7×10^{-2}		
13 psig KSII	1.91×10^{-2}		
GN_2 KSI	3.51×10^{-2}		
90° C KSII	9.84×10^{-3}		
Isobutanol 100° C (Vapor)	3.78×10^{-3}		
Iso-octane Ambient	9.26×10^{-4}		
GN_2 K 100° C		1.1×10^{-2}	9.2×10^{-3}

Figure 1-1

DECONTAMINATION RATE OF FREONS® 11 AND 113 FROM TEFLON® FEP BY GN_2 AT AMBIENT

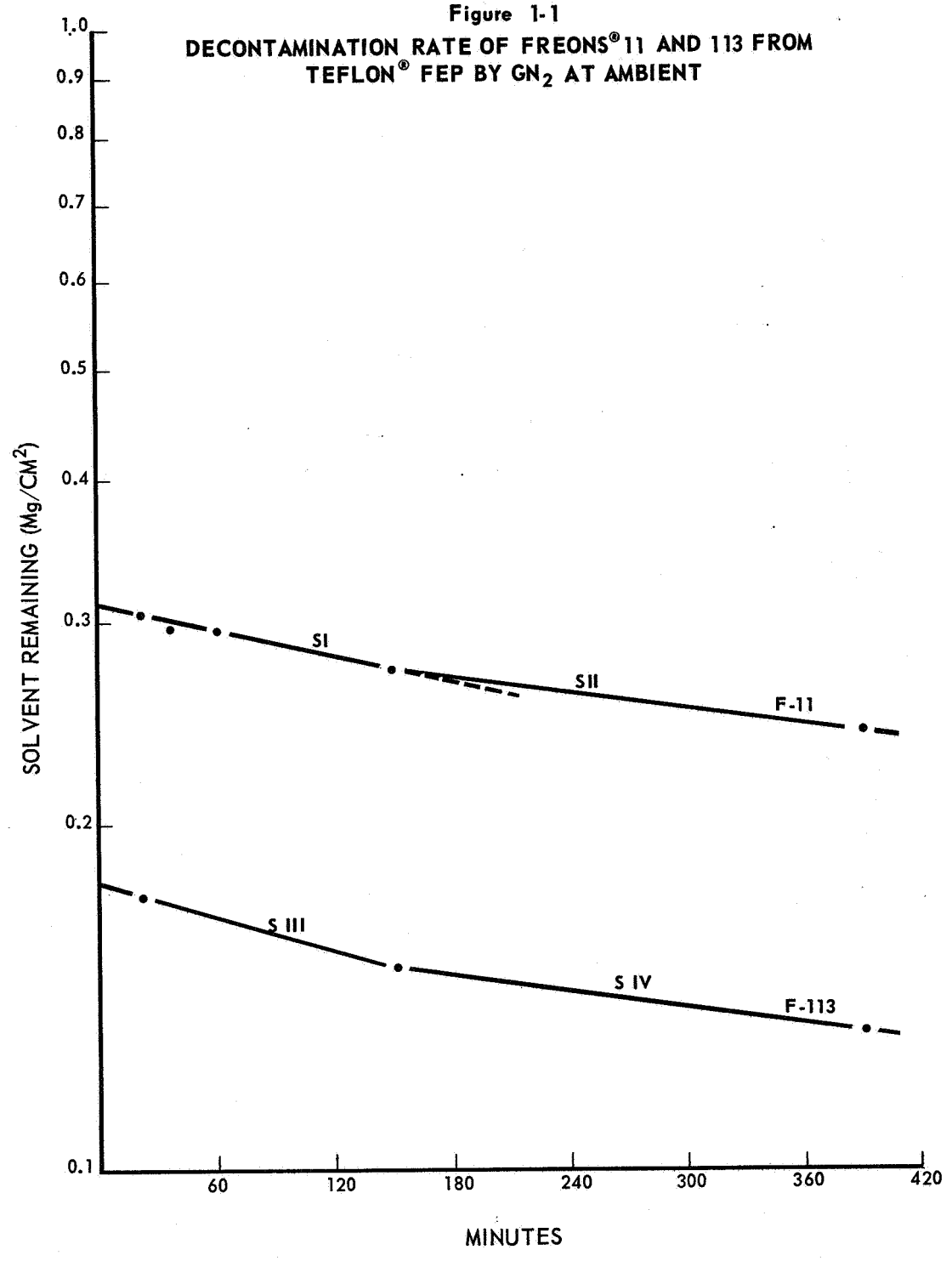


Figure 1-2

DECONTAMINATION RATE OF FREONS® 11 AND 113 FROM TEFLON® TFE BY GN_2 AT AMBIENT

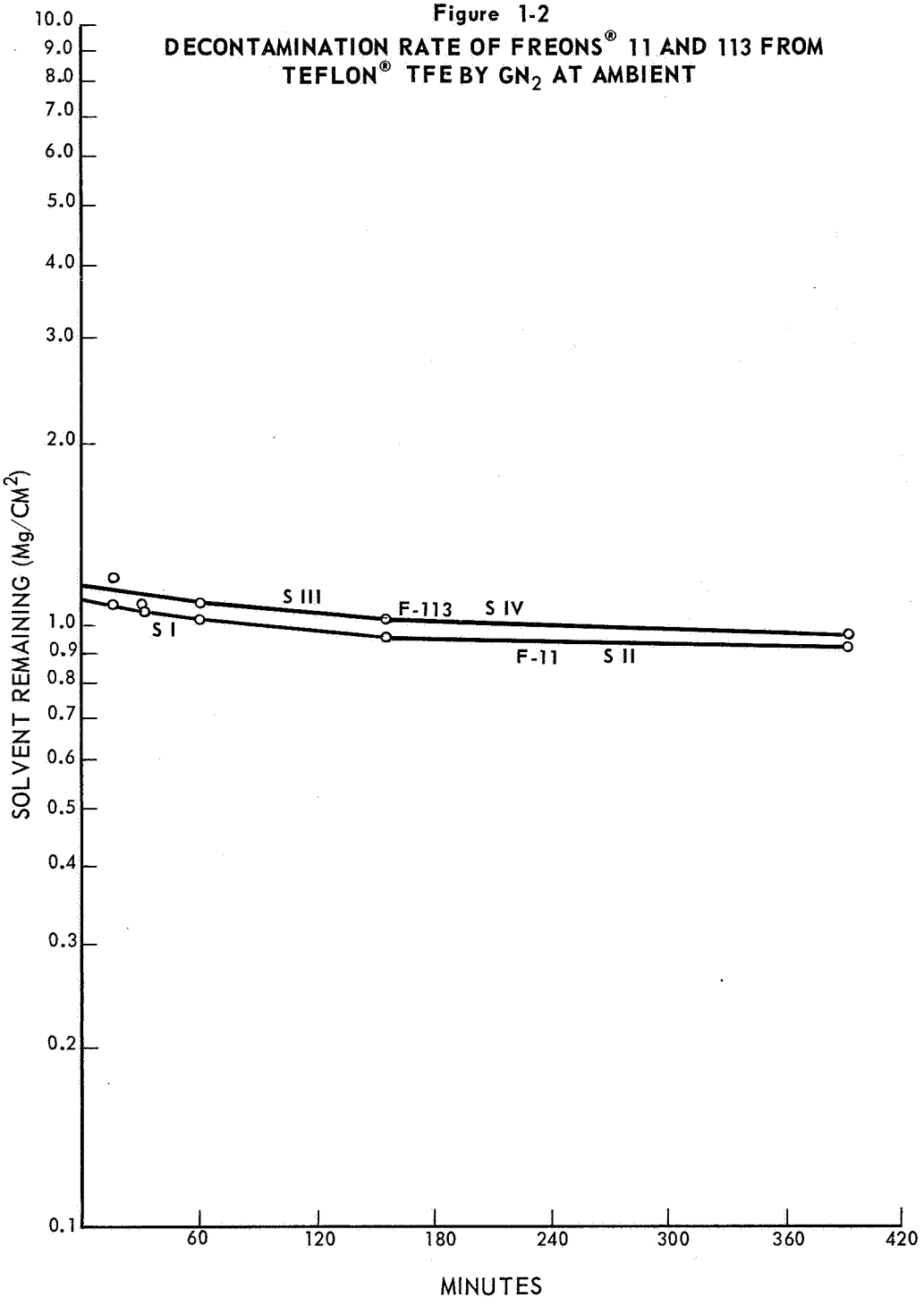


Figure 1-3

DECONTAMINATION RATE OF N_2O_4 FROM TEFLON® FEP BY GN_2 AT AMBIENT AND 65°C

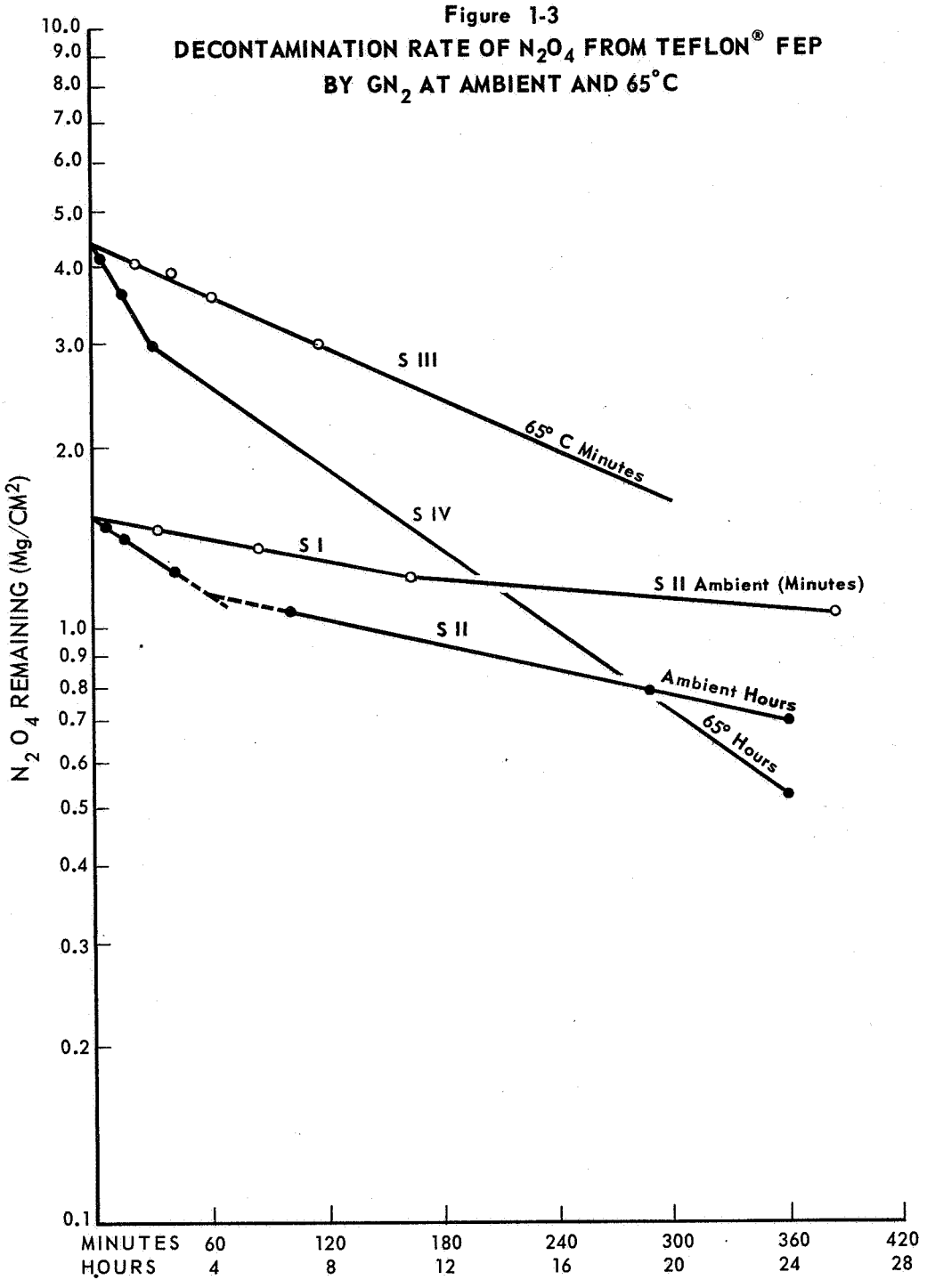


Figure 1-4

DECONTAMINATION RATE OF N_2O_4 FROM TEFLON® TFE BY GN_2 AT AMBIENT

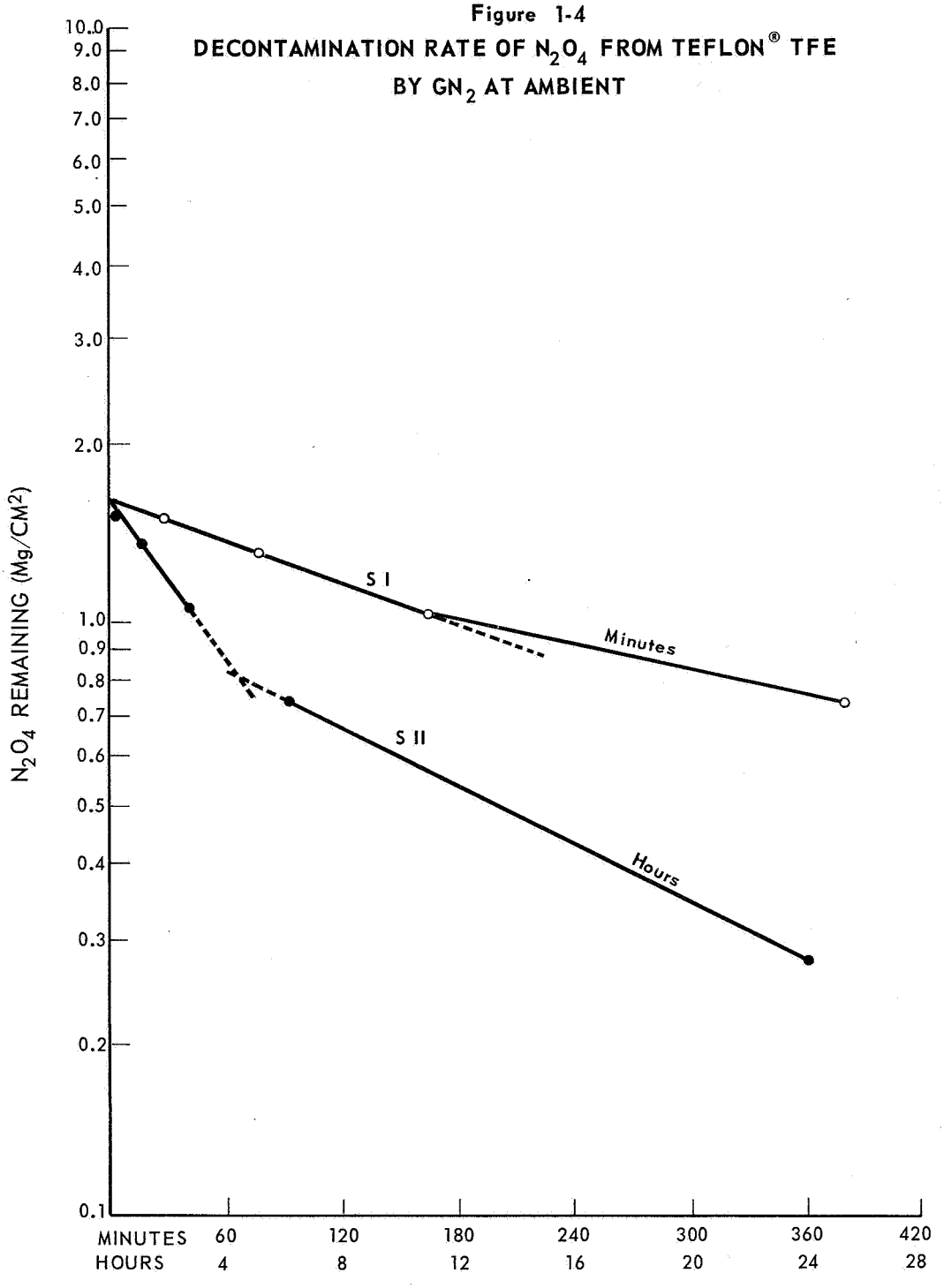


Figure 1-5

DECONTAMINATION RATE OF N_2O_4 FROM TEFLON® FEP BY VARIOUS SOLVENTS AT AMBIENT

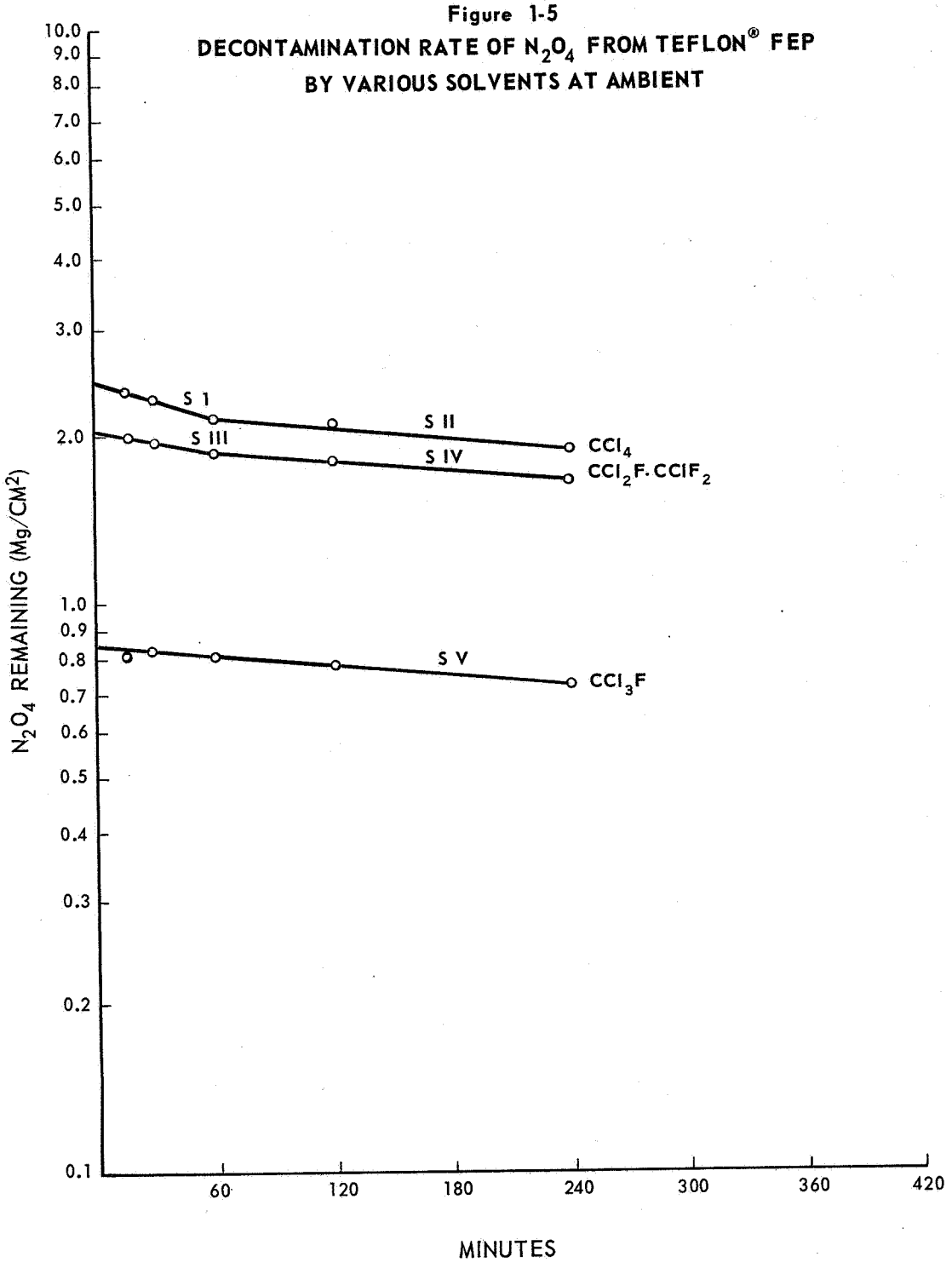


Figure 1-6

DECONTAMINATION RATE OF N_2O_4 FROM TEFLON® TFE BY VARIOUS SOLVENTS AT AMBIENT

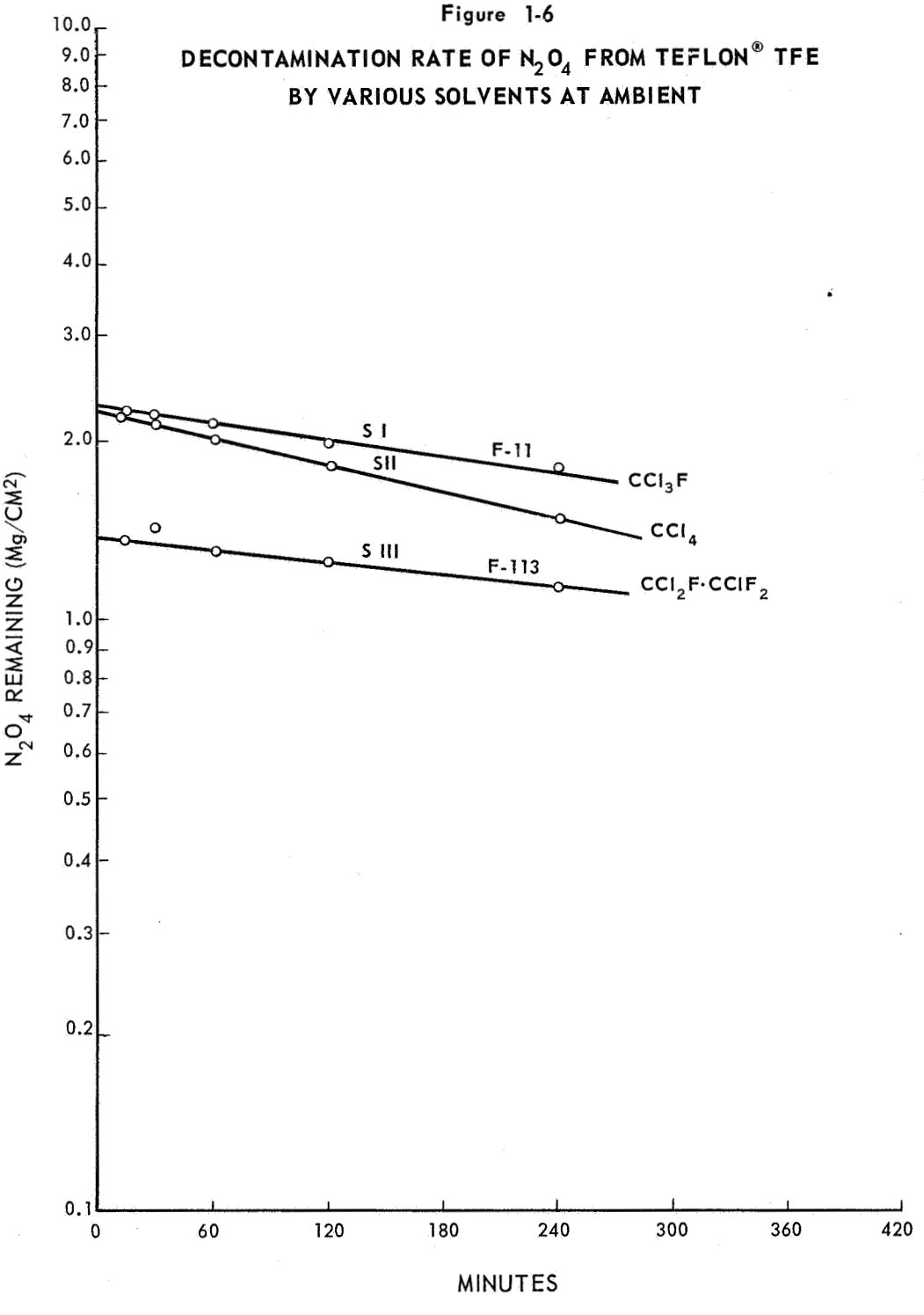


Figure 1-7

DECONTAMINATION RATE OF N_2O_4 FROM KYNAR BY VARIOUS SOLVENTS AT AMBIENT

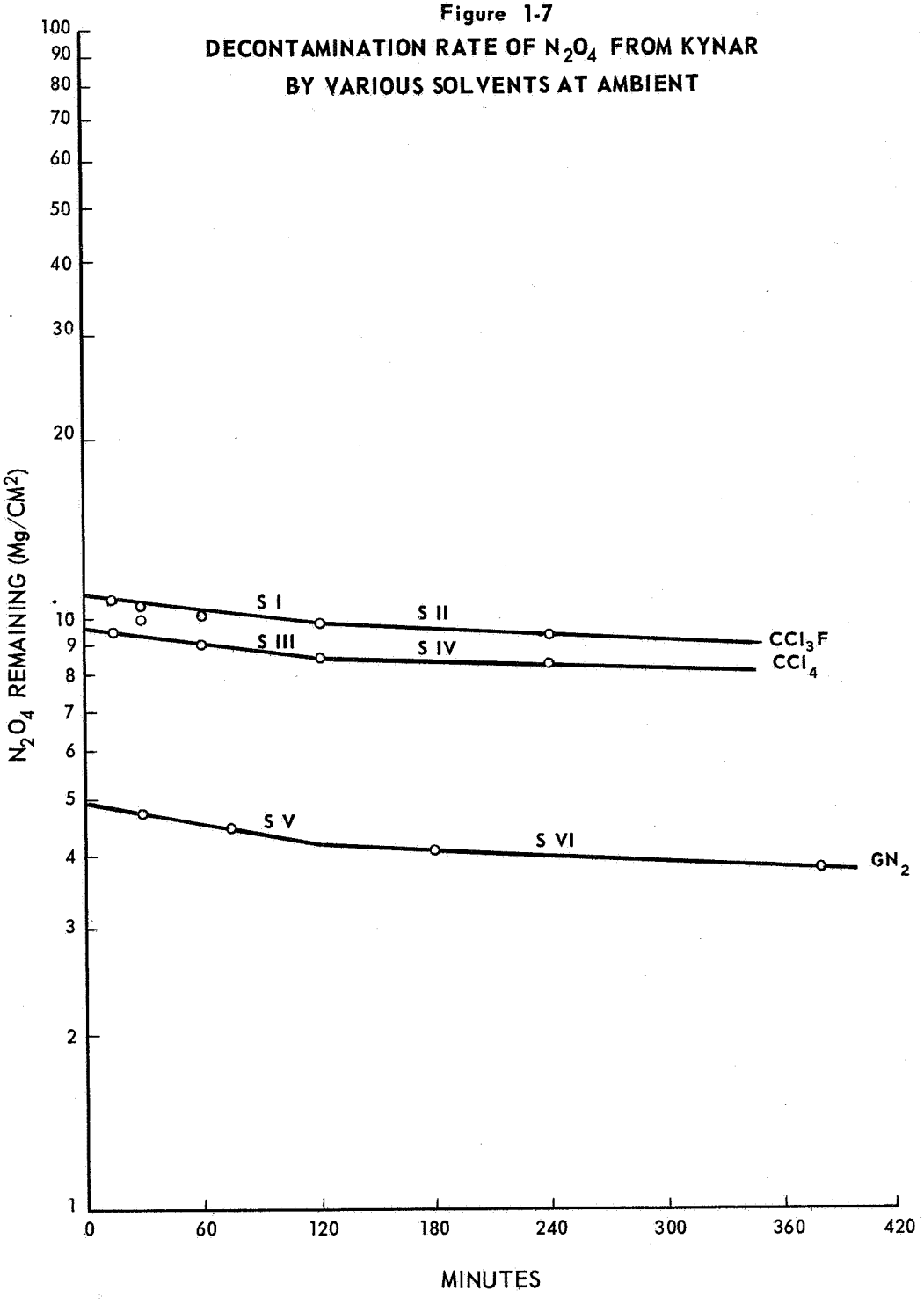


Figure 1-8

DECONTAMINATION RATE OF N_2O_4 FROM RULON BY CARBON TETRACHLORIDE, GN_2 AND FREON® 11 AT AMBIENT

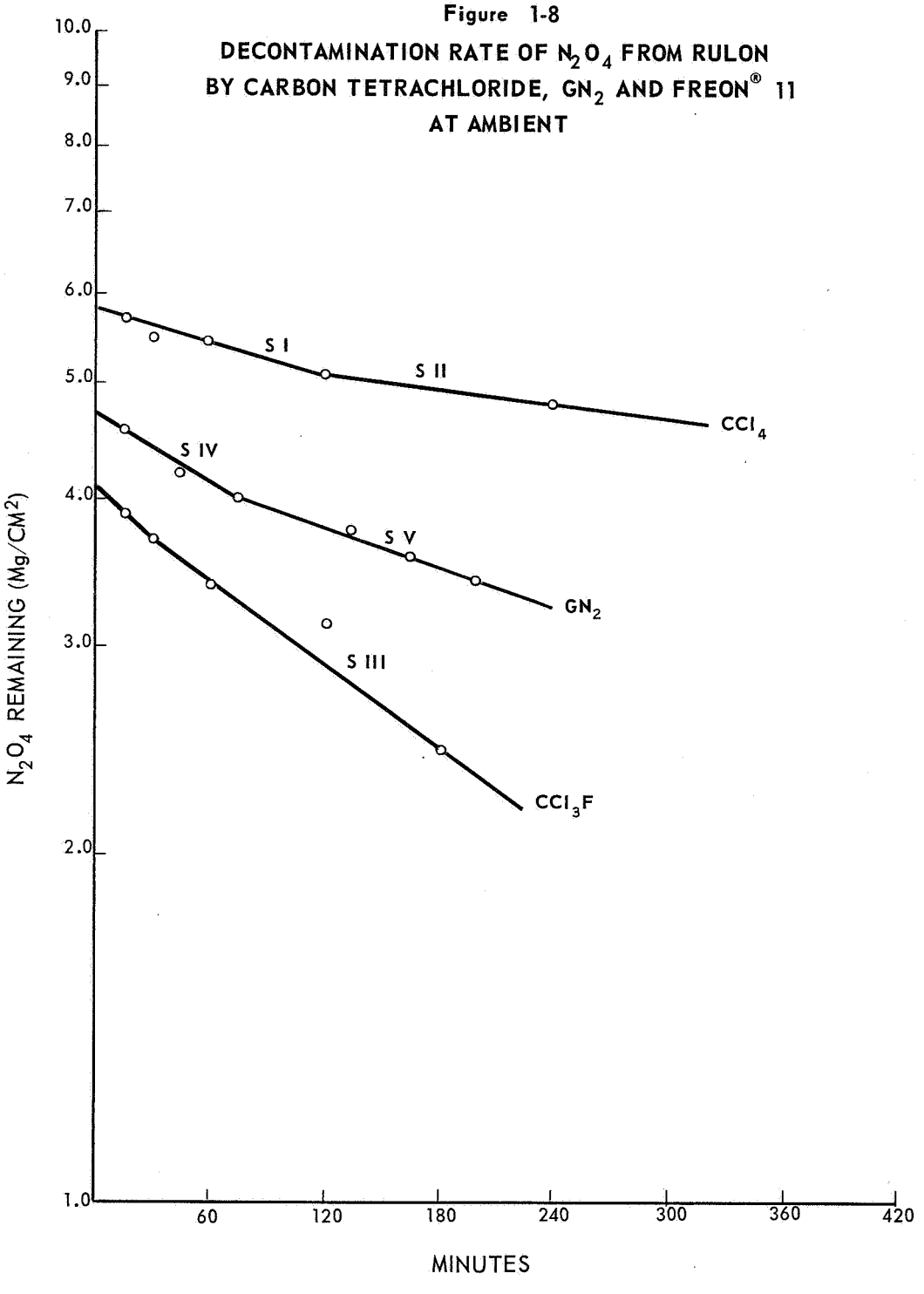


Figure 1-9

DECONTAMINATION RATE OF N_2O_4 FROM TEFLON® TFE BY GN_2 AT 100°C

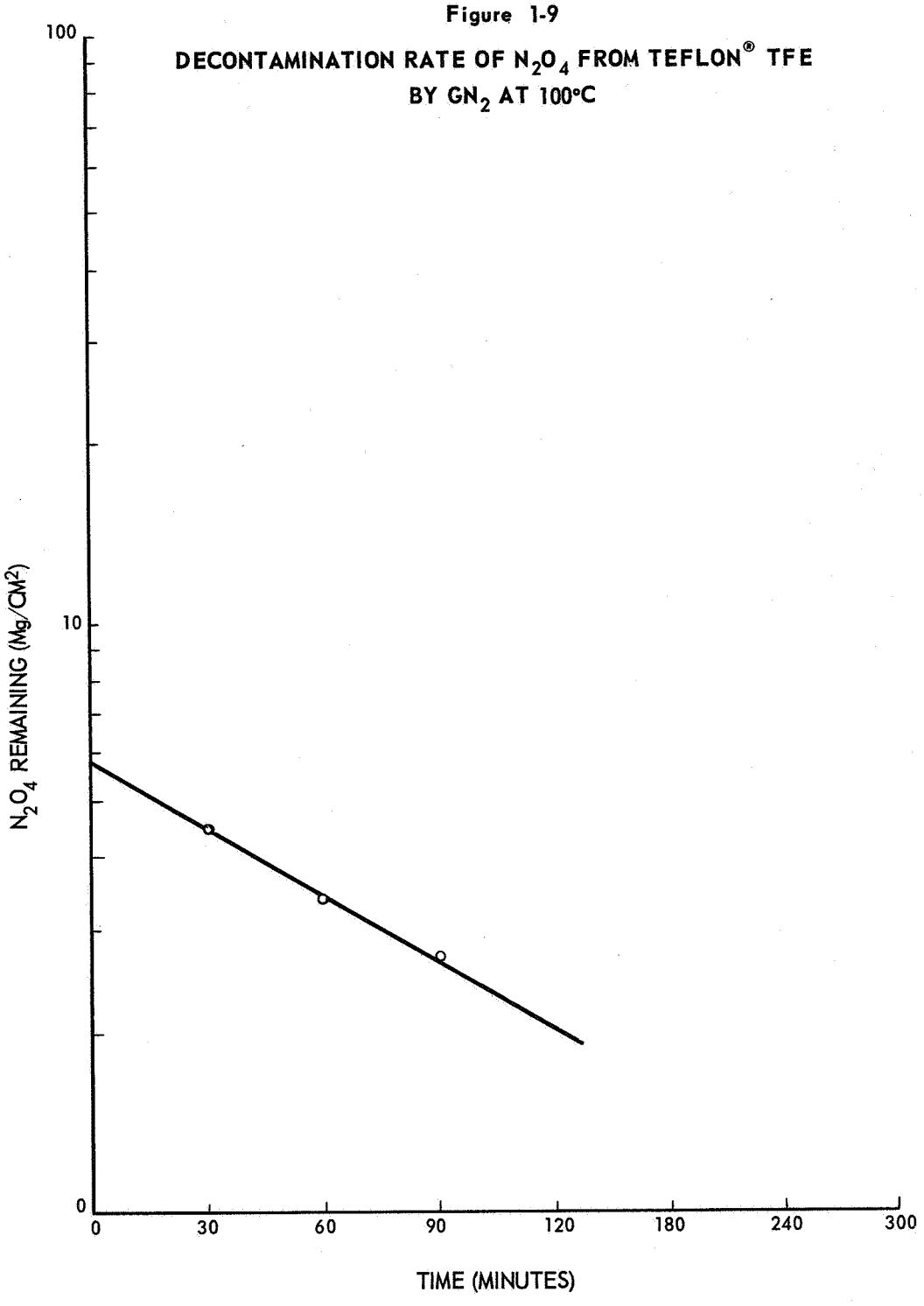


Figure 1-10

DECONTAMINATION RATE OF N_2O_4 FROM TEFLON® FEP BY GN_2 AT 100°C

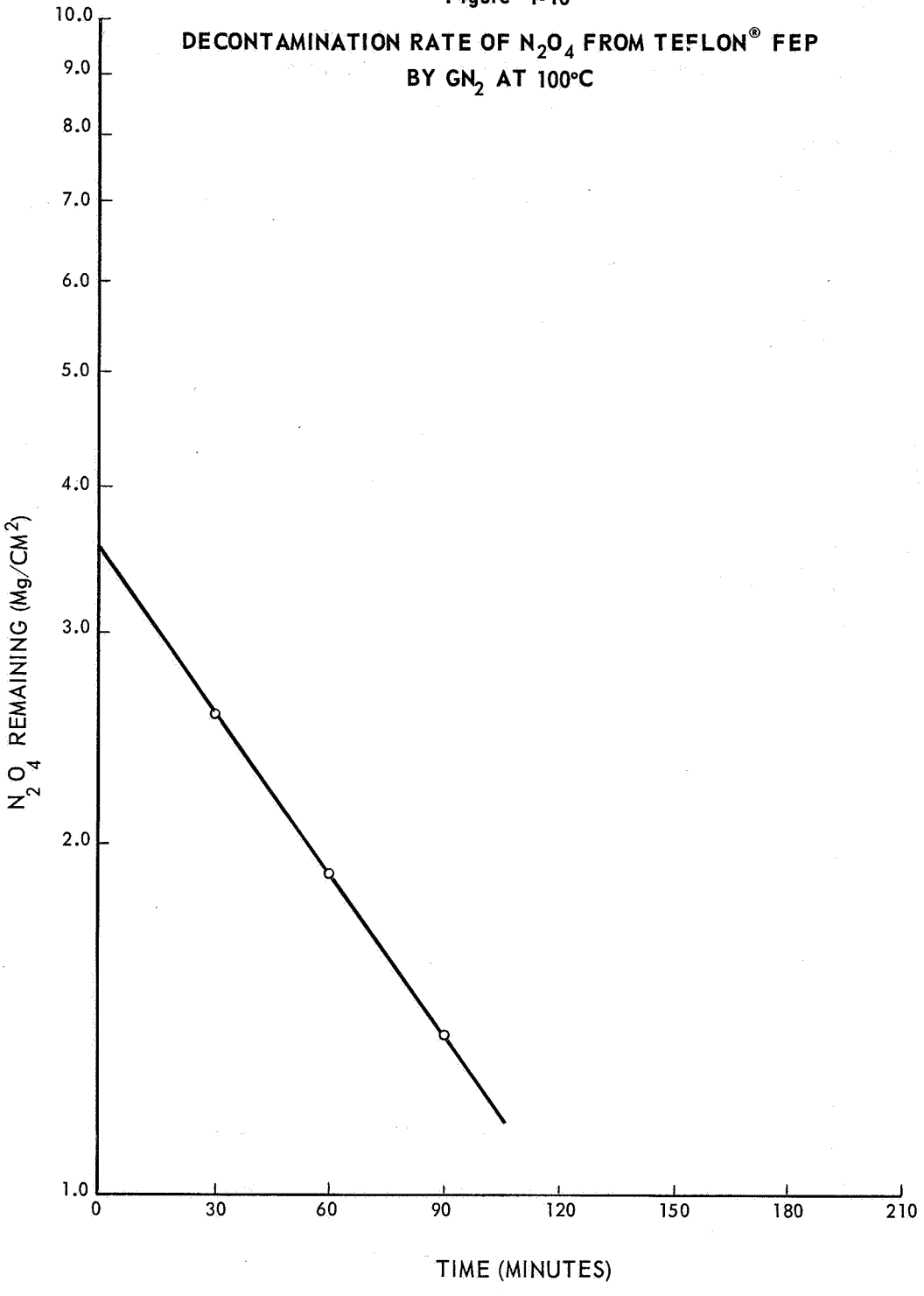


Figure 1-11

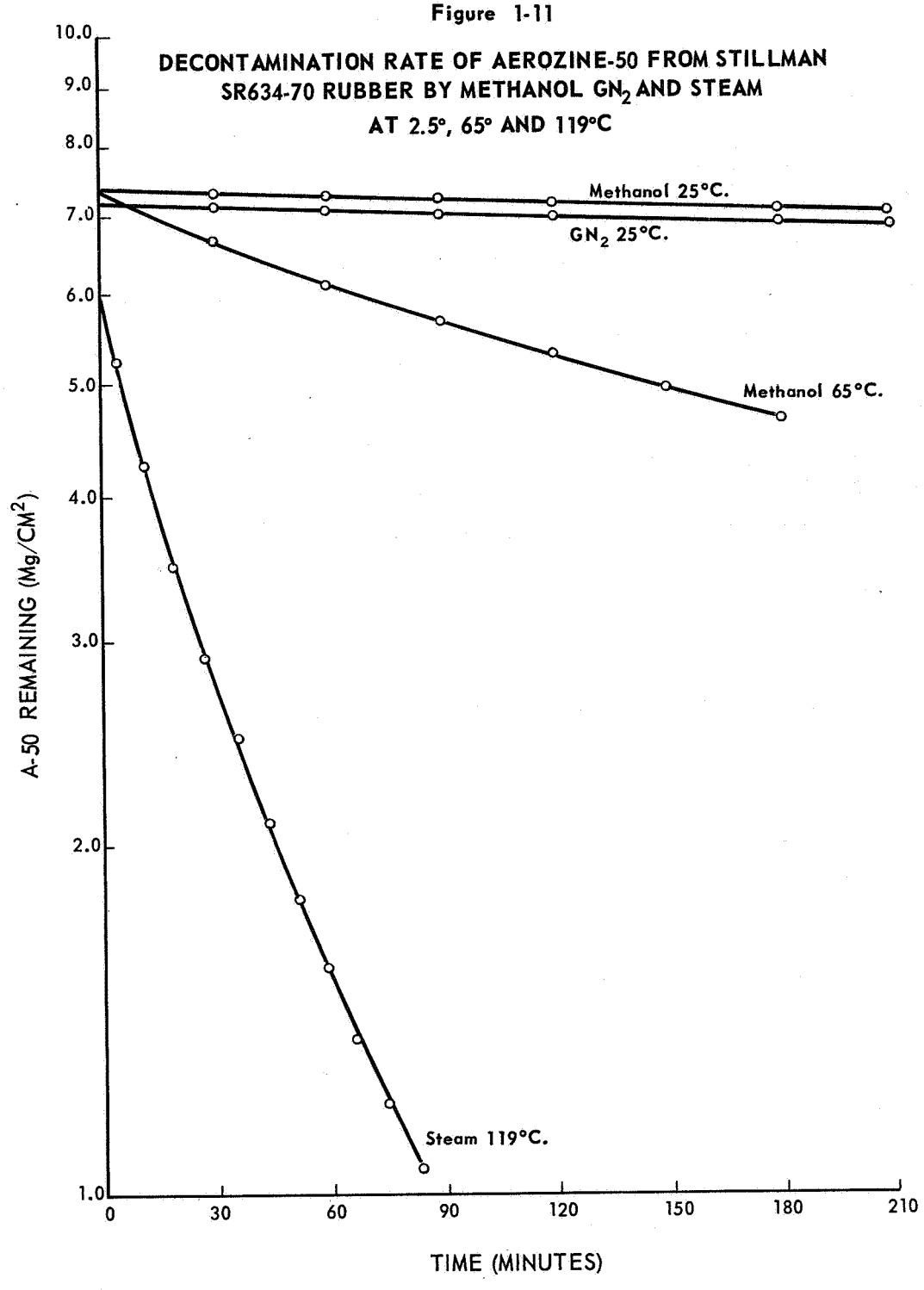

DECONTAMINATION RATE OF AEROZINE-50 FROM STILLMAN SR634-70 RUBBER BY METHANOL GN_2 AND STEAM AT 2.5°, 65° AND 119°C
Methanol 25°C.
GN_2 25°C.
Methanol 65°C.
Steam 119°C.
A-50 REMAINING (Mg/CM²)
TIME (MINUTES)
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
30
60
90
120
150
180
210

Figure 1-12

DECONTAMINATION RATE OF AEROZINE-50 FROM STILLMAN SR634-70 RUBBER BY GN_2 AT 90°C

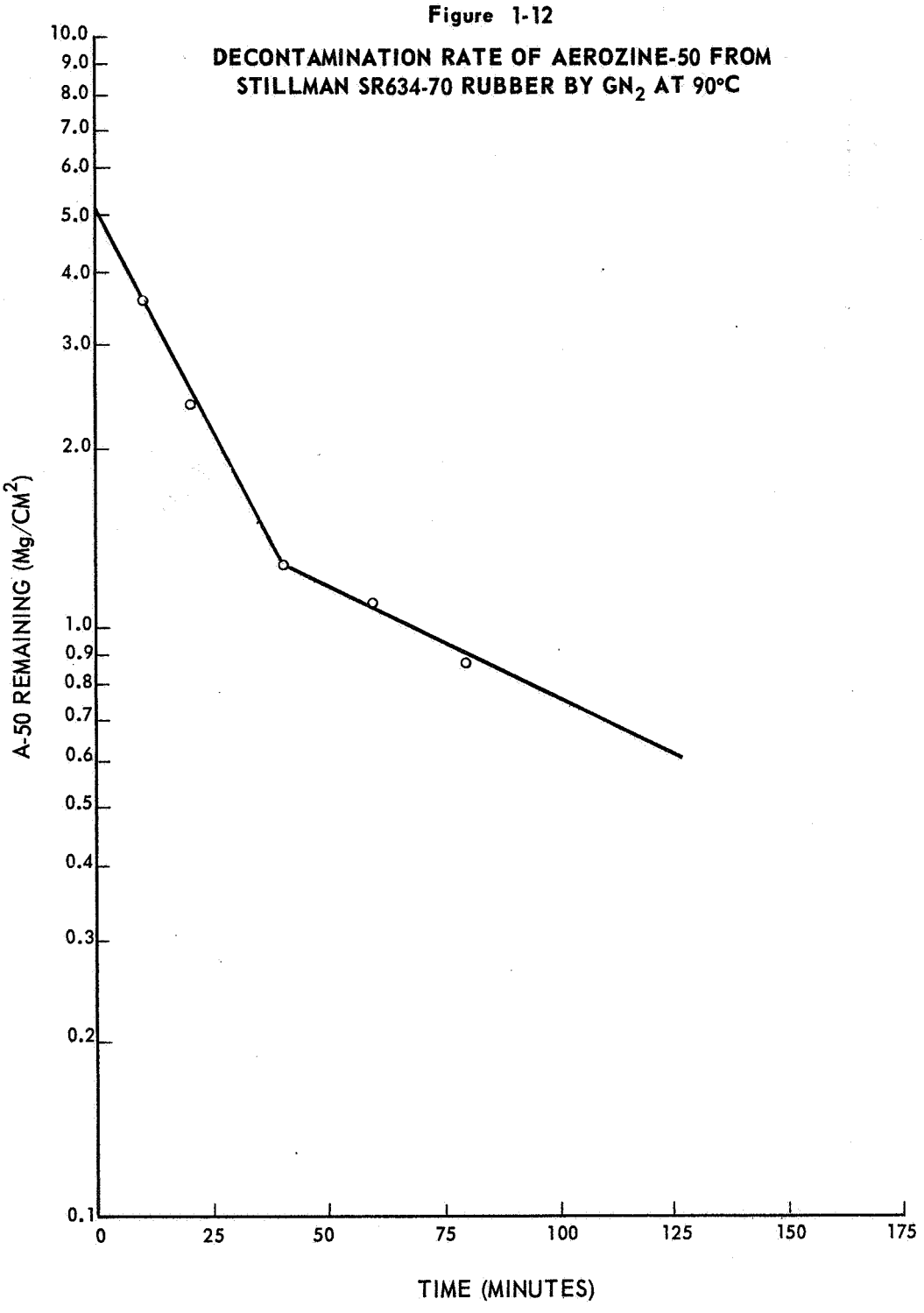


Figure 1-13

DECONTAMINATION RATE OF AEROZINE-50 FROM STILLMAN SR634-70 RUBBER BY ISOBUTANOL VAPORS AT 100°C.

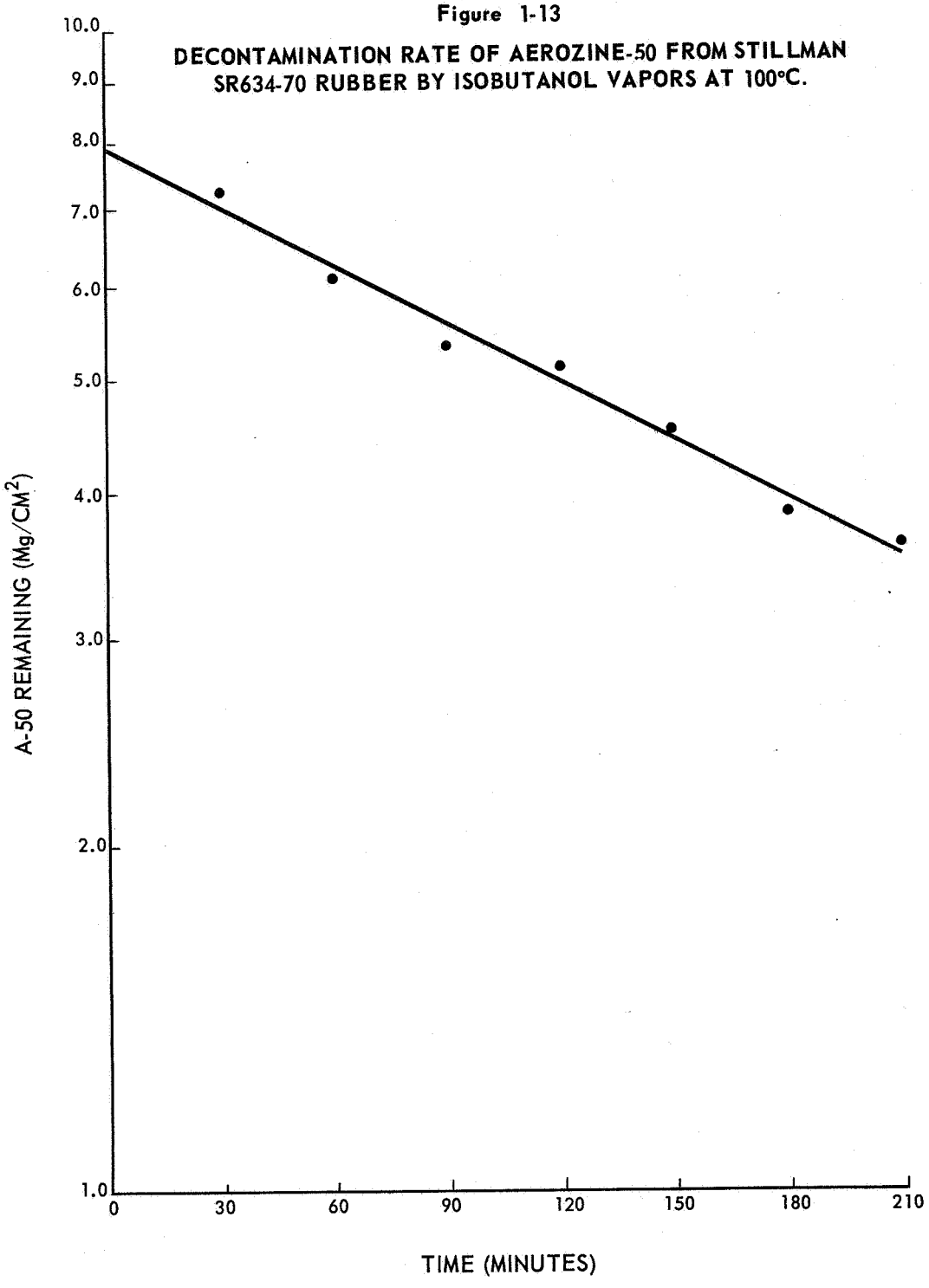
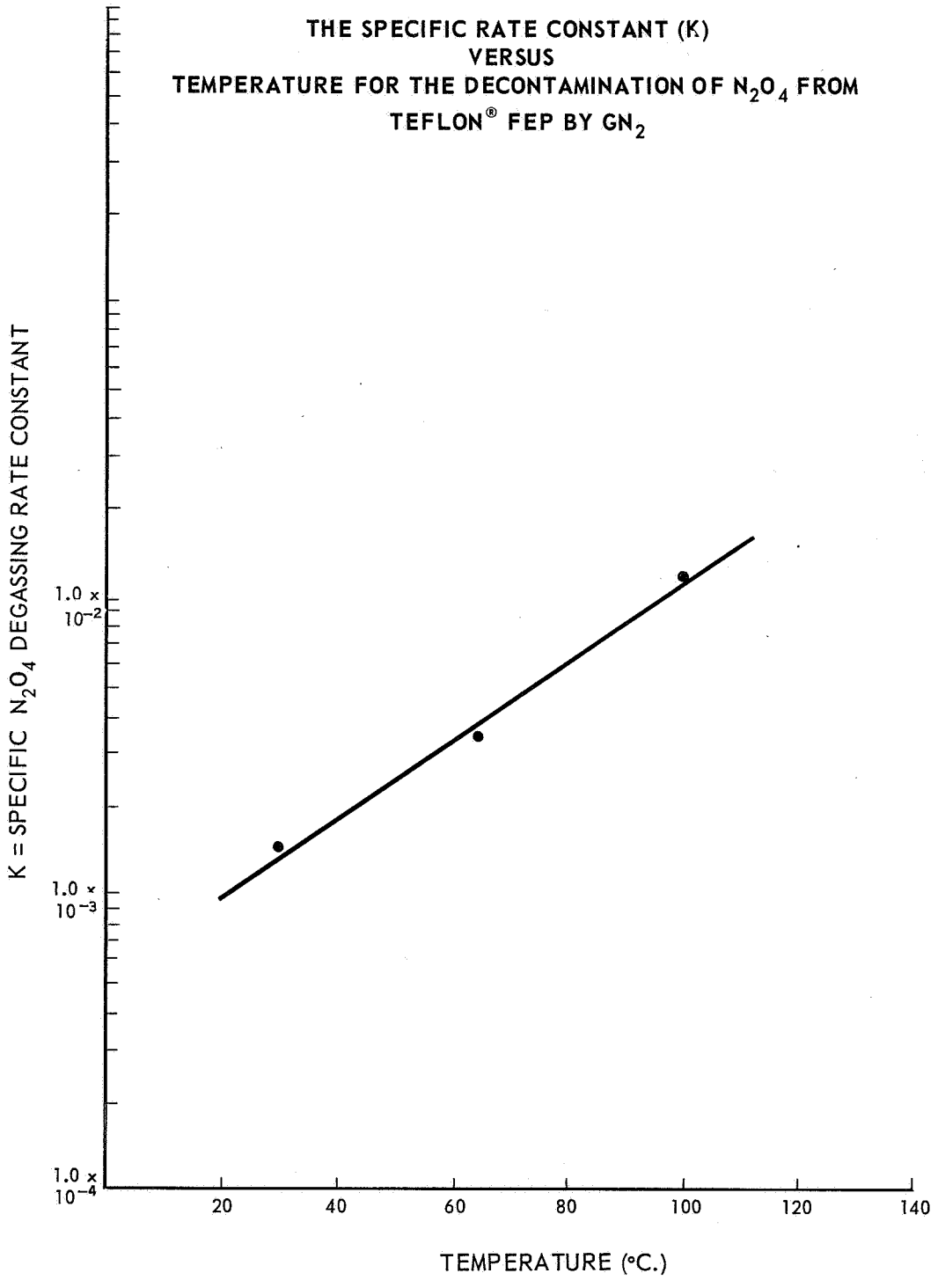


Figure 1-14

THE SPECIFIC RATE CONSTANT (K)
VERSUS
TEMPERATURE FOR THE DECONTAMINATION OF N_2O_4 FROM
TEFLON® FEP BY GN_2



VII. UNIT 2 - METHODS RESEARCH

A. Summary

1. Results obtained clearly show that the rate of desorption of N_2O_4 from the Teflons® and of Aerozine-50 from Stillman SR634-70 rubber is dependent on temperature and independent of the kind of the solvent used.

2. Cleaning of the fuel and oxidizer systems may be accomplished by heating to temperatures in the range, 80 to 105° C, for a period of 1 to 3 hours, plus some form of purging. At ambient temperature, 1 to 5 days would be required.

3. Vapor-phase cleaning is feasible with a number of solvents, preferably those boiling in the range, 45° to 105° C.

4. Vapor-phase cleaning has advantages over liquid fill-and-drain procedures as follows:

   a. Latent heat of vaporization of solvent available to heat the system uniformly throughout.

   b. Flowing film of condensed solvent vapor is effective in removing solid as well as liquid contaminants.

   c. All surfaces within the system are bathed by the flowing condensate film.

   d. Solvent required is reduced by a factor varying from 1/100 to 1/1000 of the amount required for fill-and-drain flushing.

5. From a purely technical standpoint, the best vapor-phase decontaminating solvent is Freon® E-2, a development stage compound material produced by E. I. du Pont. It is compatible with all components of both systems.

6. Other solvents that may be suitable for use in vapor-phase decontamination are:

   a. Inhibited carbon tetrachloride - oxidizer system

   b. Isopropanol - fuel system

   c. Methanol - fuel system

   The objectives of this work unit include a search for unique and improved methods of decontaminating the propulsion system; a comparison of liquid-phase flushing with a vapor-phase process, and a study of the effect of temperature on the rate of removal of the oxidizer, the fuel, and selected solvents.

B. Experimental and Results

1. Tests at Ambient Temperature (24.5° C).

The rate of absorption and desorption of several solvents in the Teflons® was measured in ordinary laboratory glassware. Tests with N_2O_4 were conducted in 4 Pyrex reaction chambers connected by stainless steel tubing to the N_2O_4 supply cylinder, to the GN_2 purge supply, and to a water scrubber.

All specimens were cut with a standard tensile test specimen cutter from sheets of the material to be tested. Dimensions are 2-1/2" long by 3/8" wide, with a necked-down section whose smallest width is 1/8". Thickness ranged from 0.030" to 0.090".

Teflon® specimens that were to be contaminated with N_2O_4 were weighed, then placed in the Pyrex test chambers. Liquid N_2O_4 was admitted, submerging the specimens for periods ranging from 16 to 20 hours, following which the N_2O_4 was drained off, the chambers purged with GN_2 for 10 minutes, the specimens were removed, the weight gain was determined, and the specimens were put through the decontaminating procedure under study.

Stillman SR634-70 rubber specimens that were to be contaminated with Aerozine-50 (A-50) were placed in small glass bottles filled with A-50 and tightly capped. Exposure time in these bottles was usually over 1 week, following which the specimens were removed, dried, the weight gain was determined, and the specimens were put through the decontamination procedure under study.

In all instances weight gain or loss is expressed as milligrams per square centimeter of specimen surface. Surface area of specimens is 11.1 square centimeters for specimens 0.031" thick and 13.4 square centimeters for specimens 0.090" thick.

In general, the original weight of the specimen is subtracted from the weight of the specimen after exposure to the contaminant or a solvent. The increase in weight, expressed in milligrams, is divided by the specimen surface area in square centimeters to give the net weight gain (or loss) in milligrams per square centimeter.

a. Fill and Drain (24.5° C)

Teflon® specimens of known N_2O_4 content were returned to the Pyrex test chambers and each specimen was flushed a given number of times after which it was removed from the chamber, dried, and weighed. Flushing solvents were water, CCl_4, and Freon® 11. Attempts to correlate weight-loss with the number of solvent flushes revealed that the controlling factor in N_2O_4 desorption from Teflon® at ambient (24.5° C) temperature is time -- not the number of flushes.

b. Prolonged Soaking in Liquid Solvents (24.5° C)

A number of Teflon® specimens of known N_2O_4 content were soaked in water, CCl_4, and Freon® 11. Individual specimens were withdrawn periodically, dried, and weighed. Weight loss was assumed to be due to desorption of N_2O_4. It was possible to correlate the diminishing N_2O_4 content with time. Plots of these data are shown appropriately labeled in Figure 2-3.

c. N_2O_4 Desorption into Gaseous Atmospheres (24.5° C)

A number of specimens of known N_2O_4 content were placed in several gaseous atmospheres: GN_2, Freon® 11, and the dry air of a desiccator. At timed intervals individual specimens were removed and weighed. Plots of these data are shown appropriately labeled in Figure 2-3.

d. Absorption of CCl_4 by Teflon® TFE (24.5° C)

Weighed specimens of Teflon® TFE (uncontaminated) were placed in an Erlenmeyer flask containing CCl_4 sufficient to cover the specimens. Individual specimens were withdrawn periodically and weighed. A plot of these data is given in Figure 2-1.

2. Tests at the Boiling Temperature of Various Solvents

These tests were performed in ordinary refluxing apparatus. Teflon® specimens contaminated with N_2O_4 or Stillman SR634-70 rubber contaminated with Aerozine-50 were suspended in the saturated vapor of the candidate solvent. To correct for solvent adsorption by the contaminated specimen an uncontaminated or "blank" specimen was paired with it. Five such pairs were usually placed in the saturated vapors of the candidate solvent and periodically a single pair was withdrawn from the column and weighed. The weight gain of the blank specimen of a given pair was assumed to be a measure of the solvent absorption by the contaminated specimen. This weight was deducted from the gross weight of the contaminated specimen with the expectation that the corrected weight of the contaminated specimen would be a reasonably accurate measure of the contaminant remaining in the specimen at the time it was removed from the column. This assumption proved to be in error in some instances, as will be shown.

a. Solvent Adsorption by Teflon® TFE at Boiling.

Weighed specimens of Teflon® TFE (uncontaminated) were suspended in the saturated vapors of CCl_4 and Freon® 112. Weight gain was measured by periodic withdrawal of single specimens and weighing. Absorption of these two solvents is plotted versus time in Figure 2-2.

b. Desorption of N_2O_4 from Teflons®

By the procedure outlined above the desorption of N_2O_4 from Teflons® suspended in the saturated vapors of CCl_4, Freon® 112 (Figure 2-3), and Freon® E-2 (Figures 2-10 and 2-11) was studied. Data are plotted in the cited figures.

c. Desorption of A-50 from Stillman SR634-70 Rubber Specimens

Desorption of A-50 from Stillman SR634-70 rubber specimens suspended in the vapors of: (Figure 2-4) a mixture of ethanol 50% with acetone 50%; (Figure 2-5) saturated steam; (Figure 2-6) methanol; (Figure 2-7) isopropanol; (Figure 2-8) perfluorodimethylcyclobutane; and (Figure 2-9) Freon® E-2 is shown by plots in the cited figures.

Inspection of these plots show that absorption of the solvent is appreciable in all cases. The absorption by the blank specimen is shown by the lower curve (originating at 0,0) labeled "Blank Specimen Absorption of Solvent," etc.

The upper curves in these plots labeled "A-50 Reflux Desorption" are the weight of the contaminated specimen after the weight gain of the blank specimen has been deducted. The curves at zero time indicate the initial amount of contaminant in the specimen. So, if notwithstanding the correction applied, these upper curves show an increased weight with time in the refluxing column, it is obvious that the contaminated specimens absorb solvent equal to (1) the weight of A-50 desorbed, plus (2) the correction applied, plus (3) the increase in weight over that at the start as indicated by the upward slope of the upper curve.

In Figure 2-6, for example, the curves developed by the above procedure originate at about 7.5 milligrams absorbed A-50 per square centimeter of specimen surface. (This is the ordinate value at zero time-from-start). The lowest curve starting from this point is a plot of the data obtained by periodic weighings of the first pair of specimens which were placed directly in the nitrogen-purged chamber. Since there was no exposure to solvent none was absorbed and this curve slopes downward from the start indicating the desorption of A-50 with time in a 50° C nitrogen purge.

The uppermost curve labeled "A-50 Reflux Desorption" is a plot of the data obtained by weighings of the paired specimens as they were removed from the reflux column. Each successive pair removed had been exposed to a longer period of solvent vapor action and the increased solvent absorption is indicated by the upward slope of this curve.

As each successive pair was withdrawn from the refluxing column it was, after being weighed, placed in the nitrogen-purged chamber where measurement of its weight change with time was continued. Plots of this data are the curves that branch downward from the upper, or "A-50 Reflux Desorption" curve.

3. Results

a. Effect of Solvent or Atmosphere on Rate of Desorption of N_2O_4 from Teflon® TFE.

Figure 2-3 shows the loss of absorbed N_2O_4 from Teflon® TFE under various conditions. All curves at 24.5° C are closely grouped considering that these are plots of the rate of N_2O_4 desorption in water, CCl_4, Freon® 11 liquid, Freon® 11 gaseous, GN_2, and in the dry air of a desiccator.

It is apparent that the nature of the solvent or of the atmosphere does not significantly affect the rate of desorption of N_2O_4 from Teflon® TFE at 24.5° C. It is believed that this also holds at other tmperatures.

b. Effect of Temperature on the Rate of Desorption of N_2O_4 from Teflons® or of A-50 from Stillman SR634-70 Rubber.

Figures 2-3, 2-10, and 3-11 show the desorption of N_2O_4 from the Teflons® in the presence of several solvents boiling at various temperatures. The time required for removal of 1/2 of the N_2O_4 is considered to be a good basis for comparison of procedures. For Teflon® TFE these 50% marks are tabulated:

Solvent	B.P.	Time for 50% Removal	Source
Average of all at	24.5° C	300 Minutes	Fig. 2-3
CCl_4	81° C	40 Minutes	Fig. 2-3
Freon® 112	93° C	20 Minutes	Fig. 2-3
Freon® E-2	101° C	15 Minutes	Fig. 2-10

From this tabulation it is apparent that temperature is the controlling factor in removal of N_2O_4 from Teflons® and that the nature of the solvent has no significant effect.

With regard to the effect of temperature on the rate of desorption of A-50 from Stillman SR634-70 rubber, this is not as readily discernable by inspection of curves as it was for N_2O_4 desorption from Teflons® because the rubber absorbed solvent to an extent that obscured the desorption of the A-50. However, some approximations are possible and these are tabulated below:

Solvent or Atmosphere	Temperature	Time for 50% Removal	Source
Perfluorodi-methylcyclobutane	45°	1,200 Minutes	Fig. 2-8
Nitrogen	50°	900 - 1,000 Minutes	Figs. 2-5 & 2-7
Isopropanol	83°	180 Minutes	Fig. 2-7
Water	100°	80 Minutes	Fig. 2-5
Freon® E-2	101°	20 Minutes	Fig. 2-9

The effect of temperature again appears to be controlling, and the nature of the solvent or atmosphere appears to be insignificant.

A comparison of Figures 2-1 and 2-2 show, also, that the rate of solvent absorption in Teflon® TFE is strongly affected by temperature. Teflon® TFE absorbed more of the solvents at their boiling points, 81 and 93°, than at 24.5° C by a factor greater than ten-fold.

c. Comments on Absorption of Solvent by A-50 Contaminated Stillman SR634-70 Rubber.

Figures 2-4 through 2-9 are useful as an indication of the effect of the cleaning solvent on the A-50 contaminated Stillman SR634-70 rubber, and of the effect on the rubber of the A-50 contaminant.

The curves starting at 0,0 are plots of the "Blank Specimen's Absorption of Solvent." In Figure 2-4, for instance, the absorption of the 50-50 solvent mixture is seen to be appreciable, more than 2 mg/cm^2. The weight of solvent absorbed by the blank specimen was deducted from the gross weight of the contaminated specimen. At 200 minutes this "corrected" weight of absorbed material was 6.8 mg/cm^2 after the 2.0 mg/cm^2 absorbed by the blank had been deducted. It is known from work done by co-workers that at 68° C the desorption of A-50 from Stillman rubber in 200 minutes is appreciable, perhaps 40% of its original content or about 2 mg/cm^2. This means the pores of the A-50 sample were so swollen by the effect of the A-50 that absorbed material had reached a (uncorrected) gross weight of 8.8 mg/cm^2 after losing 2 mg of A-5. Of the original 5 mg/cm^2 A-50 absorbed in this sample it had only 3 mg remaining. So in the process of desorbing 2 mg of A-50/cm^2 this specimen absorbed 8.8 -3.0 = 5.8 mg/cm^2 of solvent. Compare this with the blank specimen's 2.0 mg/cm^2 of solvent absorbed during the same length of time.

Another effect of A-50 on Stillman rubber is seen by inspection of Figure 2-5. Two separate tests are plotted in this figure. One test is made on specimens having an initial A-50 content of 5 mg/cm^2. Note how this curve shows a drop in corrected weight due to the action of saturated steam. The other curve represents data obtained on specimens having an initial A-50 content of 8.0 mg/cm^2. The additional swelling effect of the greater A-50 content drastically changed the characteristics of the "A-50 Reflux Desorption" curve.

Conclusion is that the A-50 is a powerful swelling agent in its effect on Stillman SR634-70 rubber.

The curves in Figure 2-7 show the results of work with isopropanol in removing A-50 from Stillman rubber. Inspection of the curves shows the A-50 is rapidly expelled if the weight change correction is applied. The Stillman rubber absorbed more isopropanol than was experienced with methanol, steam, and several other solvents.

Figure 2-8 is a plot of data obtained with perfluorodimethyl-cyclobutane. The rate of desorption of A-50 from Stillman rubber based on weight change measurements is slow, because of the low boiling temperature of this solvent, 45° C. One-half of the A-50 had been desorbed in about 1,200 minutes, which is about the same as the desorption rate of A-50 in 50° C, GN_2.

One of the more important aspects of this work is the discovery that absorption of perfluorodimethylcyclobutane into the Stillman rubber is very slight--less than 0.1 milligram per square centimeter in 24 hours at 45° C. This solvent was disqualified for use in fuel system decontamination because of the formation of a solid reaction product which appeared as a scum on the wall of the flask.

Figure 2-9 shows a plot of data obtained with a second fluorinated compound, DuPont's Freon® E-2 (b.p. = 101° C), a fluorinated ether. Contaminated test specimens suspended in the saturated vapor of boiling Freon® E-2 desorbed the A-50 in 5 to 6 hours with negligible absorption of this solvent in the specimens. This solvent appears to be ideal for use in decontamination of the fuel system. It is extremely inert and has no detrimental effects on the physical properties of Stillman rubber.

d. Desorption of N_2O_4 from the Teflons® in DuPont's Fluorinated Ether, Freon® E-2.

This experimental work is discussed separately because Freon® E-2 was tested with N_2O_4 -- Teflon® after tests with A-50 -- Stillman rubber had given extraordinarily good results. Figures 2-10

and 2-11 show plots of data obtained in tests on specimens of Teflon® TFE and FEP, respectively, desorbing N_2O_4 in the saturated vapor of Freon® E-2. The desorption proceeds rapidly. TFE is completely free of N_2O_4 in 50 minutes. FEP requires 5 to 7 hours. Adsorption of the Freon® R-2 into the Teflons® was appreciable.

e. Tables

Tables 2-I and 2-II summarize results plotted in Figures 2-1 through 2-11 and give additional information relative to the solvents tested.

C. Discussion

The general approach was based on the premise that most of the difficulties in the decontamination procedures are due to propellants absorbed into semiporous elastomers and plastic materials in the systems. Work in the unit was entirely concerned with studies to determine the most effective way to decontaminate these nonmetallic materials with the least possible detrimental effect on them or on the metallic parts.

Also, total decontamination of the nonmetallic parts was considered to be a proper goal even though not completely attainable. That is, not only were the respective propellant components to be removed but also the cleansing solvent so that the part would be free of any foreign substance.

It was at first expected that liquid or vapor flushing at ambient temperature would probably suffice for decontamination. The problem was thought to be merely that of determining which solvent was the most effective in leaching out the respective propellant components.

It is considered difficult to heat the propulsion system to the desired temperature range by flowing heated gas through the system. The sensible heat available by this means would not be sufficient to maintain the desired temperature because of radiation, conduction, and convection losses.

By vaporizing a fluid and flowing the vapor through the system, the latent heat of vaporization is available to allow uniform heating throughout the system. The vapor would condense on all surfaces colder than the boiling point of the solvent. These surfaces would be bathed in a flowing film of the condensing vapor while at the same time being heated. Heating by this means would be rapid and uniform. The uncondensed vapor flowing through the systems would sweep out the gas phase of the contaminants. The amount of solvent required for vapor-phase flushing is less by a factor of between 1/100 and 1/1000 than would be required for a liquid flush procedure. Vapor-phase flushing should be feasible for the decontamination of both the fuel and the oxidizer systems.

The most effective decontaminating solvent for use in vapor-phase flushing is Freon® E-2. However, this solvent is in the developmental stage. Vapor-phase flushing would require about 1,000 pounds for the Apollo propulsion system.

Freon® E-2 would be suitable for decontaminating both systems. It is interesting to note that Freon® E-2 has a molecular weight of 452; it has only one hydrogen atom and two oxygen atoms; otherwise, it is a totally fluorinated ether. There are not many compounds that meet all requirements, but other compounds that might be expected to have merits similar to Freon® E-2 as a decontaminant would have these properties:

1. Inertness to N_2O_4 and A-50.

2. Molecular weight in the range of 300 and up for low absorption.

3. Low freezing point, -10° C or lower.

4. Boiling point in the range, 80-101° C. This, with a large molecular weight, would also require a highly fluorinated compound.

Other solvents that may be suitable for decontamination are inhibited CCl_4, in the oxidizer system, and isopropanol, normal propanol, or methanol, in the fuel system. The Stillman rubber absorbs significant amounts of these materials and holds them tenaciously. However, it is believed that the presence of these compounds can be tolerated to the extent that they would be present in the fuel system.

Water would be excellent and cheap for use in both systems, but there are widespread objections to water because of the difficulties of complete drying.

TABLE 2-I REMOVAL OF N_2O_4 FROM TEFLONS® TFE AND FEP

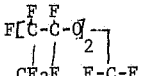
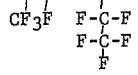
Cleaning Solvent, Vapor, or Gas Tested and Type of Teflon® Used	Plot Fig. No.	Formula	Boiling Point or Temp of Test °C	Effect of Solvent on Tensile Strength (See Note 1)	Net Weight Change of N_2O_4 Treated Specimens and Weight Gain of Blank Specimens Due to Solvent Absorption as Percent of Initial Weight of N_2O_4 Absorbed in Treated Specimens at Indicated Time Intervals From Start								Remarks
					50 Minutes		100 Minutes		300 Minutes		1,400 Minutes		
					Treated	Blank	Treated	Blank	Treated	Blank	Treated	Blank	
Carbon Tetrachloride Teflon® TFE	2-3	CCl_4	24.5	Negligible	(Loss) 17.8	(Gain) 0.61	(Loss) 24.1	(Gain) 2.0	(Loss) 44.4	2.9	--	6.2	
Water (TFE)	2-3	H_2O	24.5	Negligible	(Loss) 19.5	--	(Loss) 29.0	--	--	--	--	--	
Freon® 11 Liquid (TFE)	2-3	CCl_3F	24.5	Negligible	(Loss) 18.3	--	(Loss) 26.7	--	--	--	--	--	
Freon® 11 Vapor (TFE)	2-3	CCl_3F	24.5	Negligible	(Loss) 13.9	--	(Loss) 20.5	--	--	--	--	--	
Nitrogen Purge (TFE)	2-3	GN_2	24.5	None	(Loss) 22.0	--	(Loss) 32.7	--	--	--	--	--	
Desiccator (TFE)		Dry Air	24.5	None	(Loss) 27.3	--	(Loss) 34.5	--	--	--	--	--	
Carbon Tetrachloride (TFE)	2-3	CCl_4	81°	Negligible	(Loss) 61.1	(Gain) 6.7	(Loss) 76.1	(Gain) 12.8	(Loss) 100.0	(Gain) 32.0	--	--	100% Desorption at 260 minutes
Freon® 112 (TFE)	2-3	$C_2Cl_4F_2$	93°	Negligible	(Loss) 66.1	(Gain) 12.8	(Loss) 78.9	(Gain) 19.4	(Loss) 100.0	(Gain) 37.2	--	--	Extrapolated Curve would be at 100% Desorption at 200 minutes
Freon® E-2 (TFE)	2-10		101°	Negligible	(Loss) 100	(Gain) 25.0	--	--	--	--	--	--	
Freon® E-2 (FEP)	2-11		101°	Negligible	(Loss) 60.0	(Gain) 6.0	(Loss) 78.0	(Gain) 16.0	(Loss) 96.0	(Gain) 36.0	(Loss) 100.0	--	100% Desorption at 500 minutes

TABLE 2-II REMOVAL OF AEROZINE-50 FROM STILLMAN SR634-70 RUBBER

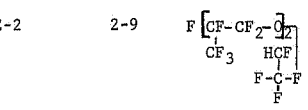
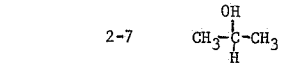
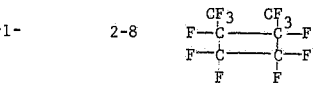
Cleaning Solvent, Vapor or Gas Tested	Plot Fig. No.	Formula	Boiling Point or Temp of Test	Aerozine-50 Absorbed by Specimens mg/cm^2 (Avg.)	Net Weight Change of Refluxing Specimens Treated with A-50 and Weight Gain of Blank Specimens as Percent of Initial Weight of A-50 Absorbed in Treated Specimens at Indicated Time Intervals								Remarks
					50 Minutes		100 Minutes		300 Minutes		1,400 Minutes		
					Treated	Blank	Treated	Blank	Treated	Blank	Treated	Blank	
Du Pont Freon® E-2	2-9		101° C	7.5	(Loss) 65.3	(Gain) 0	(Loss) 78.6	(Gain) 0	(Loss) 92.0	(Gain) 0	(Loss) 100	(Gain) 6.7	Suitable for cleaning both fuel and oxidant systems
Saturated Steam	2-5	H_2O	100° C	8.0	(Gain) 5.0	(Gain) 3.7	(Gain) 4.4	(Gain) 5.6	(Gain) 2.5	(Gain) 9.4	--	--	Suitable for cleaning both fuel and oxidant systems
Mixture: 50% Ethanol 50% Acetone	2-4	C_2H_5OH $CH_3-CO-CH_3$	68° C	5.0	(Gain) 26.0	(Gain) 20.0	(Gain) 32.0	(Gain) 26.0	(Gain) 44	(Gain) 42.0	--	--	Not suitable
Methanol	2-6	CH_3OH	65° C	7.5	(Gain) 9.5	(Gain) 2.0	(Gain) 11.4	(Gain) 3.3	(Gain) 11.7	(Gain) 5.3	--	--	Suitable for cleaning fuel system only
Isopropanol	2-7		83° C	8.0	(Loss) 35.0	(Gain) 15.0	(Loss) 47.5	(Gain) 20.4	(Loss) 66.2	(Gain) 32.0	--	--	Suitable for cleaning fuel system only
Nitrogen	2-5 2-6 2-6	GN_2	50° C	8.0	(Loss) 5.5	(Gain) 0.0	(Loss) 8.75	(Gain) 0.0	(Loss) 23.1	(Gain) 0	(Loss) 58.7	(Gain) 0	Suitable for cleaning both fuel and oxidant systems
Perfluorodimethyl-cyclobutane	2-8		45° C	8.5	(Loss) 8.9	(Gain) 0	(Loss) 12.3	(Gain) 0	(Loss) 23.6	(Gain) 0	(Loss) 42.1	(Gain) 1.76	Might be suitable for cleaning oxidant system forms solid reaction product with A-50 contaminated Stillman rubber. Disqualified for fuel SiOE cleaning.

Figure 2-1

ABSORPTION OF CCl_4 BY TEFLON® TFE AT 24.5°C.
VERSUS
TIME

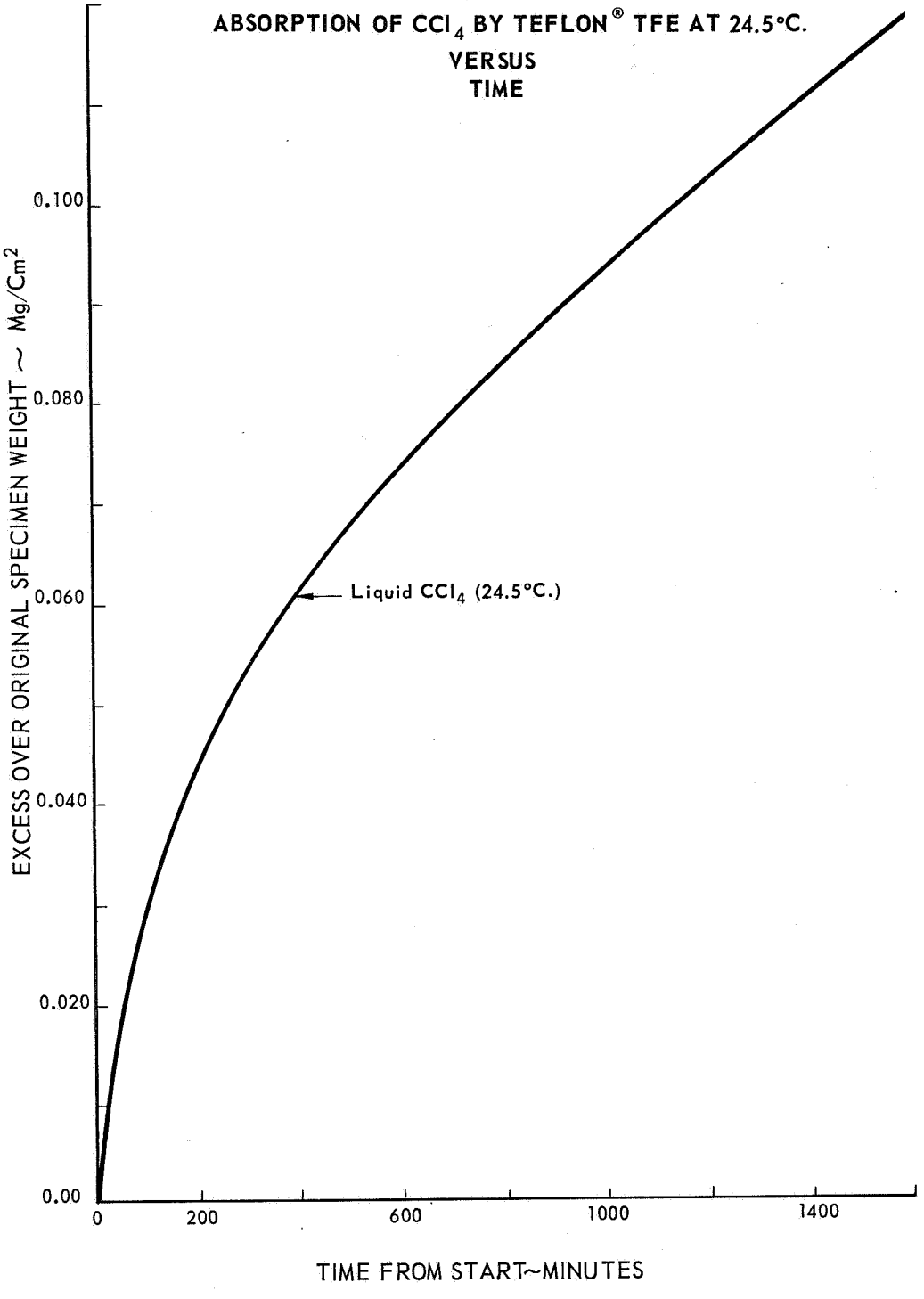


Figure 2-2

ABSORPTION OF SOLVENTS BY TEFLON® TFE
VERSUS
TIME

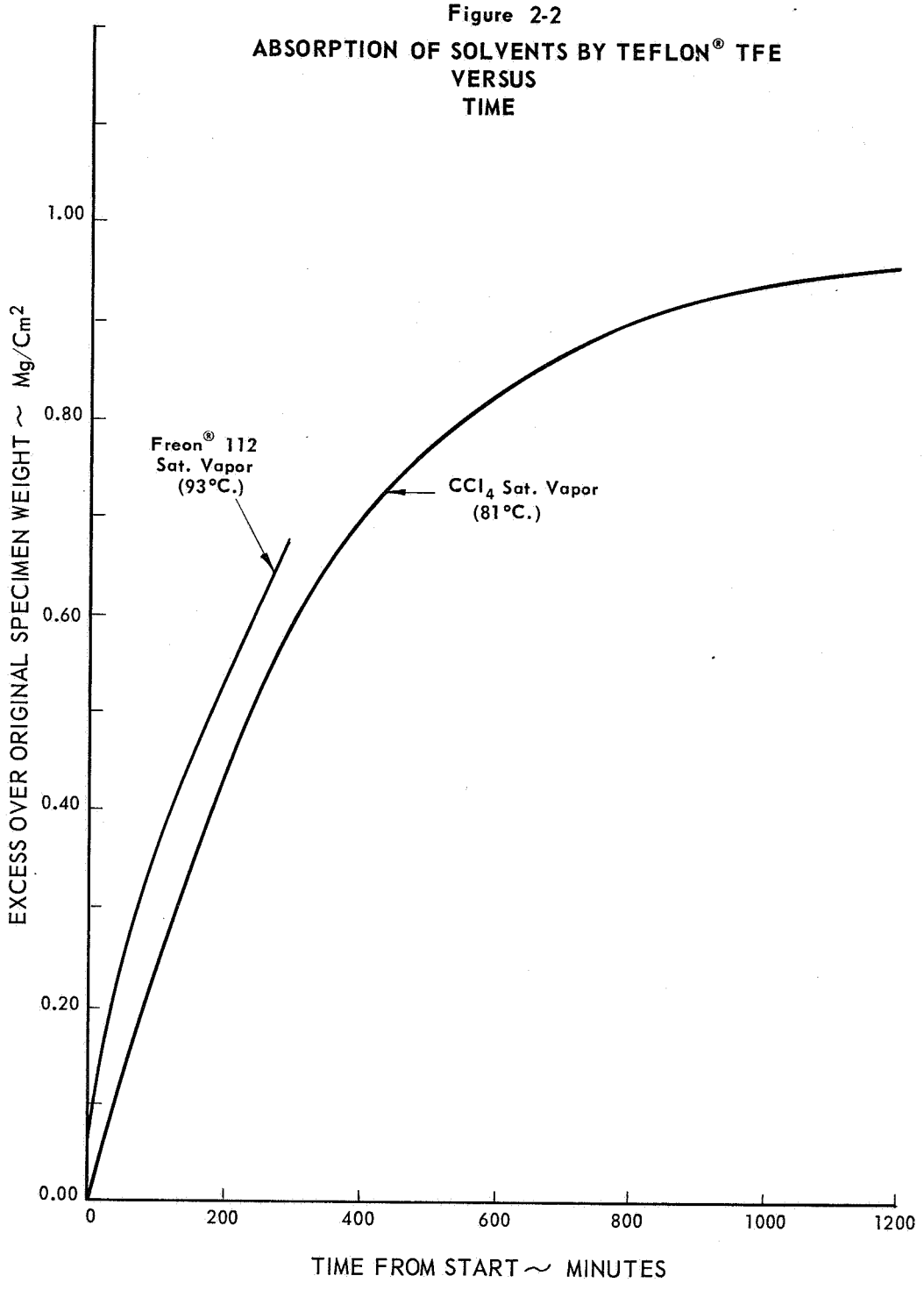
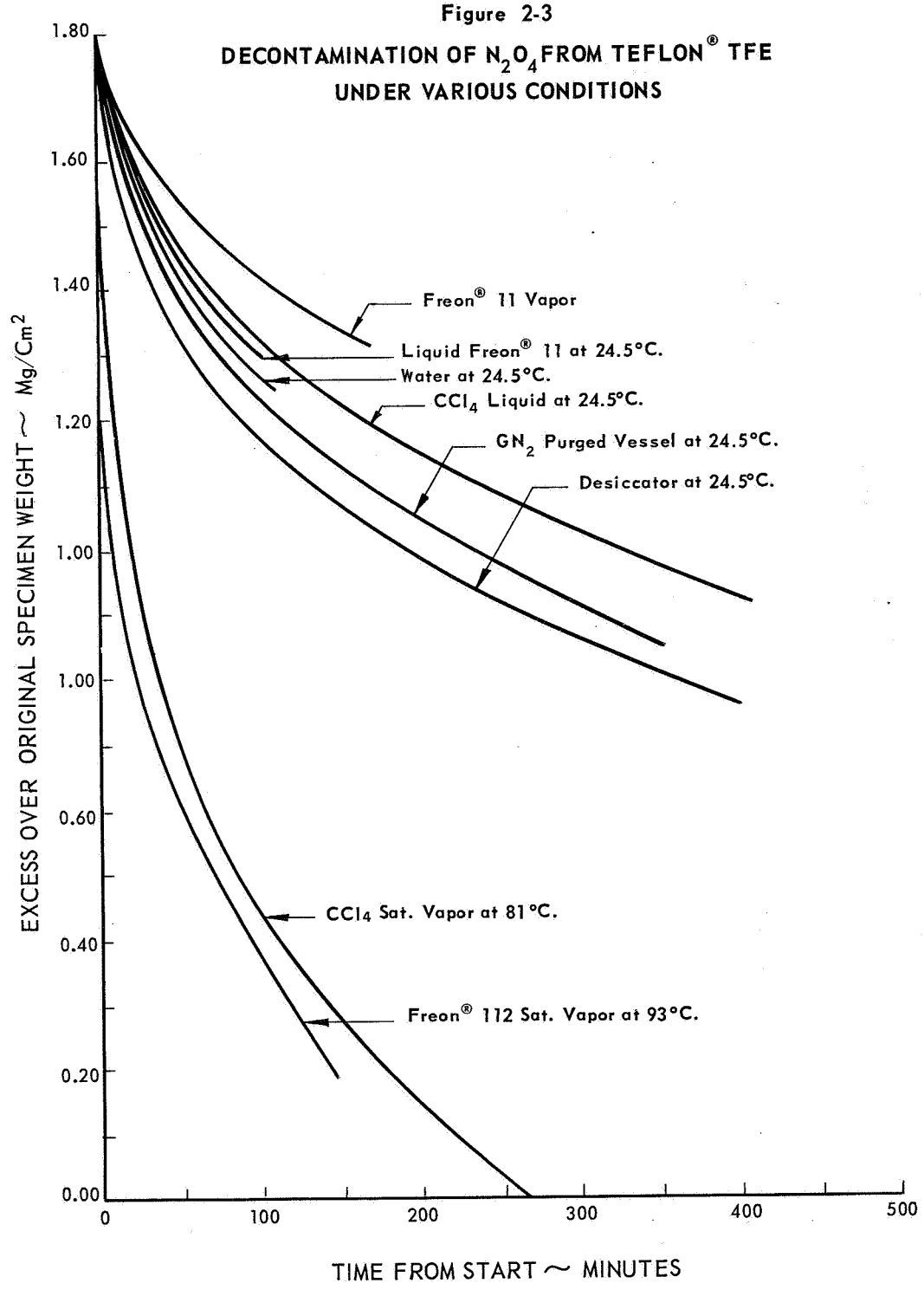


Figure 2-3

DECONTAMINATION OF N_2O_4 FROM TEFLON® TFE UNDER VARIOUS CONDITIONS



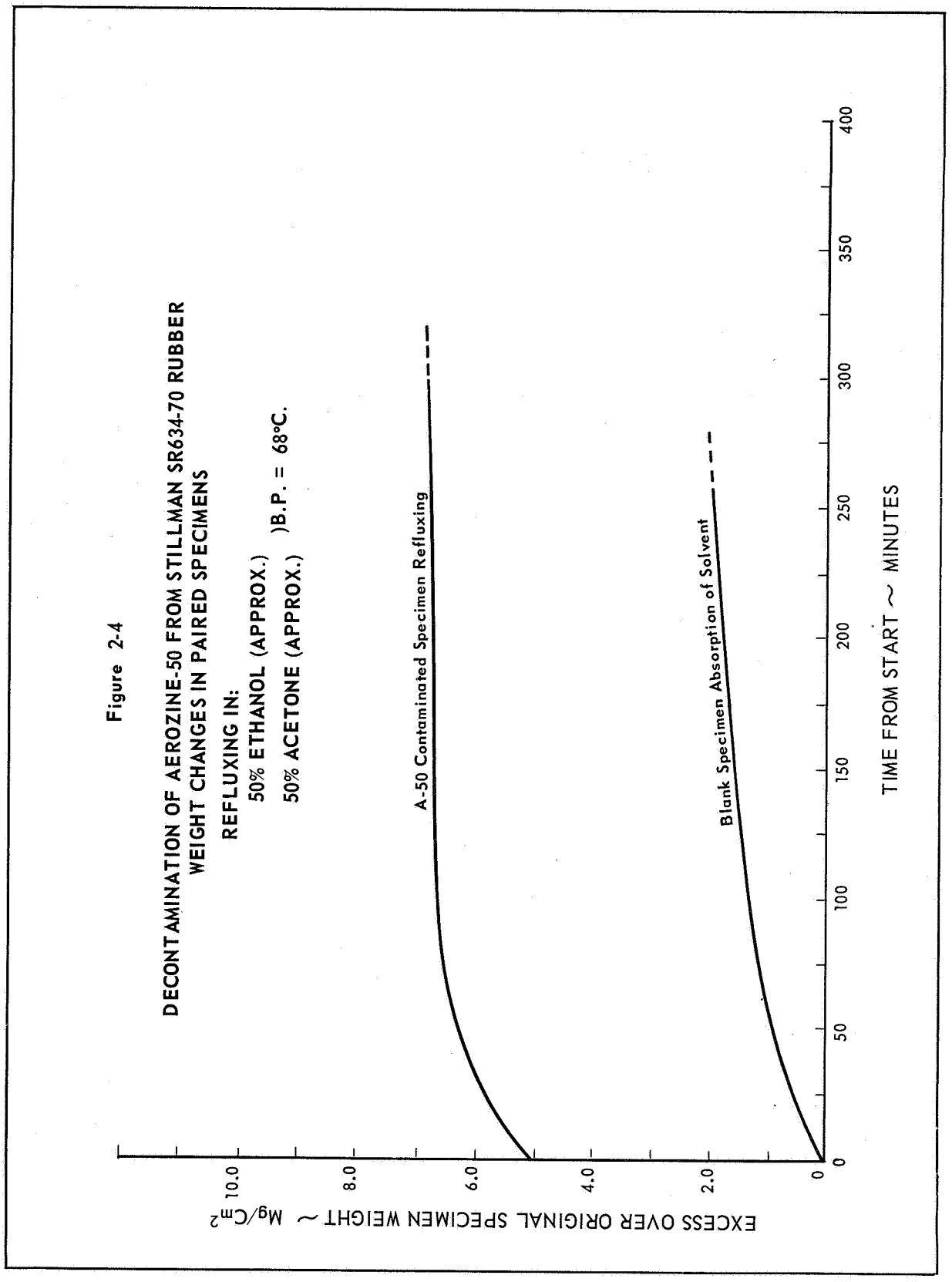


Figure 2-4
DECONTAMINATION OF AEROZINE-50 FROM STILLMAN SR634-70 RUBBER
WEIGHT CHANGES IN PAIRED SPECIMENS
REFLUXING IN:
50% ETHANOL (APPROX.)
50% ACETONE (APPROX.))B.P. = 68°C.
A-50 Contaminated Specimen Refluxing
Blank Specimen Absorption of Solvent
EXCESS OVER ORIGINAL SPECIMEN WEIGHT ~ Mg/Cm²
10.0
8.0
6.0
4.0
2.0
0
0
50
100
150
200
250
300
350
400
TIME FROM START ~ MINUTES

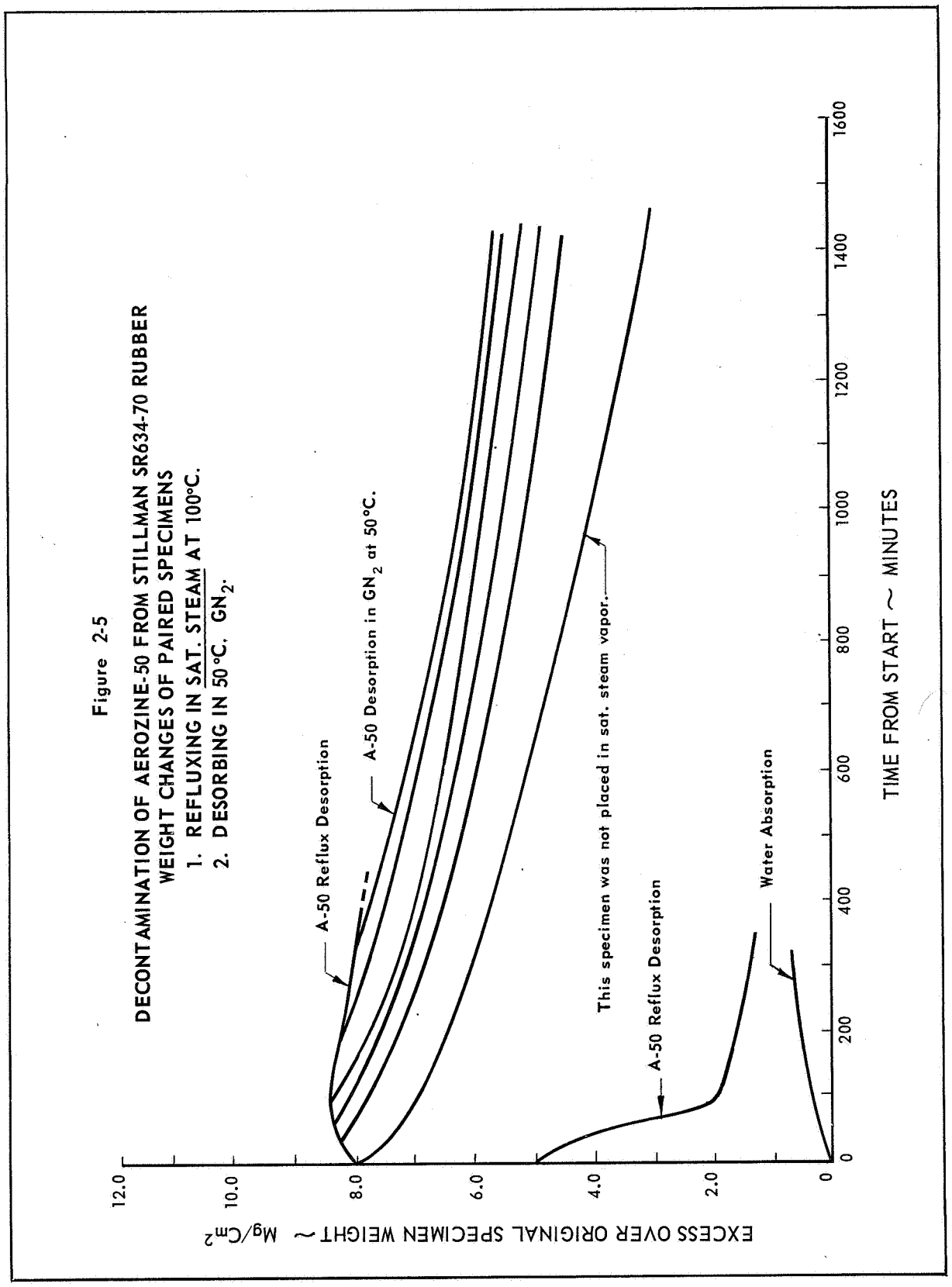
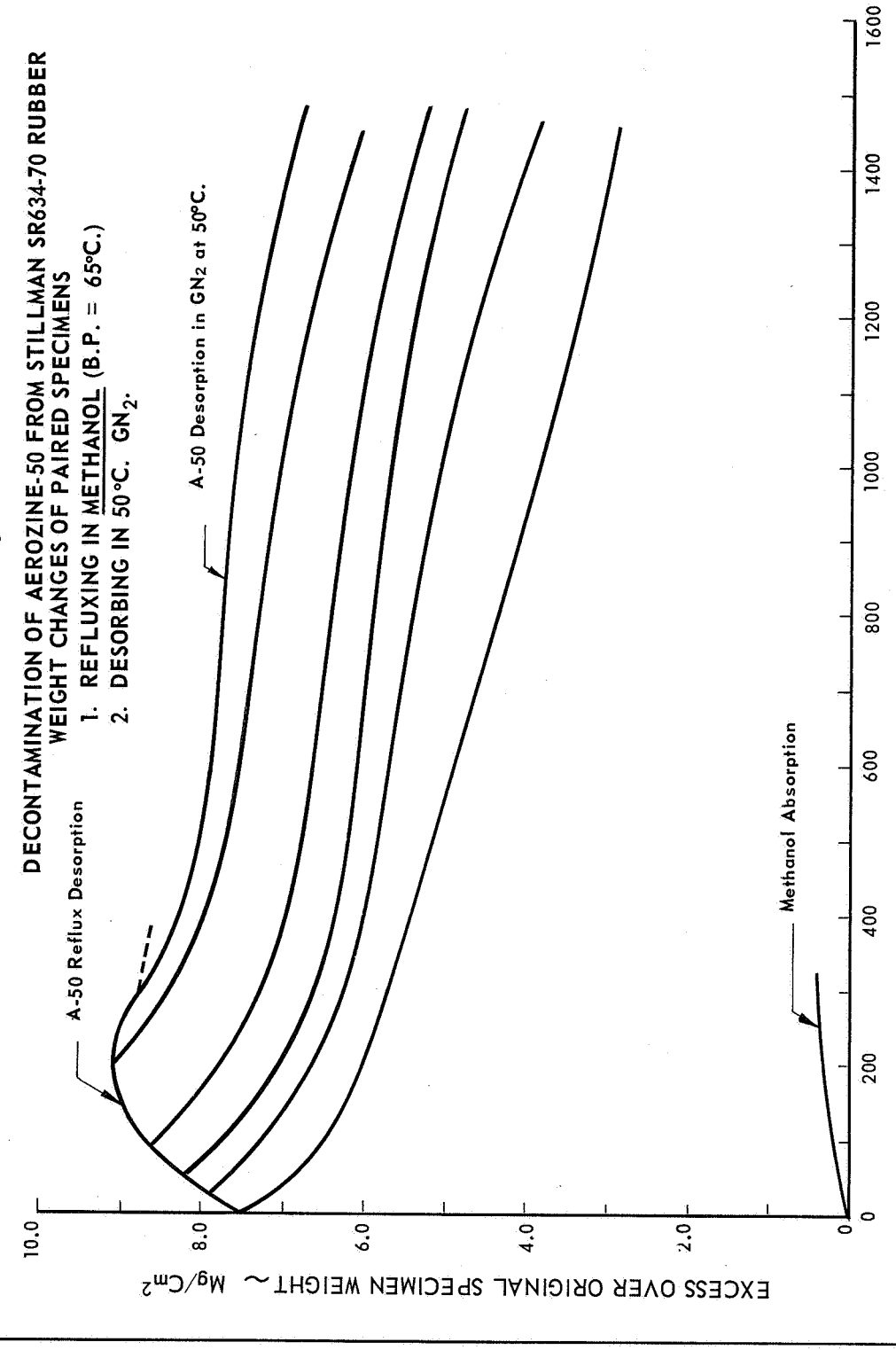


Figure 2-5
DECONTAMINATION OF AEROZINE-50 FROM STILLMAN SR634-70 RUBBER
WEIGHT CHANGES OF PAIRED SPECIMENS
1. REFLUXING IN SAT. STEAM AT 100°C.
2. DESORBING IN 50°C, GN_2.
EXCESS OVER ORIGINAL SPECIMEN WEIGHT ~ Mg/C_m^2
12.0
10.0
8.0
6.0
4.0
2.0
0
0
200
400
600
800
1000
1200
1400
1600
TIME FROM START ~ MINUTES
A-50 Reflux Desorption
A-50 Desorption in GN_2 at 50°C.
This specimen was not placed in sat. steam vapor.
A-50 Reflux Desorption
Water Absorption

Figure 2-6

DECONTAMINATION OF AEROZINE-50 FROM STILLMAN SR634-70 RUBBER
WEIGHT CHANGES OF PAIRED SPECIMENS

1. REFLUXING IN METHANOL (B.P. = 65°C.)
2. DESORBING IN 50°C. GN_2.



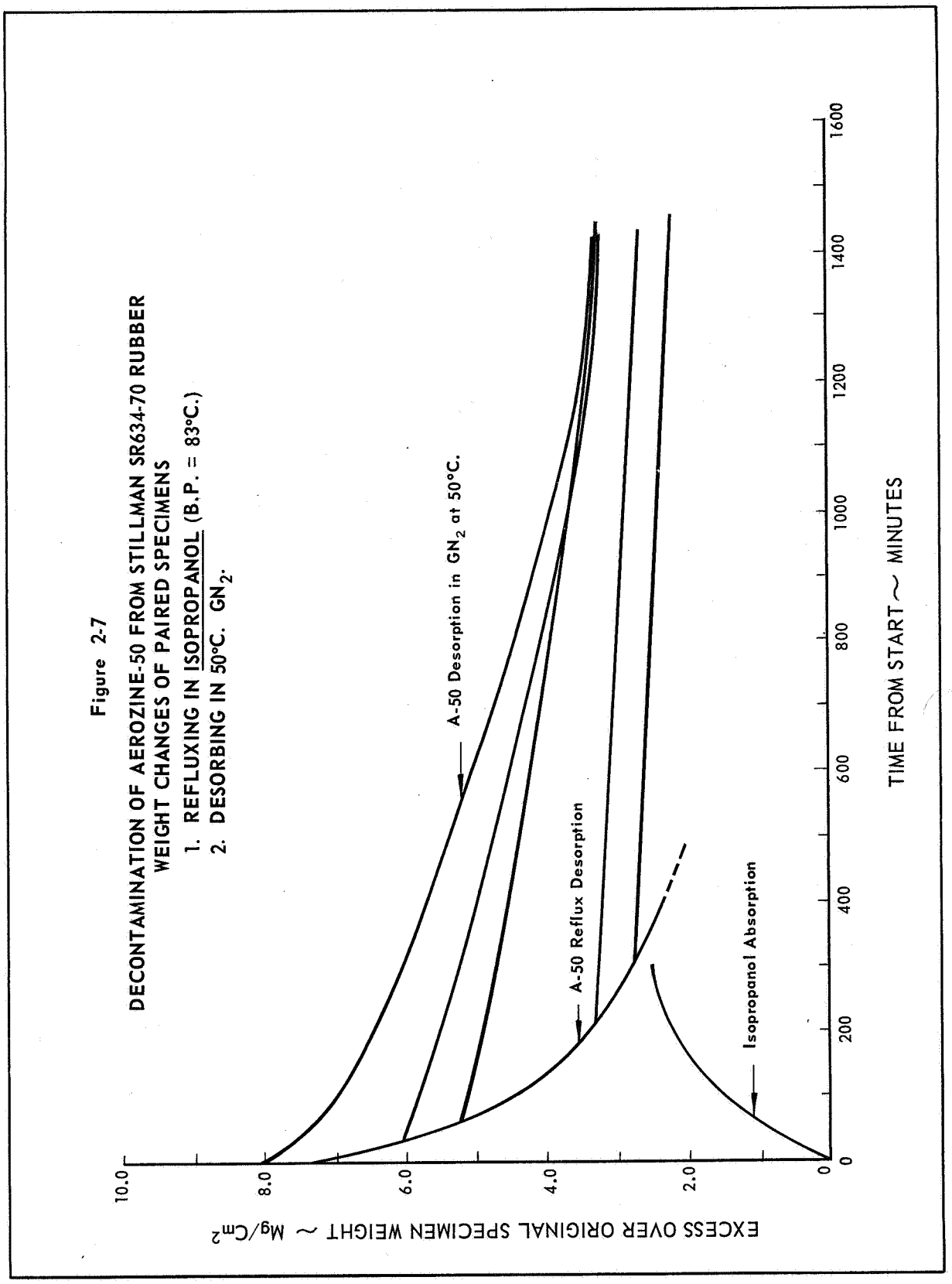


Figure 2-7
DECONTAMINATION OF AEROZINE-50 FROM STILLMAN SR634-70 RUBBER
WEIGHT CHANGES OF PAIRED SPECIMENS
1. REFLUXING IN ISOPROPANOL (B.P. = 83°C.)
2. DESORBING IN 50°C. GN_2.
A-50 Desorption in GN_2 at 50°C.
A-50 Reflux Desorption
Isopropanol Absorption
EXCESS OVER ORIGINAL SPECIMEN WEIGHT ~ Mg/Cm^2
10.0
8.0
6.0
4.0
2.0
0
0
200
400
600
800
1000
1200
1400
1600
TIME FROM START ~ MINUTES

Figure 2-8

DECONTAMINATION OF AEROZINE-50 FROM STILLMAN SR634-70 RUBBER
WEIGHT CHANGES OF PAIRED SPECIMENS

1. REFLUXING IN PERFLUORODIMETHYLCYCLOBUTANE AT 45°C.
2. DESORBING IN 50°C. GN_2.

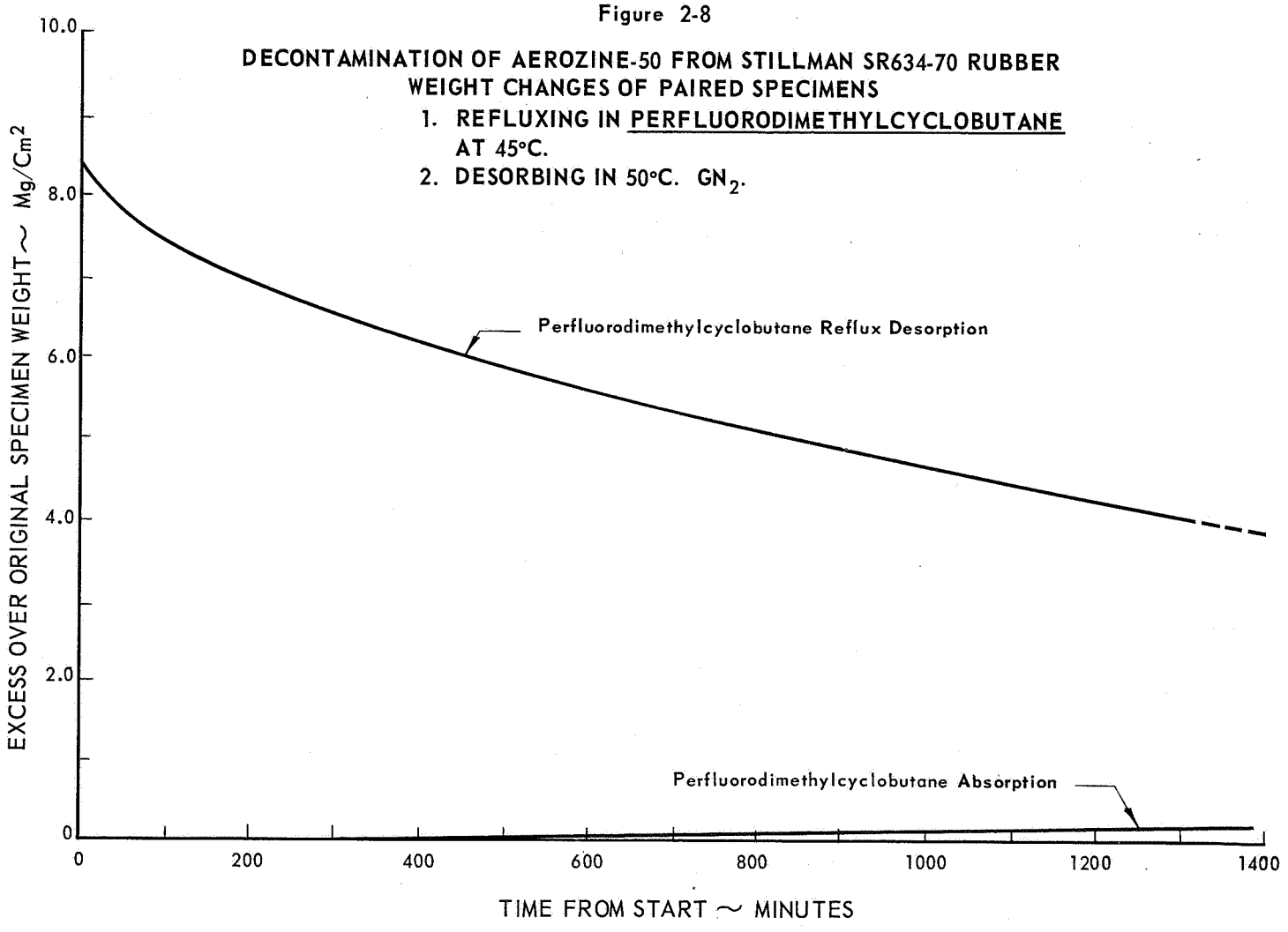


Figure 2-9

DECONTAMINATION OF AEROZINE-50 FROM STILLMAN SR634-70 RUBBER
WEIGHT CHANGES OF PAIRED SPECIMENS

1. REFLUXING IN FREON® E-2 (B.P. = 101°C.)
2. DESORBING IN 50°C. GN_2.

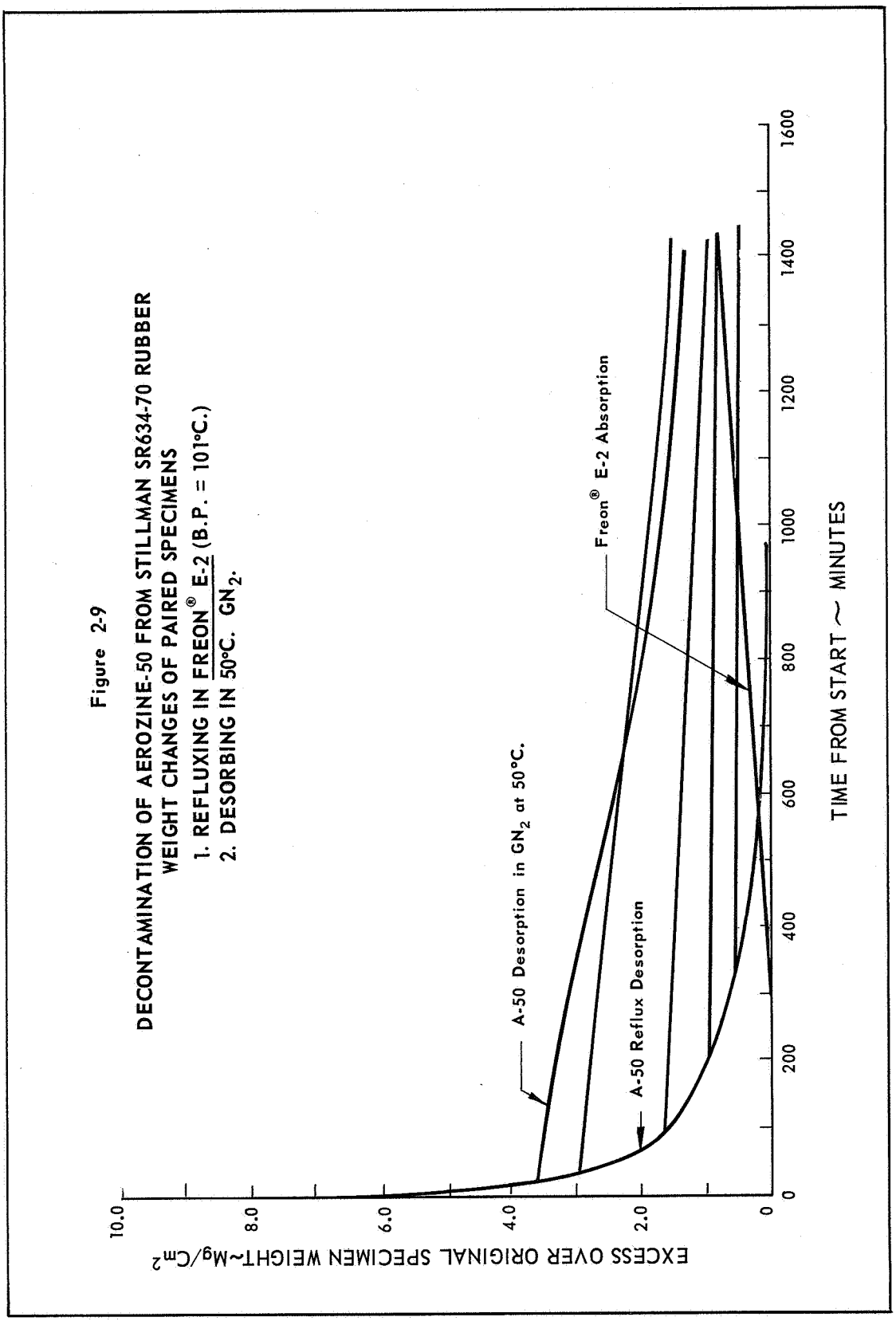
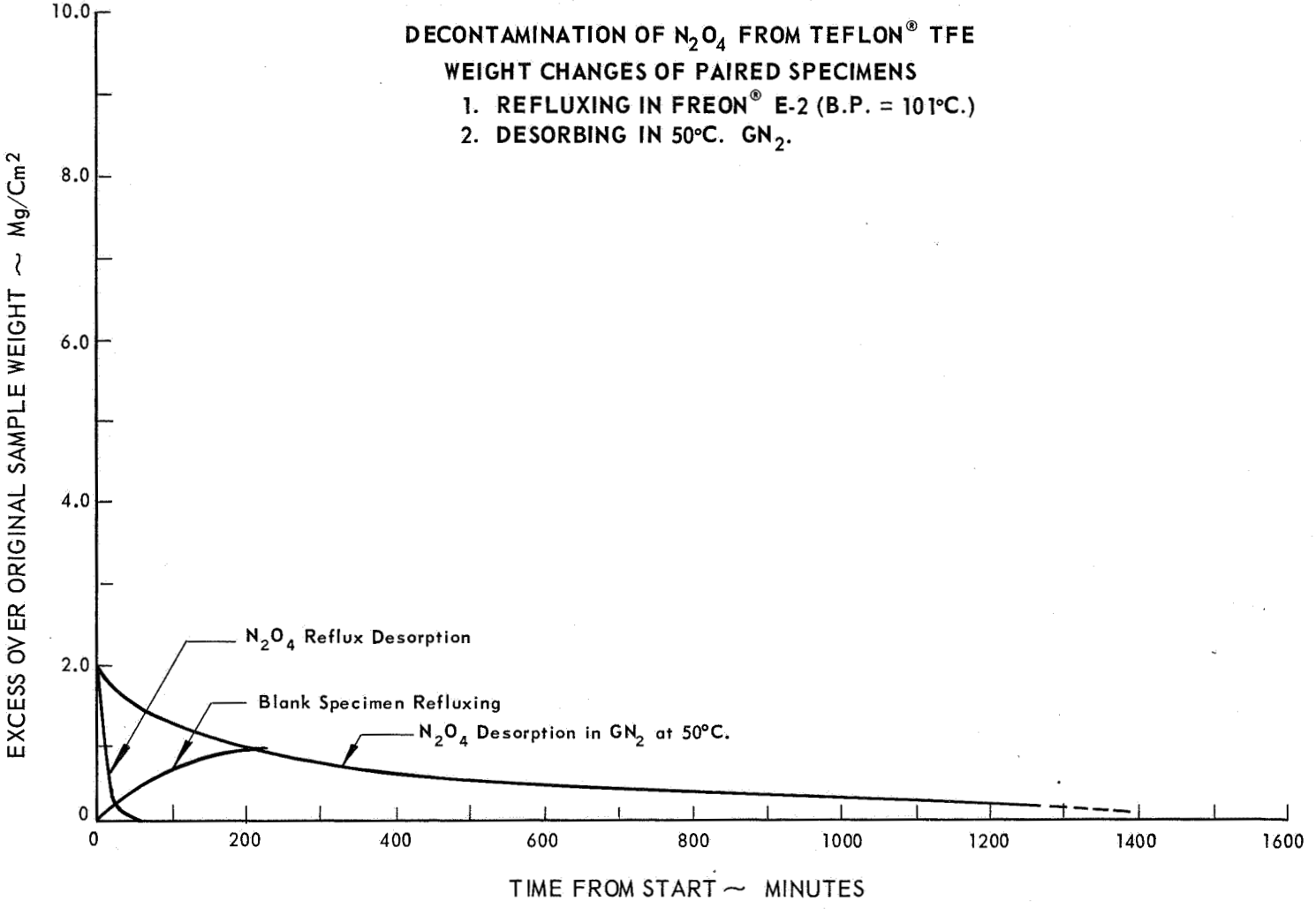


Figure 2-10

DECONTAMINATION OF N_2O_4 FROM TEFLON® TFE
WEIGHT CHANGES OF PAIRED SPECIMENS
1. REFLUXING IN FREON® E-2 (B.P. = 101°C.)
2. DESORBING IN 50°C. GN_2.



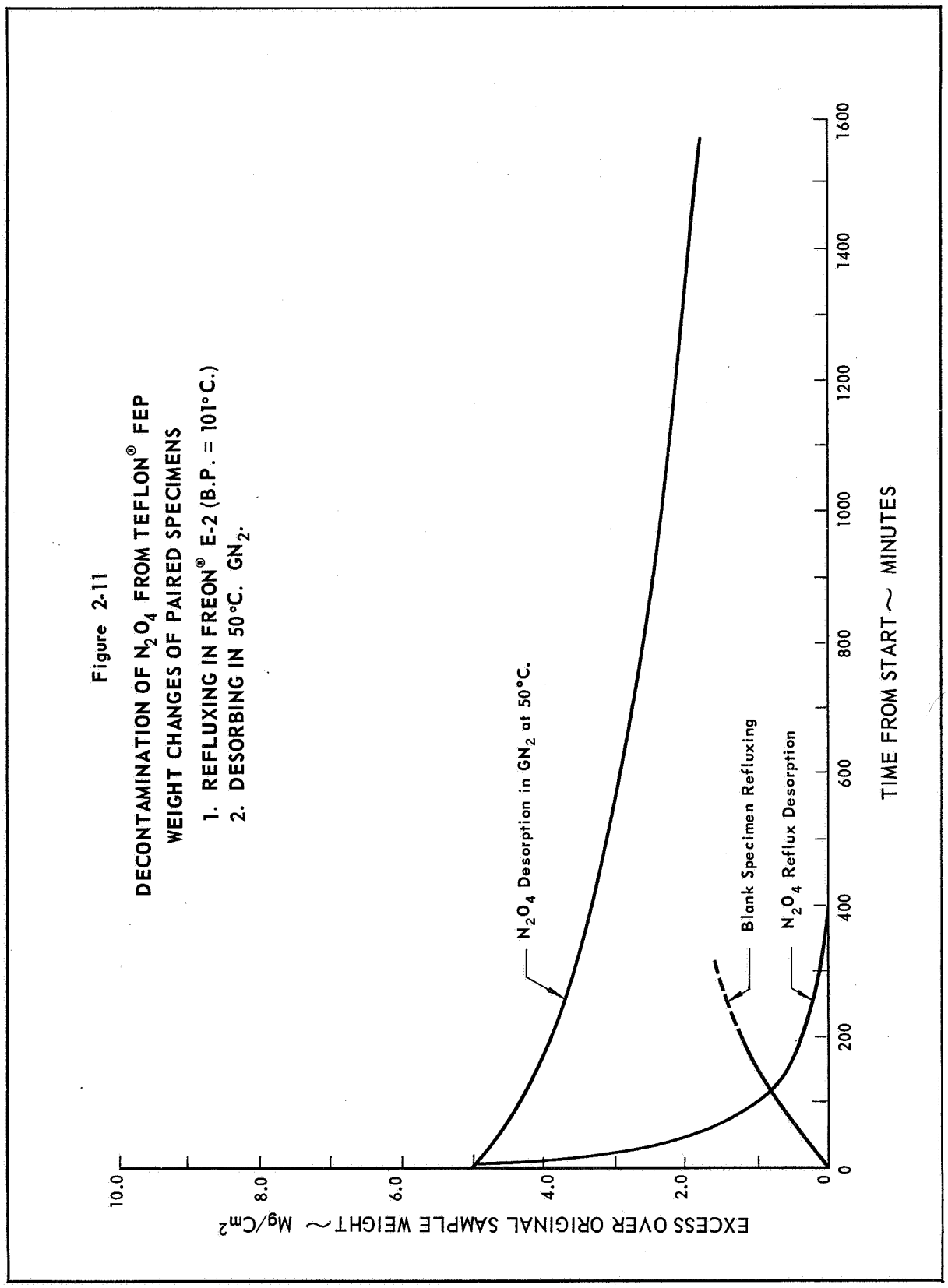


Figure 2-11
DECONTAMINATION OF N_2O_4 FROM TEFLON® FEP
WEIGHT CHANGES OF PAIRED SPECIMENS
1. REFLUXING IN FREON® E-2 (B.P. = 101°C.)
2. DESORBING IN 50°C. GN_2.
EXCESS OVER ORIGINAL SAMPLE WEIGHT ~ Mg/Cm^2
10.0
8.0
6.0
4.0
2.0
0
N_2O_4 Desorption in GN_2 at 50°C.
Blank Specimen Refluxing
N_2O_4 Reflux Desorption
0
200
400
600
800
1000
1200
1400
1600
TIME FROM START ~ MINUTES

VIII. UNIT 3 - SOLVENT REGENERATION TECHNIQUES

A. Summary

1. Hydrazine and unsymmetrical dimethyl hydrazine (UDMH) may be efficiently removed from polar (methanol) or non-polar (Freon® 113) solvents by cation exchange resins (Dowex® 50W-X8, 50-100 mesh, H^+). This is the recommended procedure.

2. Silica gel, water-swollen, and containing dissolved sodium hydroxide, is a very effective extractant. It appears to offer no particular problem. This appears the most satisfactory of the column extraction methods for N_2O_4.

3. Water extraction is very effective for N_2O_4.

4. Blowing-out of N_2O_4 by use of air or nitrogen reduces acids to low levels, with residuals being components other than N_2O_4. Blowing-out equipment could be constructed and operated quite simply. Blowing out followed by extraction with caustic laden silica gel is the recommended procedure.

As a portion of the total effort under this contract, it was deemed desirable to develop methods for removal of active fuel and oxidizer agents, viz. hydrazines and nitrogen tetroxide, from flushing solvents. The purposes are twofold: (1) to permit repeated recycling of solvent as flush to propulsion system, and (2) to minimize disposal problems of contaminated solvents.

Several ideas were considered in the original contract proposal which involved such extraction techniques as ion exchange, liquid-liquid extraction, adsorption, and gel-water extraction. This report discusses the experimental results of these studies and includes comments on additional concepts which were tested.

B. Experimental and Results

1. Source of Materials

The solvents used were commercial grade methanol and Freon® 113 obtained from du Pont. They were used as received. Preliminary attempts to use Freon® 11 were discontinued because its high volatility made laboratory operations without special equipment very difficult.

Anhydrous hydrazine and unsymmetrical dimethyl hydrazine (UDMH) were obtained from Olin and FMC respectively. These were transferred by pipet into clean bottles and diluted with solvent to give approximately 500 ppm solutions. Nitrogen tetroxide (N_2O_4) was obtained in a 5-lb. cylinder from Matheson. A small volume was transferred to a chilled bottle and diluted with cold Freon® 113 to give a stock solution which was diluted to 500 ppm as needed.

The two major resins used were Dowex® 50W-X8, 50-100 mesh, H^+ form (Lot 07285-W2) and Dowex® 21K, 50-100 mesh, Cl^- form (Lot 03124-668). One ml of the resin as received was washed into a column made by putting a glass-wool plug in a 2 ml graduated pipet. The 1 ml bed of resin had a height of about 9.7 cm and a cross-sectional area of approximately 0.1 cm^2.

The molecular sieves were grade 5A from Linde. The silica gel was grade 42 from Davison, 6-16 mesh. The desired water content was achieved by placing the adsorbents and water in separate shallow dishes in a desiccator and allowing sufficient time for equilibration. In the case of the silica gel containing NaOH, this adsorbent was prepared by immersing silica gel containing about 9% water in a 1 N solution of NaOH.

2. Analytical Methods

Both the hydrazines and the N_2O_4 were determined by acid-base titration. When the solvent was immiscible with water, the titration was carried out in a stirred two-phase system with the electrodes in the water phase. In the case of the hydrazines, it was necessary to perform the titration on the recording titrator since the break was quite shallow and tended to vary in pH with concentration and solvent ratio. Equilibrium was obtained relatively rapidly. The N_2O_4 solutions were titrated to pH 7 using a standard pH meter. However, in most cases, they were very slow to come to equilibrium, often requiring at least 15 minutes to obtain a pH of 7 which did not drift. It is not known whether this is a characteristic of the N_2O_4 or is due to the presence of some trace acidic component in the system. The latter seems more likely.

3. Fuel Side

a. UDMH from Freon® 113 by Ion Exchange

The excess water was blown out of the 1 ml column of Dowex® 50W, H^+ and a 450 ppm (0.012 N) UDMH in Freon® 113 solution was passed through it. The effluent was collected in appropriate cuts and titrated. The first 160 ml contained 4 ppm or less of UDMH. After an additional 30 ml, the concentration was about 100 ppm. There was no observable water phase in any of the cuts. The flow rate was very uneven but averaged roughly 1 ml/minute which is equivalent to 2.5 gpm/sq.ft. or 7.5 gpm/cu.ft.

As a check on the ion exchange capacity of the column, it was regenerated with 5 ml of N HCl, rinsed and exhausted with a $NaNO_3$ solution. The effluent was titrated for H^+ giving an exchange capacity of 1.63 meq.

The column was regenerated with 10 ml N HCl, rinsed, and the UDMH-Freon® 113 run repeated. The flow rate was held fairly constant at 1 ml/minute in this run. The effluent concentration is shown in Figure 3-1. A volume of 150 ml was obtained in which the UDMH concentration was less than 2 ppm and an additional 20 ml at less than 5 ppm, followed by a fairly sharp breakthrough to feed concentration. Thus, in each of these runs the resin is removing approximately 160 x 0.012 = 1.9 meq of UDMH, or slightly more than the exchange capacity. The water-swollen resin apparently has some sorptive capacity for UDMH in the Freon® 113 system.

b. UDMH-Hydrazine from Methanol by Ion Exchange

When the information was received that methanol was the current solvent of choice on the fuel side, the above runs were repeated with a UDMH-methanol solution. The column was refilled with new resin and the water was displaced from the resin by a methanol wash prior to the run. The feed solution was a 400 ppm (0.0054 N) solution of UDMH in methanol. The flow rate varied from 0.5 to 1.0 ml/minute. The first three 100 ml cuts collected contained 2, 4, and 8 ppm UDMH, respectively. After this, the effluent concentration increased to feed concentration within the next 100 ml. The capacity obtained was slightly greater than 300 x 1.0054 = 1.6 meq.

The column was regenerated with 50 ml of N/4 methanolic HCl prepared by adsorbing HCl gas in methanol. The UDMH in the regenerant effluent was estimated, by titration after the addition of excess base, to be 1.6 meq. This determination is subject to considerable error if the base added contains any carbonate.

This regenerated column was again exhausted with the UDMH-methanol solution at a flow rate of about 0.5 ml/minute with the following results:

Cut No.	Volume	Concentration of UDMH
1	250 ml	1.5 ppm
2	25	16
3	25	64
4	25	160
5	25	250
6	25	400

While the breakthrough occurred slightly earlier, the total UDMH picked up was 1.7 meq. Regeneration with 50 ml of N/4 HCl in methanol removed 1.7 meq of UDMH.

A sample of anhydrous hydrazine was obtained at this time and a new feed solution was made up containing equal parts by weight of hydrazine and UDMH. This feed solution behaved identically with the previous UDMH-methanol solution in the column experiments. A series of runs were made in an attempt to optimize the regeneration conditions using methanolic HCl. Acid concentration was varied from 2 N to N/8, amount of acid from 10 to 20 meq, and contact time from 10 to 40 minutes. The results were erratic, partially as a result of analytical difficulties, and possibly partially because of kinetic problems in the non-aqueous system. Certainly more work would be required before the best conditions for such a non-aqueous regeneration scheme could be set.

The original intent in using an all methanol cycle was to avoid contaminating the solvent with water with the subsequent necessity for a drying step. Such a scheme would be attractive if the process were to be run on a frequent cyclic basis. However, in the current use, where the system is to be used only intermittently, rough economic estimates indicate that a disposable resin bed, or even discarding of the methanol might be more attractive overall.

c. UDMH from Freon® 113 Using Molecular Sieves

Batch equilibrium studies were carried out to determine equilibrium adsorption of UDMH at various UDMH concentrations. The results, shown in Figure 3-2, show that UDMH is not strongly adsorbed by molecular sieves containing about 9% water. A column experiment in which Freon® 113 containing 500 ppm UDMH was passed through a column of molecular sieves containing about 9% water, gave similar results, namely poor adsorption of UDMH.

d. UDMH from Freon® 113 Using Silica Gel

Batch equilibration of 500 ppm UDMH solution in Freon® 113 with silica gel containing about 9% water showed rather strong adsorption of UDMH. These results are shown in Figure 3-3. A column experiment, using a 2 ml measuring pipet containing 2.0 ml silica gel (9% water content) as the column, gave evidence of good adsorption of UDMH, although air pockets in the column caused operating problems. Another column run,

using 3.4 ml of silica gel in a column 3/8" x 8", showed good pickup of UDMH with little leakage of UDMH. The results of this run are shown in Figure 3-4, where it can be seen that 73 bed volumes can be treated to a 5 ppm UDMH breakthrough, or 88 bed volumes to a 10 ppm UDMH breakthrough. When word was received that methanol would probably be used as the solvent for the fuels, work on this type adsorbent was discontinued, since the use of adsorbents containing water require an immiscible solution for application.

4. Oxidizer Side

a. N_2O_4 from Freon® 113 by Ion Exchange

A column containing 1 ml of Dowex® 21K, Cl^-, was regenerated with 10.0 ml of N NaOH. The Cl^- eluted was 1.05 meq. The excess water was blown out of the column and a 380 ppm (0.013 N) solution of N_2O_4 in Freon® 113 was passed through it. The flow rate varied from 0.5 to 2.0 ml/minute. The acid in the effluent averaged about 3 ppm (expressed as N_2O_4) for the first 275 ml collected. This represents an acid pickup of over 3.5 meq on a column with an exchange capacity of 1.05 meq. There was no breakthrough to feed concentration at this point. Instead, the effluent concentration rose to about 45 ppm and held there for another 300 ml of effluent at which point the run was stopped. This represents the pickup of approximately another 3.5 meq of acid. At this point the column was regenerated with 25.0 ml of N NaOH and the regenerant effluent and rinse-back titrated with standardized HCl. This titration indicated that 5.8 meq of anion was stripped from the column, which substantiates the 7.0 meq picked up.

The water swollen Dowex® 21K obviously has a considerable sorptive capacity for N_2O_4 in this system, enough so that it would appear potentially hazardous in that the organic resin might easily accumulate enough N_2O_4 to trigger a violent oxidation. There was a chemical reaction in the resin as shown by a slow continuous generation of gas in the column. This gas evolution appeared to continue even after the regeneration with NaOH. Attempts to detonate a few beads of the loaded resin with a hammer failed. When ignited in a flame they did not show any tendency to sputter or pop.

Removal of N_2O_4 from Freon® 113 was also tried using Dowex® 44, an ammonia-epichlorohydrin condensation resin. The resin was converted to the free-base form and

thoroughly rinsed. One ml of the resin was placed in the column and a 500 ppm N_2O_4 in Freon® 113 was passed through it. A volume of 125 ml was collected with a residual acid of about 5 ppm N_2O_4. By the end of this volume the flow had practically stopped because of increased pressure drop in the bed. After standing overnight, the upper portion of bed was found to be softened and even partially liquified.

b. N_2O_4 from Freon® 113 by Degassing

In working with the N_2O_4-Freon® 113 solutions, it was observed that N_2O_4 was lost from solution at an appreciable rate if the container was left open to the atmosphere. It therefore seemed logical to try a degassing or desorption scheme.

A small desorption unit was set up as in Figure 3-5. The size of the packed column was roughly 8" x 1" and the packing was 1/4" saddles. The liquid distribution was quite poor and it tended to run down the sides of the column. The sweep gas was plant nitrogen; the flow rate was measured by means of a small rotameter, and controlled at roughly 5 ml/second. The exit gas was bubbled through a solution of standardized caustic.

In the first run the feed solution contained 712 ppm of N_2O_4. Two 100 ml cuts were obtained:

Cut No.	Ave. Flow Rate	Residual Acid	As N_2O_4
1	1.65 ml/minute	0.00148 $\underline{N}$	43 ppm
2	2.2 ml/minute	0.00137 $\underline{N}$	40 ppm

There was no color left in the product. The amount of caustic neutralized in the scrubber was 4.5 meq. The approximate amount of acid removed from the product =

$$V\Delta C = 200 \text{ ml } (0.0244 \underline{N} - 0.0014 \underline{N}) = 4.6 \text{ meq}$$

In a second more extended run air was used as the sweep gas and the feed contained 506 ppm N_2O_4. A total of 4,314 g of product (I) was collected at an average flow rate of 1.2 g/minute ($\sim$0.8 ml/minute). This had a residual content of 0.0021 $\underline{N}$ (61 ppm as N_2O_4). In a third run using the same feed but at an average flow rate of 13.2 g/minute (8.4 ml/minute), 1,320 g of product (II) was obtained with a residual acid content of 0.0043 $\underline{N}$ (125 ppm as N_2O_4). This product had a trace of the brownish N_2O_4 color left in it. There was no appreciable amount of Freon® 113 collected in the gas scrubber in any of the runs.

Several techniques were tried for the reduction of the residual acidity from the degassed product. A portion of product (I) was passed through a 1 ml column of Dowex® 21K which had been regenerated with 5.0 ml of N NaOH. (Cl^- eluted = 0.84). A total of 1,100 ml was put through the bed and the effluent concentration was still less than 1×10^{-4} N. Total acid picked up was approximately 2.2 meq on an exchange capacity of 0.84 meq. Rinsing the bed with about 70 ml of acetone at this point eluted considerable yellow color and 0.93 meq of acid. There was no noticeable degradation of the resin.

A 200 ml sample of product (I) was allowed to evaporate in a tared dish. The residue was 0.10 g or about 0.03%.

Another portion of product (I) was flash distilled until 98-99% of the material had gone overhead. The residue was found to contain only a trace of acid while the distillate was 0.0015 N, as compared with 0.0019 N before distillation.

A 250 ml portion of product (II) was shaken with 25 ml of water and separated. The Freon® phase was found to have an acid content of only 9×10^{-5} N after this extraction.

As a final step these samples were examined by means of their visible and UV adsorption spectra using a Cary Recording Spectrophotometer. The results are shown in Table 3-I. The strong peak at 340 μ is the major contribution of the N_2O_4. The absence of any adsorption at this wavelength in product (I) indicates that N_2O_4 can be removed completely by careful degassing and that the residual acid is not N_2O_4. The distillation experiment shows that the residual acid base volatility approached that of Freon® 113. The extreme slowness with which it titrates, probably due to a slow diffusion from the organic into the aqueous phase, suggests a rather hydrophobic material. This might be a halogenated organic acid formed from the action of the N_2O_4 on some impurity in the Freon® 113. It is not present in the original Freon® 113.

Another unknown impurity which shows an adsorption at 275 μ is a higher boiler than Freon® 113 and may represent an impurity in the N_2O_4, a reaction product of N_2O_4 and Freon® 113, or simply some material such as stopcock grease picked up in processing the sample.

c. N_2O_4 from Freon® 113 Using Molecular Sieves

Freon® 113 containing about 500 ppm N_2O_4 was passed through an 8" high bed of molecular sieves containing

10.6% water. The pickup of N_2O_4 was very poor, the first effluent cut being about 55% of the feed concentration, with subsequent cuts being of even higher concentrations. Next, some molecular sieves were saturated with water prior to loading in an 8" high column. This increased waste content of the molecular sieves resulted in much stronger adsorption of N_2O_4. While the leakage level was not as low as desired, approximately 175 bed volumes were treated to yield an overall N_2O_4 concentration of 10 ppm.

A problem of molecular sieve degradation appeared during this run. The sieves at the top of the column were reduced to a powder and the sieves were observed to be quite friable when the column was unloaded. In addition, the effluent during the water regeneration, produced a white flocculent precipitate when it was titrated to a neutral pH. X-ray diffraction of the ignited precipitate indicated that it was Al_2O_3, thus confirming the belief that the flocculent precipitate was $Al(OH)_3$. Thus, molecular sieves do not appear to have sufficient chemical stability for this application.

The use of a bed of dry molecular sieves as an adsorbent for N_2O_4 from Freon® 113 was also investigated. In this case, the molecular sieves would act as an adsorbent of polor molecules rather than as a support for water. This system was found to be ineffective however, the first effluent cut containing 12 ppm N_2O_4, the next cut containing 55 ppm N_2O_4.

d. N_2O_4 from Freon® 113 Using Silica Gel

Two series of equilibration experiments were carried out using silica gel containing about 9% and about 16.7% water. In both cases, the adsorption was not very strong at low concentrations of N_2O_4, although strong adsorption was observed at higher concentrations. The adsorbent with the higher water content showed the stronger adsorption of N_2O_4, as can be seen from Figure 3-6, which shows the results for both adsorbents.

In a column contact of 500 ppm N_2O_4 solution with silica gel containing about 9% water, the effluent showed a gradual increase in N_2O_4 concentration; only the first fraction was at a N_2O_4 level below 10 ppm. The next column experiment, with silica gel containing 21.9% water, gave lower N_2O_4 levels in the effluent than in the previous run, but again showed a steady increase in N_2O_4 leakage from the start of the run. Again, only the final fraction contained less than 10 ppm N_2O_4. The elution of the adsorbed N_2O_4 with

water showed complete removal, with most of the desorbed material coming off in the first fraction.

In an attempt to increase the adsorption of the N_2O_4, a quantity of silica gel was equilibrated with 1 N NaOH solution. After removal of the gel from the NaOH solution, it was placed in an 8" high column and rinsed with Freon® 113, prior to passage of Freon® 113 containing about 500 ppm N_2O_4 through the column. This adsorbent was found to give much lower N_2O_4 levels in the effluent. Approximately 140 bed volumes of effluent were treated to a breakthrough of 5 ppm N_2O_4. Removal of the adsorbed material was attempted by eluting the bed with water. The first fraction was acidic, and titration of this acid accounted for 63% of the N_2O_4 adsorbed. Subsequent fractions were alkaline, due to the NaOH leaking from the bed. It should be noted that the adsorbent held material in excess of that neutralized by the NaOH trapped in the gel.

In order to determine whether any of the NaOH in the silica gel might diffuse into the Freon® solution as it passes through the column, an experiment using radioactive sodium was run. The 1 N NaOH solution was spiked with Na^{22} prior to equilibration of the solution with the silica gel. The gel was then dried on a paper towel to remove excess solution. The radioactivity of the gel was determined and compared to the radioactivity of the solution before contact with the gel. The activity on the gel was 71.5%. The gel was then placed in an 8" high column and rinsed with Freon® 113. No activity was detected in this Freon® 113. Next, a 500 ppm solution of N_2O_4 in Freon® 113 was passed through the column and fractions collected. In order to concentrate the Na^{22} activity, each 100 ml fraction was shaken with 2.0 ml of a hydrogen form cation exchange resin (Dowex® 50W-X4, 50-100 mesh). After contact, the resin was filtered, rinsed with water, and transferred to a test tube for counting. The results are given in Table 3-II, which gives the activity of the samples, the Na^+ concentration calculated from the activity, and the concentration of N_2O_4 or hydrolysis products in the fractions. The erratic behavior observed is unexplained, although the amount of Na^+ leaked out by the Freon® 113 is certainly below maximum allowable limits.

Water elution was used to desorb the N_2O_4 and hydrolysis products. Most of the Na^{22} activity eluted in the first fraction. The gel was counted after water elution and found to contain no Na^{22} activity. A material balance

on the Na^{22} activity was not obtained because of the resin contact method for concentrating the activity. In the effluent samples during the water elution, the high acid concentration prevented complete pickup of the Na^+ ions on the resin.

To investigate the effect of a higher flow rate on the pickup of N_2O_4 by silica gel containing NaOH, a run was made at a higher flow rate. The silica gel was equilibrated as before with 1 N NaOH. The column was ~17" high and 0.342" in diameter. The flow rate averaged 11.1 ml/minute, which is equivalent to 4.6 gallons/sq.ft./minute. At this high flow rate, it was visually noted that the leading edge of the adsorption band was fairly broad, approximately 6" in width. The results of this run are shown in Figure 3-7, where it can be seen that the lowest concentration of N_2O_4 in the effluent was 7 ppm.

e. N_2O_4 Extraction from Freon® 113 with Water

In order to study the feasibility of extraction of N_2O_4 from Freon® 113 with water, the partition of N_2O_4 between these two phases was studied. (This was accomplished by shaking water with a solution of N_2O_4 in Freon® 113 until equilibrium was obtained, followed by an analysis of N_2O_4 concentration in each phase. Various points on the curve were generated by varying the ratio of the two phases.) The results are shown in Figure 3-8. It can be seen that the N_2O_4 concentration in the water phase is directly proportional to its concentration in the Freon® 113 phase with a distribution coefficient of 157, i.e. the N_2O_4 concentration in water divided by the N_2O_4 concentration in Freon® 113. The rate of extraction of N_2O_4 from Freon® 113 was studied by shaking a 500 ppm N_2O_4 solution in Freon® 113 with water at a phase ratio of 10:1 (organic:aqueous), followed by analysis of the N_2O_4 concentration in each phase. The results are shown in Figure 3-9, where it can be seen that extraction is virtually complete after 5 minutes.

C. Conclusions

Hydrazine-UDMH from Methanol

Cation exchange resin removal is recommended.

Resin: Dowex® 50W-X8, 50-100 mesh, H^+.

Operation: One cycle; no regeneration.

Capacity: 1075 gal. 500 ppm feed/cu.ft.

Flow Rate: 3 gpm/ft.^{2}

Bed Depth: 3-5 ft.; diameter as needed.

Pre-Rinse: 5 bed volumes methanol.

Column Design: Standard, fixed bed.

Breakthrough: Analysis by pH.

N_2O_4 from Freon® 113

Choice to be made between (1) caustic in silica gel, (2) water extraction, or (3) degassing or combination of (3) with (1) or (2).

TABLE 3-I

Spectral Properties of Degassed Samples

Sample	Residual Acid (At N_2O_4)	Spectral Characteristics	Adsorption at 340 μ	Adsorption at 275 μ
Freon 113	---	No adsorption above 250 μ, opaque below 230 μ	0	0
550 ppm N_2O_4 in Freon 113	500	Increasing adsorption from 600 μ to 380 μ, strong peak at 340 μ, opaque below 290 μ	1.59	?
Degassed, Product I	61	No adsorption above 300 μ, distinct peak at 275 μ	0	0.86
Degassed, Product II	125	Small peak at 340 μ, sharp peak at 275 μ	0.11	1.07
Product I + Ion Exchange	<1	Unchanged from Product I	0	0.87
Product I + H_2O Extraction	2.6	Unchanged from Product I	0	0.99
Product II + Distillation	43.5	No absorption above 300 μ, small adsorption 280-250 μ	0	0.03

TABLE 3-II

Na^{22} LEAKAGE FROM NaOH TREATED SILICA GEL

Fraction(1)	N_2O_4 Concentration	Na^{22} Activity(2)	Na Concentration
1	-	496 counts/min. (510)	Nil
2	.00037 N 10.8 ppm		
3	.00018 N 5.3 ppm	507 (510)	Nil
4	.00004 N 1.2 ppm	901 (510)	6.6×10^{-6} N .084 ppm
5	-	614 (510)	1.8×10^{-6} N .025 ppm
6	.00006 N 1.8 ppm	440 (425)	2.5×10^{-7} N .0035 ppm
7	.00037 10.8 ppm	524 (425)	1.7×10^{-6} N .024 ppm

(1) All fractions 100 ml volume.

(2) Figures in parentheses are background counts.

Figure 3-1

FEED CONCENTRATION

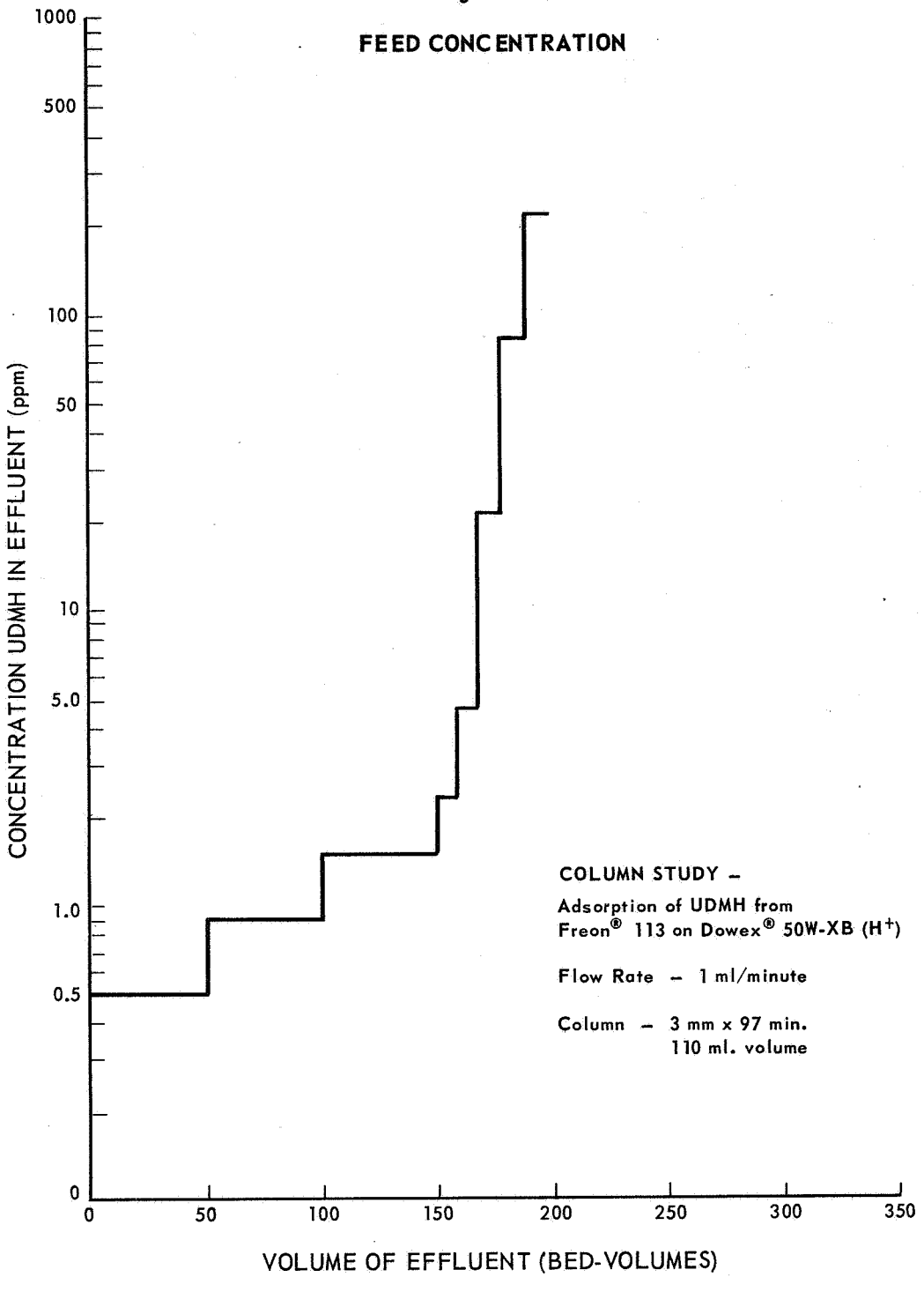


Figure 3-2

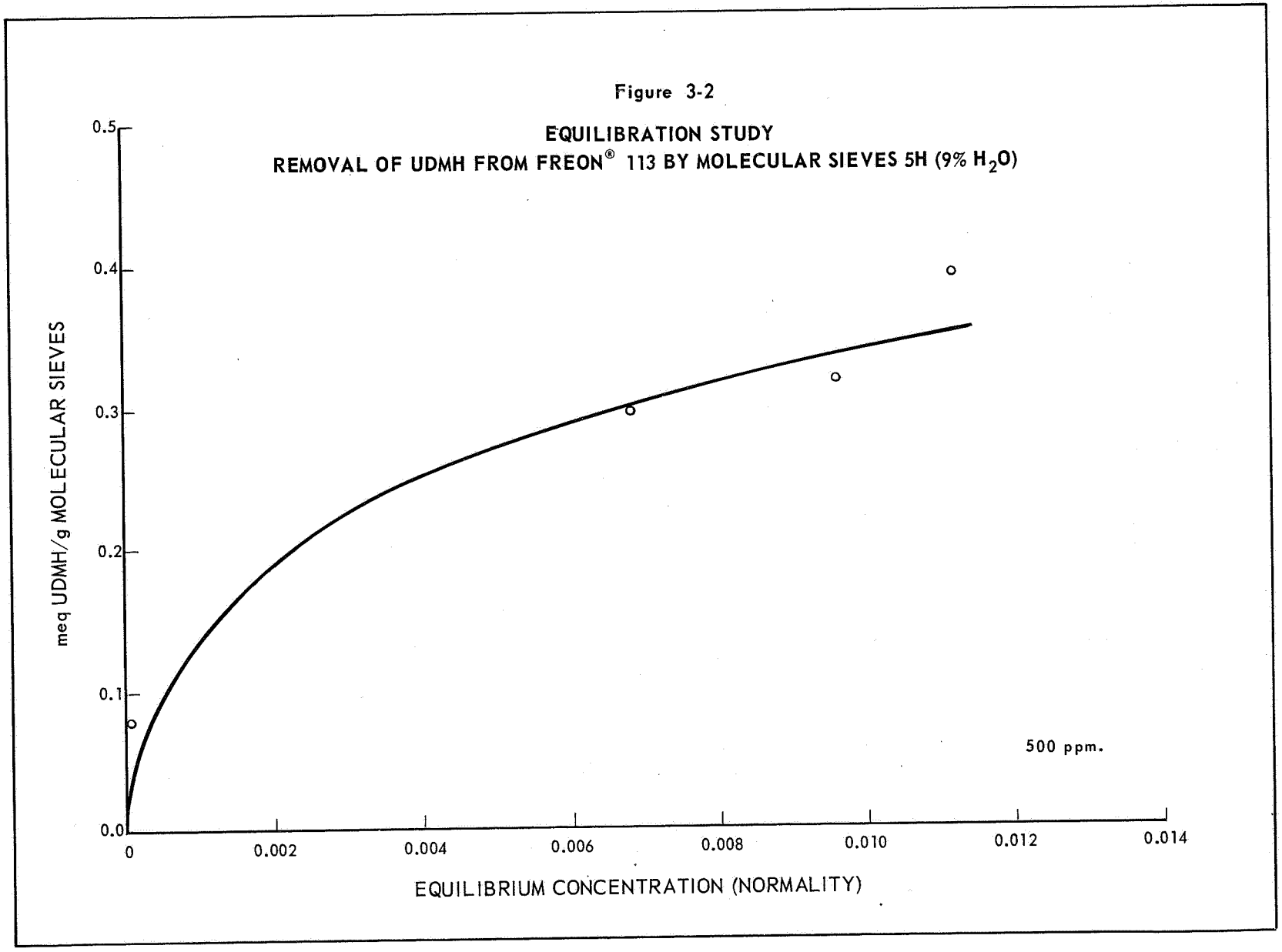

EQUILIBRATION STUDY
REMOVAL OF UDMH FROM FREON® 113 BY MOLECULAR SIEVES 5H (9% H_2O)
meq UDMH/g MOLECULAR SIEVES
0.5
0.4
0.3
0.2
0.1
0.0
500 ppm.
0
0.002
0.004
0.006
0.008
0.010
0.012
0.014
EQUILIBRIUM CONCENTRATION (NORMALITY)

Figure 3-3

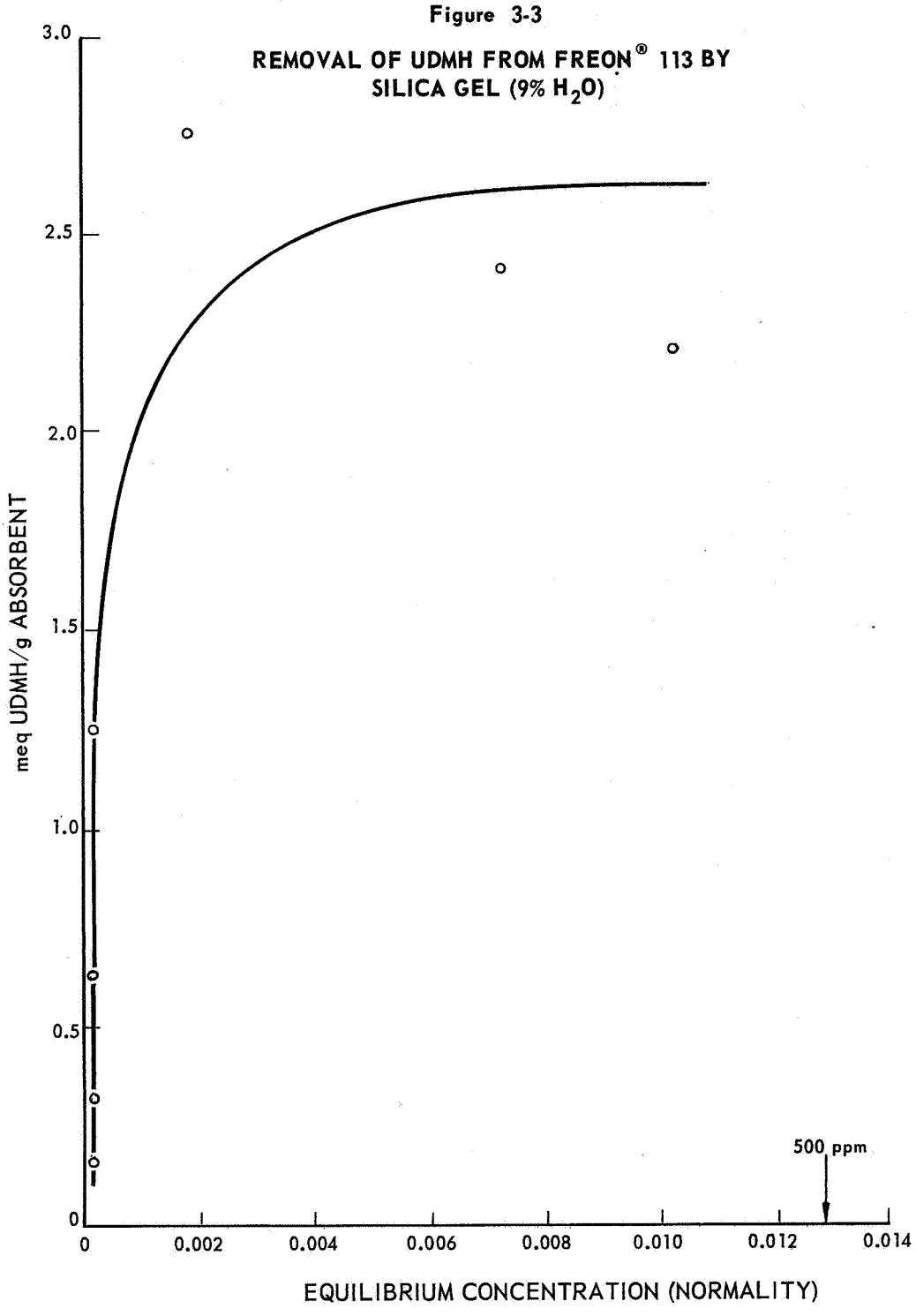

REMOVAL OF UDMH FROM FREON® 113 BY SILICA GEL (9% H_2O)
3.0
2.5
2.0
1.5
1.0
0.5
0
meq UDMH/g ABSORBENT
500 ppm
0
0.002
0.004
0.006
0.008
0.010
0.012
0.014
EQUILIBRIUM CONCENTRATION (NORMALITY)

Figure 3-4

COLUMN STUDY
REMOVAL OF 500 PPM UDMH IN FREON® 113
SILICA GEL COLUMN
(3.4 ml, 2.915 g)
9% H_2O in Silica Gel

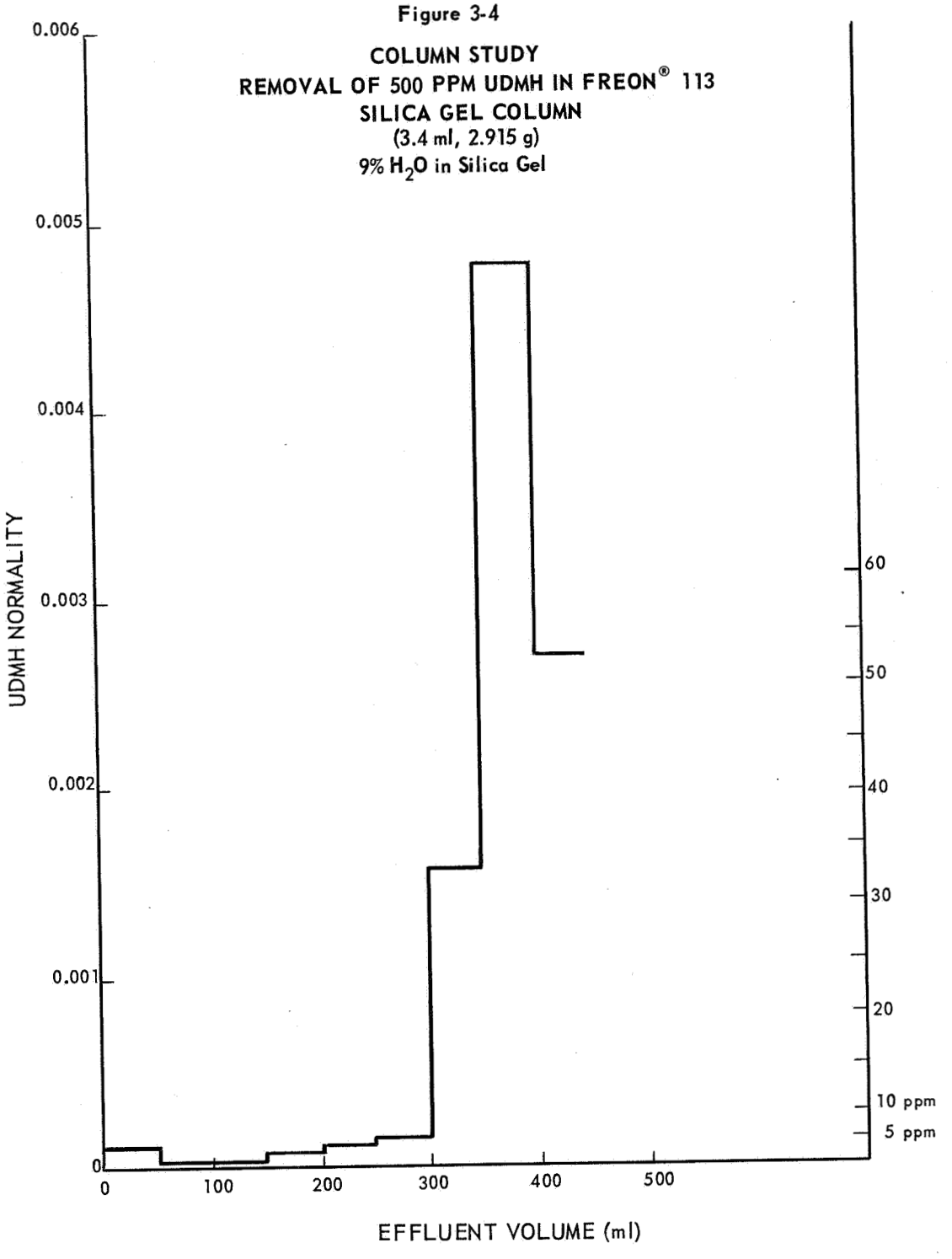


Figure 3-5
EXTRACTION APPARATUS

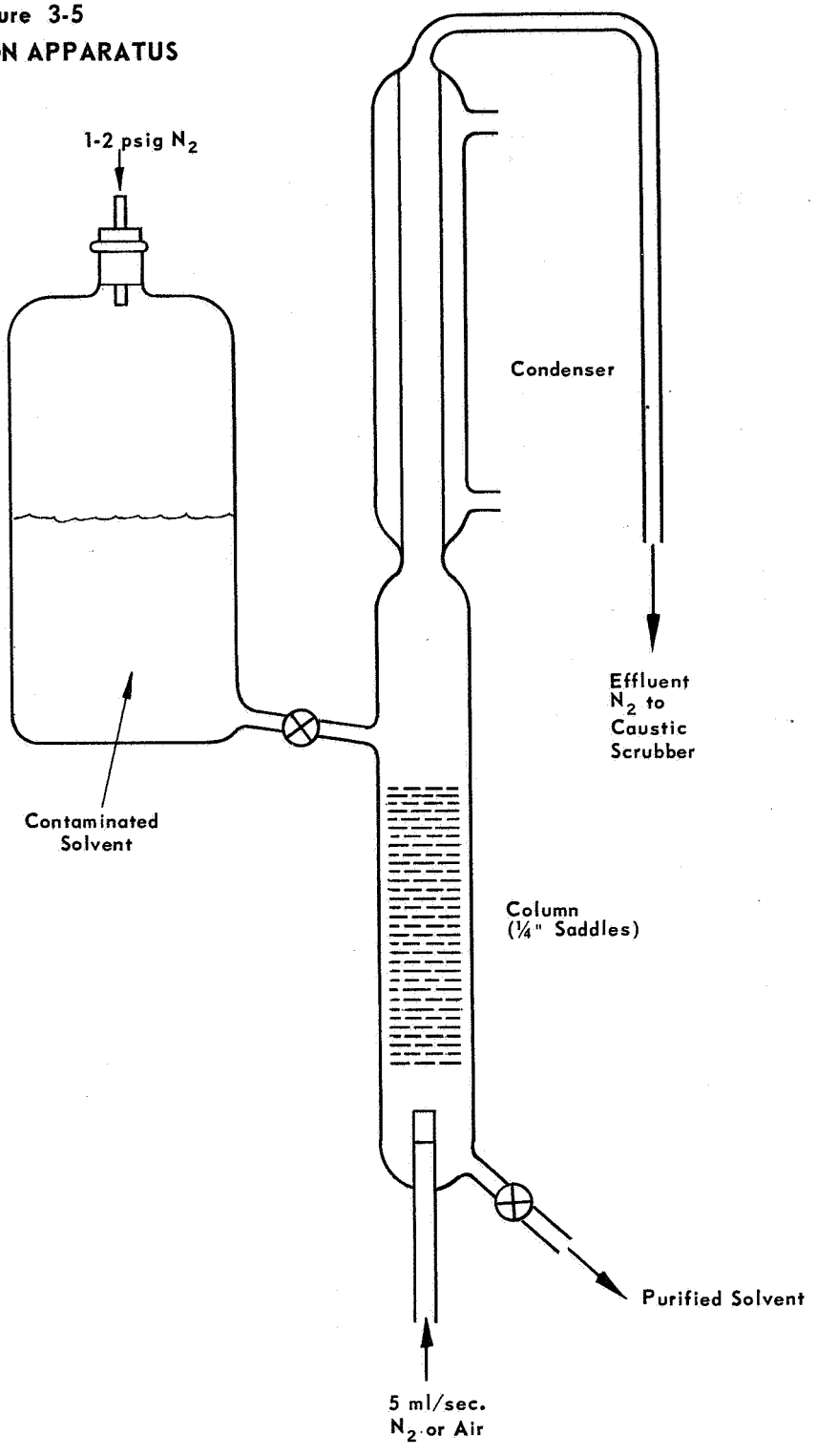


Figure 3-6

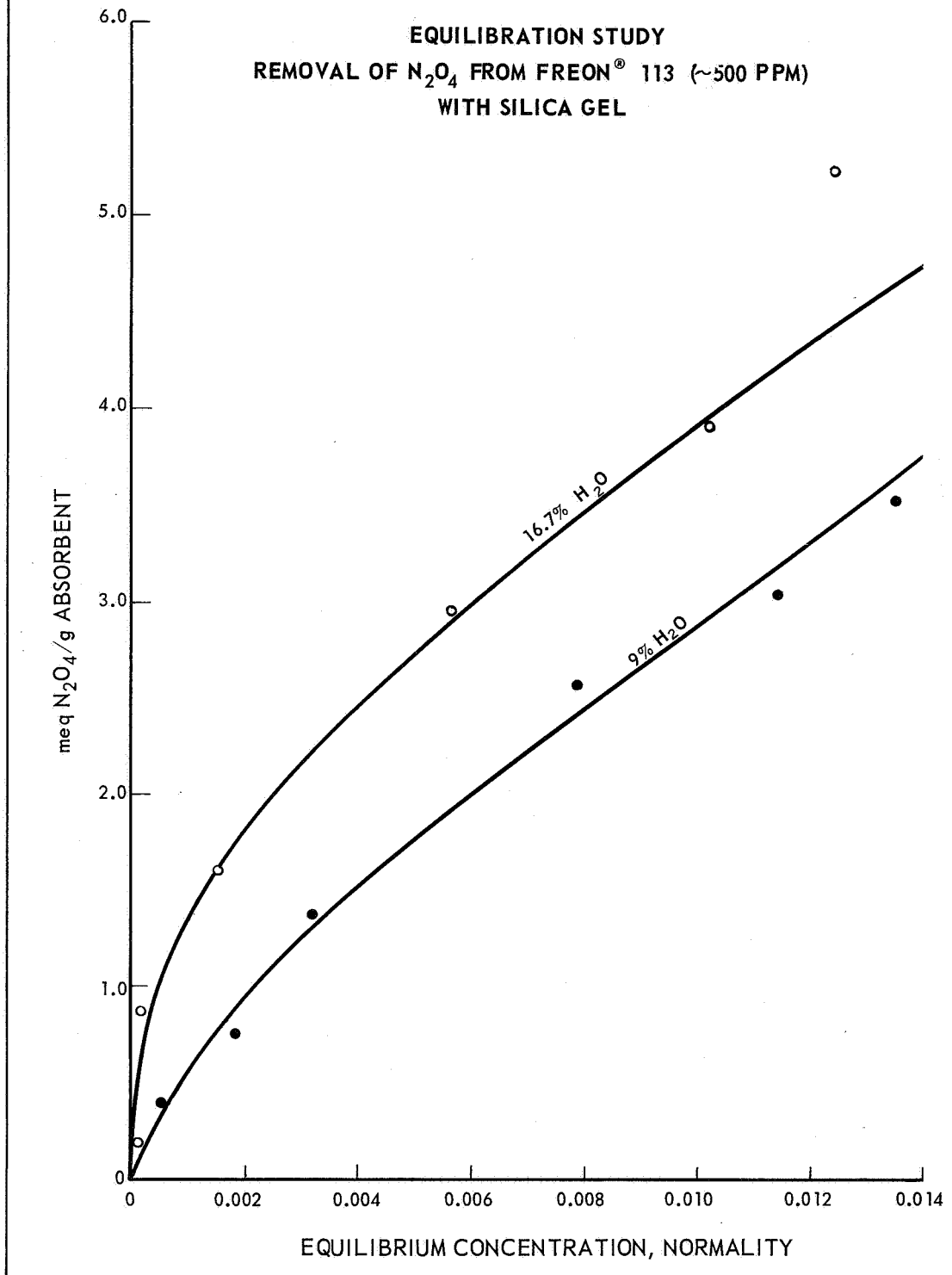

EQUILIBRATION STUDY
REMOVAL OF N_2O_4 FROM FREON® 113 (~500 PPM)
WITH SILICA GEL
meq N_2O_4/g ABSORBENT
6.0
5.0
4.0
3.0
2.0
1.0
0
16.7% H_2O
9% H_2O
0
0.002
0.004
0.006
0.008
0.010
0.012
0.014
EQUILIBRIUM CONCENTRATION, NORMALITY

Figure 3-7
COLUMN STUDY
ABSORPTION OF N_2O_4 FROM FREON® 113
WITH SILICA GEL (NaOH TREATED) AT HIGH FLOW RATE

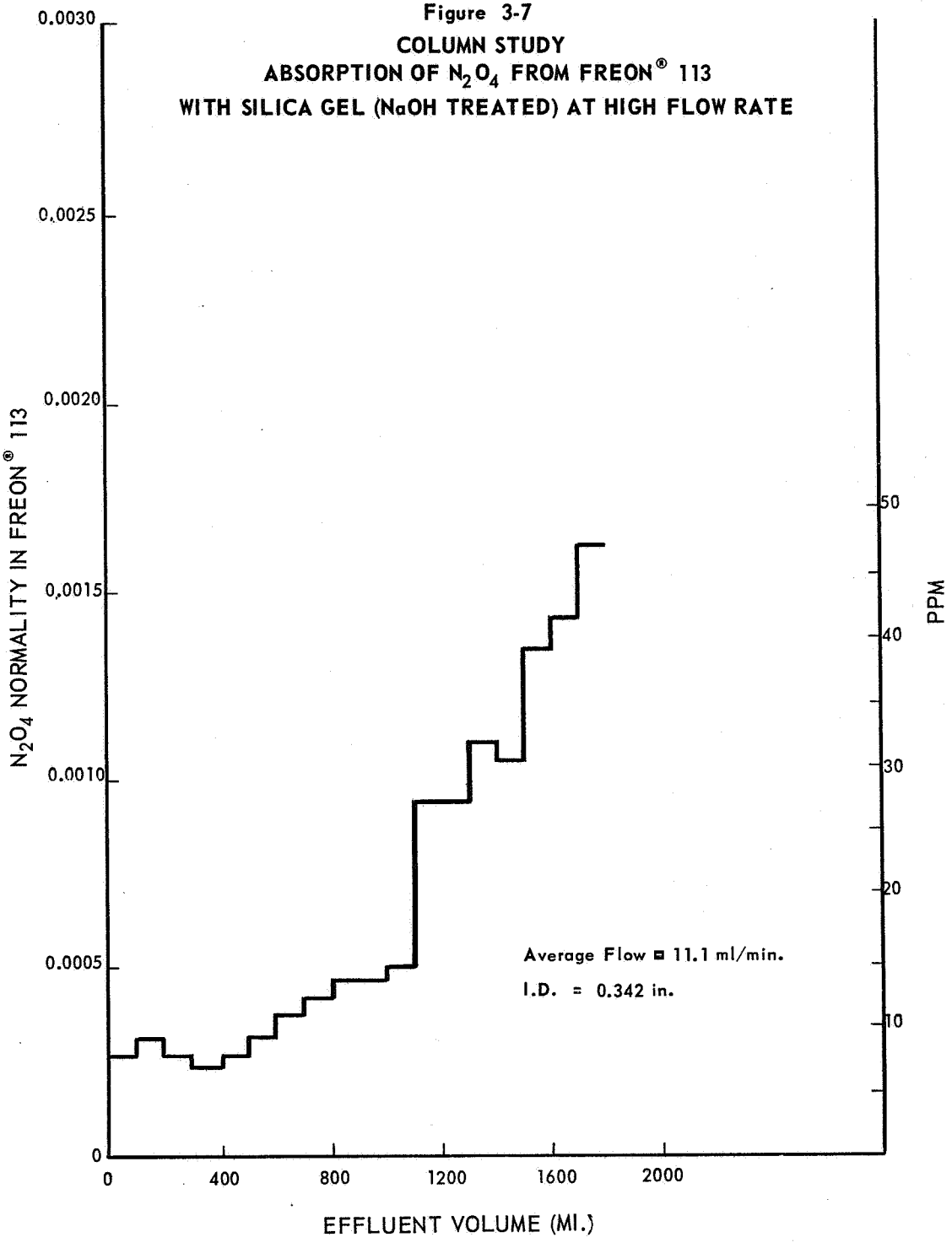


Figure 3-8

DISTRIBUTION OF N_2O_4 BETWEEN H_2O AND FREON® 113

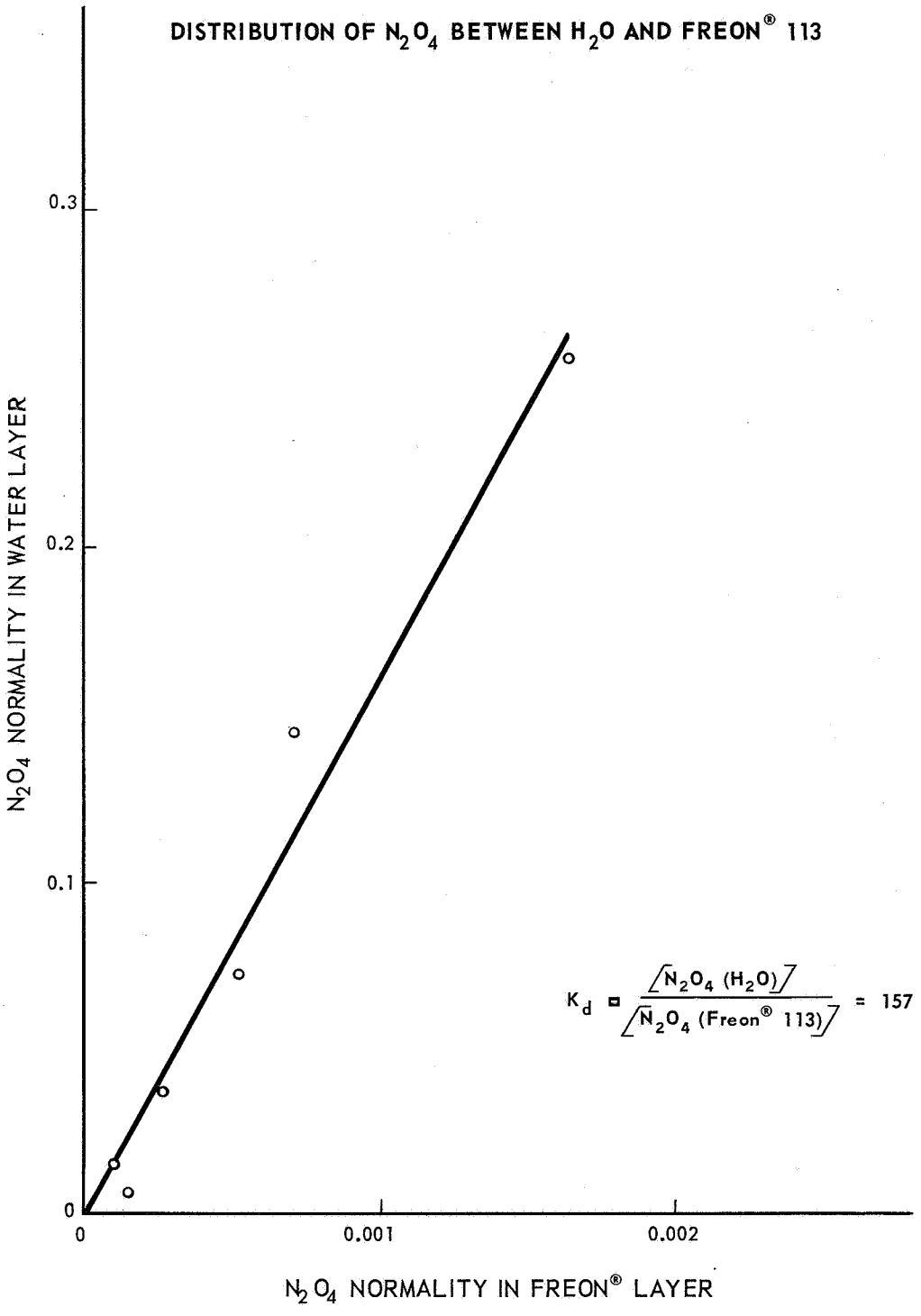
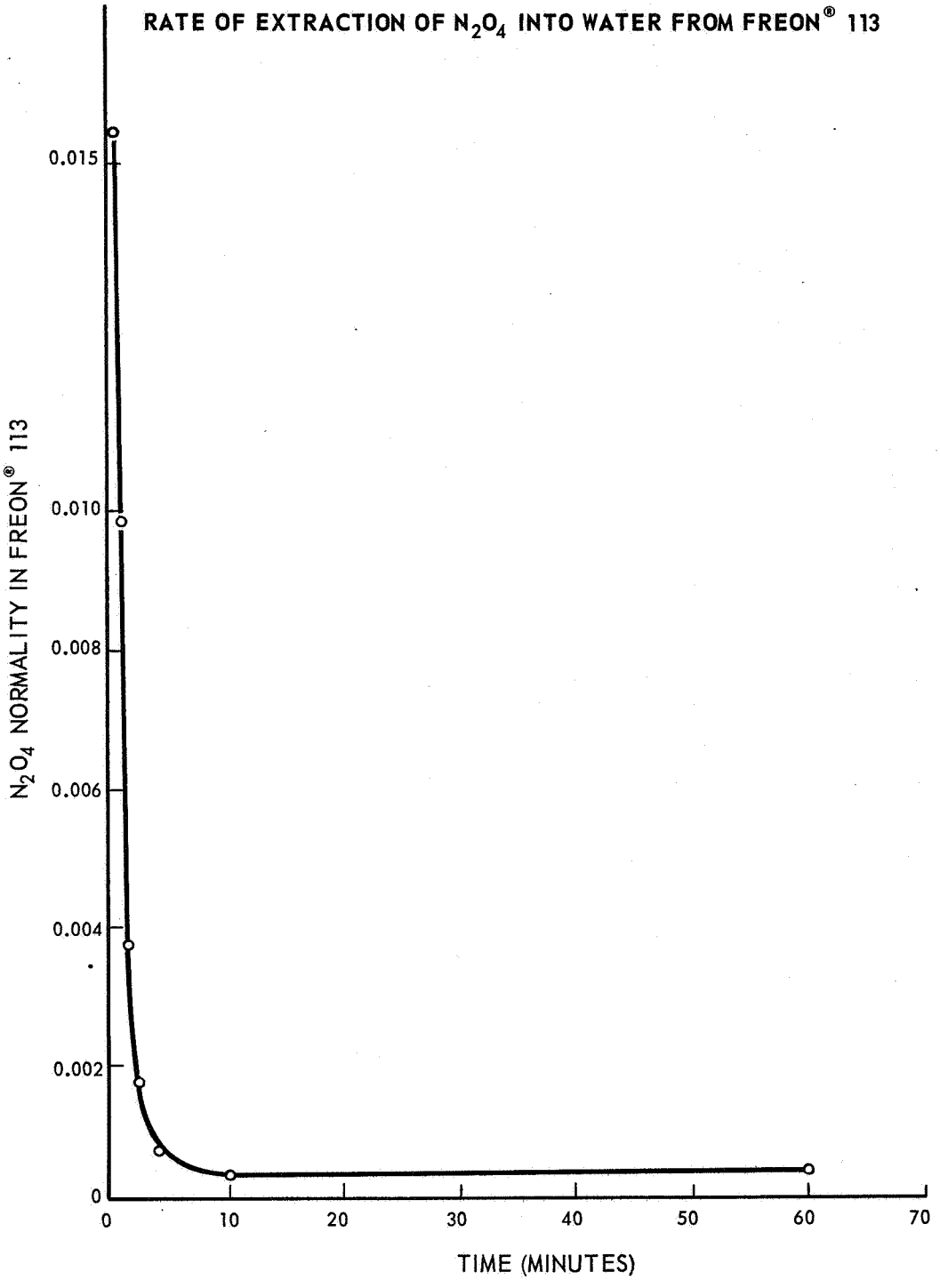


Figure 3-9


RATE OF EXTRACTION OF N_2O_4 INTO WATER FROM FREON® 113
N_2O_4 NORMALITY IN FREON® 113
0.015
0.010
0.008
0.006
0.004
0.002
0
0
10
20
30
40
50
60
70
TIME (MINUTES)

IX. ANALYTICAL PROCEDURES

A. Determination of Nitrogen Tetroxide in Aqueous Solution

1. Scope

This method is applicable to the determination of nitrogen tetroxide in the range of 20 ppm or more in aqueous solution.

2. Principle

In aqueous solution nitrogen tetroxide forms nitric and nitrous acids which are titratable with standard sodium hydroxide.

3. Reagents

(a) Sodium hydroxide, standard 0.1 N, 0.01 N and 0.001 N solutions. Dilute 8 grams of clear 50% sodium hydroxide solution with distilled water and make to one liter volume. Standardize against 0.1 N hydrochloric acid which has been standardized against primary standard sodium carbonate. Prepare the 0.01 N and 0.001 N NaOH by diluting the 0.1 N solution with carbonate-free distilled water.

(b) Phenolphthalein indicator - 0.1% in ethanol.

4. Interferences

Any acid or base present will represent an interference.

5. Procedure

Pipet into a flask a volume of sample such that it contains a minimum of 250 micrograms of nitrogen tetroxide. Add two or three drops of phenolphthalein indicator and titrate to the first faint pink color that is stable for about 20 seconds. Use the most appropriate strength solution of sodium hydroxide. Calculate ppm nitrogen tetroxide.

6. Calculation

$$\frac{\text{ml titrant} \times \text{normality titrant} \times 46{,}000}{\text{ml sample} \times \text{density sample}} = \text{ppm nitrogen tetroxide}$$

B. Determination of Nitrogen Tetroxide in Organic Solvents

1. Scope

This method may be used to determine nitrogen tetroxide in organic solvents down to the 20 ppm level.

2. Principle

Standard alcoholic potassium hydroxide is used to titrate N_2O_4 or its acidic decomposition products. The end point of the titration is determined potentiometrically.

3. Interferences

As this is a simple acid-base titration, other acids or bases present will interfere.

4. Apparatus

pH meter, Leeds and Northrup 7401, or equivalent, equipped with glass and calomel electrodes.

5. Reagents

(a) Ethanol, 95 to 100%.

(b) Potassium hydroxide, standard 1 N, 0.01 N and 0.001 N solutions. Dissolve 16.7 grams of low-carbonate potassium hydroxide in ethanol and dilute to 250.0 ml. Standardize against primary standard benzoic acid. Prepare solutions of 0.01 N and 0.001 N potassium hydroxide by dilution with alcohol.

6. Procedure

(a) Set up the pH meter so that the solution to be titrated may be continuously monitored. Provision for continuous stirring of the sample is desirable.

(b) Place 10 ml of ethanol in a 100 ml tall-form beaker. Add 15.0 ml of sample by pipette.

(c) Titrate with standard alcoholic potassium hydroxide. At intervals record pH and volume of standard base. Near the end point, add the potassium hydroxide in small increments and wait for a constant reading of the pH meter.

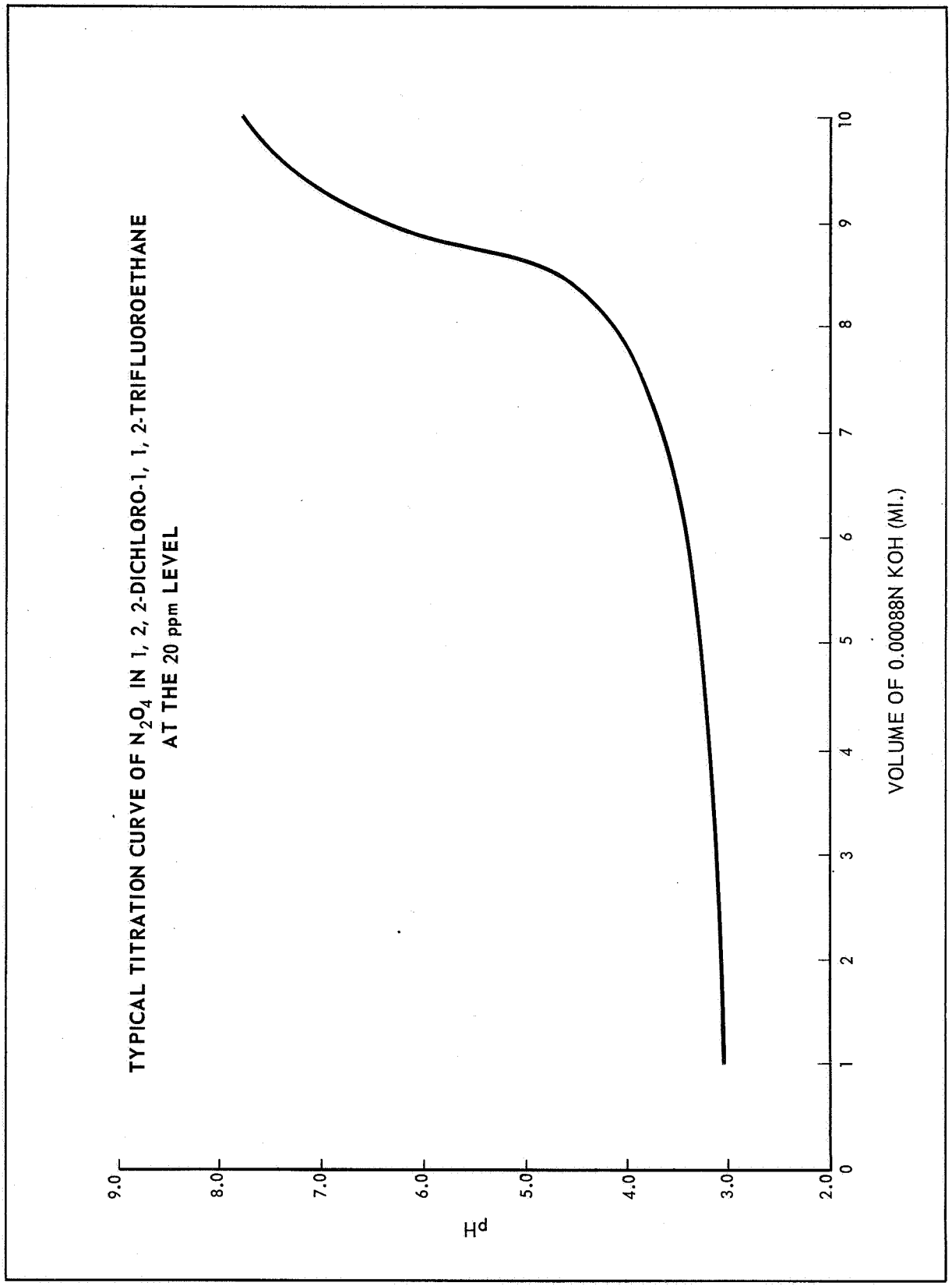
(d) From the plot of pH versus volume of standard potassium hydroxide, determine the volume of standard solution required for the titration and the pH at the end point. Use this indicated pH as the end point in subsequent titrations.

(e) Titrate a blank sample consisting of 10 ml alcohol and 15 ml of organic solvent which is free of N_2O_4 contamination. Correct the sample titration for this blank.

7. Calculation

$$\%N_2O_4 = \frac{V \times N \times 4.6}{15 \text{ ml} \times D}$$

where, V = net milliliters of standard base
N = normality of standard base
D - density of organic solvent in grams/ml


TYPICAL TITRATION CURVE OF N_2O_4 IN 1, 2, 2-DICHLORO-1, 1, 2-TRIFLUOROETHANE
AT THE 20 ppm LEVEL
pH
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
0
1
2
3
4
5
6
7
8
9
10
VOLUME OF 0.00088N KOH (ML.)

8. Notes

(a) Since the N_2O_4 may react with the solvent, samples should be titrated immediately upon receipt.

(b) Gas space in the sample bottle should be held to a minimum to reduce loss of N_2O_4 to the vapor phase.

C. Determination of 1,1-Dimethylhydrazine in Aqueous Solution

1. Scope

This method is suitable for the determination of 20 ppm or more 1,1-dimethylhydrazine in aqueous solution.

2. Principle

1,1-Dimethylhydrazine is titrated as a base using a strong acid as a titrant. The end point is determined using a pH meter.

3. Interferences

Any acid or base will represent an interference.

4. Apparatus

(a) pH meter.

(b) Magnetic stirrer and stirring bars.

5. Reagents

Hydrochloric acid, standard 0.1 N, 0.01 N, 0.001 N, and 0.0005 N solutions. Dilute 8.5 ml of concentrated hydrochloric acid to one liter with distilled water. Standardize against primary standard sodium carbonate. Prepare the 0.01 N, 0.001 N, and 0.0005 N solutions by diluting the 0.1 N solution with carbonate-free distilled water.

6. Procedure

Pipet into a beaker a volume of sample such that it contains a minimum of about 500 micrograms of 1,1-dimethylhydrazine. Place a stirring bar in the beaker and set beaker on a magnetic stirrer. Immerse electrodes in the solution and record initial pH. Add small measured portions of the appropriate standard hydrochloric acid and record pH and volume of titrant after each addition. Plot the titration curve to locate the end point and calculate ppm 1,1-dimethylhydrazine.

7. Calculation

$$\frac{\text{ml titrant} \times \text{normality titrant} \times 60{,}000}{\text{ml sample} \times \text{density sample}} = \text{ppm 1,1-dimethylhydrazine}$$

D. Determination of 1,1-Dimethylhydrazine in Nonaqueous Media

1. Scope

This method is suitable for the determination of 20 ppm or more of 1,1-dimethylhydrazine in nonaqueous media.

2. Principle

1,1-Dimethylhydrazine is titrated in nonaqueous solution by perchloric acid. The end point is determined by plotting the apparent pH as a function of volume of standard perchloric acid added.

3. Interferences

Any acid or base will represent an interference.

4. Apparatus

(a) pH meter.

(b) Magnetic stirrer and stirring bars.

5. Reagents

(a) Standard perchloric acid in ethanol, 0.1 N, 0.01 N, 0.001 N, and 0.0005 N solutions. Dilute 17.1 ml of 60% perchloric acid to one liter with 2B ethanol. Standardize against primary standard grade trishydroxymethylaminomethane using the pH meter to locate the end point. This primary standard is available from Fisher Scientific Company, Fair Lawn, New Jersey. Prepare 0.01 N, 0.001 N and 0.0005 N perchloric acid by diluting the 0.1 N solution with 2B ethanol which has been titrated to its end point with perchloric acid in ethanol.

(b) Anhydrous 2B ethanol.

6. Procedure

Pipet into a beaker a volume of sample such that it contains a minimum of about 400 micrograms of 1,1-dimethylhydrazine. Add at least an equal volume of 2B ethanol for the lower concentrations and enough to make a total volume of about 50 ml for the higher concentrations. Place a stirring bar in the beaker and set beaker on a magnetic stirrer with the pH meter electrodes immersed in the solution. Record the initial apparent pH. Add small measured portions of the appropriate standard perchloric acid and record apparent pH and volume of titrant after each addition. Plot the titration curve and determine ml of titrant at the equivalence point. Calculate ppm 1,1 dimethylhydrazine.

7. Calculation

$$\frac{\text{ml titrant} \times \text{normality titrant} \times 60{,}000}{\text{ml sample} \times \text{density sample}} = \text{ppm 1,1-dimethylhydrazine}$$

X. TECHNOLOGY SURVEY

A. Introduction

This is a summary of a literature search for the specific technology directly related to the decontamination or the removal of trace amounts of the propellant, nitrogen tetroxide, and Aerozine-50 from propulsion systems.

The topics covered were: propellants, nitrogen tetroxide, hydrazine, and unsymmetrical dimethyl hydrazine. The subtopics were: analytical procedures, decontamination methods, hazards and toxicity, hydrazine reactions, hydrazine and related compounds' use and preparation, propellant systems storage and design, N_2O_4 physical properties and reactions, and propellant compatibility.

The abstracting journals searched were: Chemical Abstracts (1955-65), Governmentwide Index, Technical Abstracts Bulletin (1961-65), Applied Science and Technology Index, Engineering Index, International Aerospace Abstracts, Scientific and Technical Aerospace Reports, Business Periodical Index, and Dow's Central Research Index.

The literature search, made under directions of Dr. Levis Hatch, Professor at the University of Texas, is included as an addendum to this technology survey.

B. Decontamination Methods

The strategic missile race demands a propulsion system having instant readiness. These missiles use storable liquid propellants. The oxidizers are N_2O_4 and white or red fuming nitric acid. The fuels are hydrazine, unsymmetrical dimethyl hydrazine (UDMH), monomethyl hydrazine (MMH), and Aerozine-50. The missiles of today are large and complex in comparison with those of earlier times. They are regularly test-fired, disassembled, inspected, and put back in standby condition. A part of this program is the decontamination of the propulsion system prior to disassembly. This requires more than passing care because the fuel and the oxidant components are highly toxic and corrosive. Both penetrate into the pores of the elastomers and the plastic materials in the propulsion system and are difficult to remove. The oxidizers form explosive mixtures with a number of solvents not normally thought of as explosive, and the fuels form explosive mixtures with air and with other oxidizing materials. Reactions between the two components and the cleansing compounds, including water, have produced undesirable solids within the systems at times. In order to maintain reliability of operation, cleanliness requirements have become more and more stringent as the complexity and size of the rockets have increased.[11] A discussion of some of the cleaning methods attempted and in use today follows.

1. Decontamination by Heated GN_2 Purge

N_2O_4 Removal: Of the various storable propellants, N_2O_4 is most effectively removed by this method. However, as the N_2O_4 is volatilized, the slight amount of water present as

in impurity in the N_2O_4 lags behind and concentrates. Enough moisture can remain to form a 70% nitric acid azeotrope. This highly corrosive liquid accumulates in small crevices and cannot be removed in a reasonable time period.

A-50 Removal: Because of the higher boiling points and greater moisture content of the various fuels and blends, decontamination of the fuel system is not feasible by heated GN_2 purge.(11)

2. Vacuum Drying

The first objection is that few systems can tolerate a vacuum. Furthermore, N_2O_4 and A-50 have relatively high freezing temperatures: 12° and 18° F, respectively. Application of a vacuum causes freezing. If precautions are taken in application of vacuum to prevent freezing, moisture present as an impurity remains to form corrosive acidic or basic concentrates.

3. Steam Cleaning

This method has been tried in a number of instances. Although it offered several advantages, it was not considered to be wholly successful. Advantages are: a heating source to volatilize the contaminants, a purge gas to sweep the same out of the system, and a flowing liquid film flush. Disadvantages are: the formation of corrosive acidic and basic products not removable at low pressure steam temperature, and the detrimental effect of temperature in the range 212° to 250° F on nonmetallic parts.

4. Volatile Neutralization

Decontamination by use of volatile materials such as NH_3 and CO_2 were considered. However, the neutralization products are solids. In general, it was concluded that the interior of the propellant systems is no place to allow a chemical reaction producing solids to occur.

5. Serial Dilution

This method is a sequential filling and draining with the same water. It was found to be adequate for removing propellants to levels that are safe for experienced personnel to perform disassembly out of doors but was considered unsafe for indoor disassembly.

6. Use of Neutralizing Solutions

This decontamination procedure was studied by investigators at Aerojet-General Corporation for cleaning of Titan II engines. A neutralization concentrate was prepared for the oxidant and the fuel. The oxidant flushing concentrate included triethanolamine as the neutralizer, a freezing point depressant, deionized water, a wetting agent, and an antifoam agent. The fuel cleaning concentrate used as a similar formulation, but hydroxyacetic acid was substituted for triethanolamine. Also, a corrosion inhibitor

was added. The concentrates were diluted with ten parts of water and flushed through the respective systems, followed by water. The systems were dried with anhydrous methanol followed by hot GN_2.[11]

7. Tri-Flush Method

This is a slight modification of the procedure discussed above except that a methylene chloride was added to the procedure.

The tri-flush method was an improvement over previously used procedures but had disadvantages as follows:

a. Multi-flush procedure required storage and handling of large quantities of the several flushing fluids.

b. Time-consuming.

c. Drying was not complete.

d. Residual antifoaming agent polymerized with solvent materials to form particulate solids.

e. Significant corrosion was apparent.[24]

8. Single-Flush Method

A new approach to decontamination was made by investigators at McDonnel Aircraft Corporation for the Gemini program which uses N_2O_4 and monomethyl hydrazine as propellants. It was proposed to use a volatile solvent in single-stage flushing of both sides of the propulsion system. Freon® MF was chosen as the flushing fluid for the following reasons:

a. It is compatible with both components.

b. Freon® MF has low viscosity and good penetration power.

c. The solvent adds no water to the system and is easily dried.[24]

Present decontamination of the Apollo service module uses a modification of the above system. Freon® 11 was not found to be sufficiently miscible with Aerozine-50, nor was it compatible with the materials of construction used in the fuel system. Methanol was adopted as the single flush fluid for the Aerozine system, and Freon® MF was retained for the N_2O_4 system.[5]

9. Other Methods

Other methods were tried, many of which are not published. An unexpected development was the discovery that trichloroethylene could form an explosive mixture with N_2O_4. Such a mixture was accidentally detonated and produced a violent explosion at Rocketdyne in 1963.[23] This explosion plus dissatisfaction with

the cleansing procedures in general, has led to renewed effort in the search for a truly satisfactory cleaning procedure.

C. Propellant-Solvent Compatibility

In November 1963, a violent explosion resulting in the loss of two lives occurred at the Rocketdyne Company during the decontamination of an N_2O_4 propellant system. It is believed that an inadvertant mixing of a trace of Aerozine-50 with N_2O_4 loaded trichloroethylene detonated the solvent-oxidizer mixture.(4) Following this event, interest in compatibility testing increased. The procedure most widely followed made use of standard blasting caps in trials to determine whether a given solvent mixed in various proportions with N_2O_4 would detonate. It was found that maximum sensitivity, or the tendency to explode, was obtained by placing the cap below the liquid level of a 50-50 mixture of the solvent being tested with liquid N_2O_4. A number of solvents not previously thought to be detonatable were found to be unsafe in mixtures with N_2O_4.(4,41,16) The presence of hydrogen in a solvent reduces its stability in contact with N_2O_4; chloroform ($CHCl_3$) is on the borderline but is not incompatible with N_2O_4.(16) Completely halogenated compounds such as Freon® TF (Freon® 113) and Freon® MF (Freon® 11) and carbon tetrachloride were found to be safe.(16)

D. Properties and Reactions of the Propellants

1. Aerozine-50

a. Properties and Reactions

Aerozine-50 is a 50/50 mixture of unsymmetrical dimethyl hydrazine (UDMH) and hydrazine (N_2H_4). This blend is a clear, colorless, hygroscopic liquid with a characteristic fishy ammoniacal odor. The components of the mixture are miscible in all proportions. On combination, there is an immediate tendency for each to desolve in the other. But layering of the mixture can occur, with UDMH above the N_2H_4, because of the significant difference in density.(1) When first introducing UDMH and N_2H_4 in a vessel or upon rapid chilling, the mixture will separate, forming an interface. Many ways of mixing the components have been studied. However, once the components have been satisfactorily blended, no appreciable stratification is observed.(46)

Aerozine-50 is soluble in water, ammonia, and alcohols; it is a strong reducing agent, and is also weakly alkaline. It will react slowly with air and CO_2 to form several products and salts. Rags, sawdust, and other materials with large surface areas on prolonged exposure to the vapor, may absorb enough A-50 to ignite spontaneously.

Aerozine-50 is a stable liquid under the extremes of heat and cold expected in storage. Upon freezing, the mixture contracts in volume. Thermal decomposition of N_2H_4 begins at about 320° F; UDMH is stable up to about 700° F. The fuel blend is not shock sensitive, but the vapors are flammable over a wide range of concentrations. A mixture of these vapors with air can be detonated by a small spark. Furthermore, some metals such as copper, molybdenum, or iron oxide will catalyze decomposition at room temperature.

Studies of the liquid-vapor equilibrium have revealed no azeotropic mixtures.[29] The two components of A-50 interact endothermically on mixing. Supercooling and freezing point depressant data on N_2H_4 is reported by Leonard.[18] Decomposition kinetics of N_2H_4 were studied by McHale[25] who reported a simple non-chain reaction and proposes several possible mechanisms.

Tables 4-I to 4-VII and Figures 4-1 to 4-7 summarize the more important physical properties of the fuel blend and also give some of the outstanding properties of the individual components.

b. Hazards and Toxicity

The fuel blend is toxic by inhalation, ingestion, or by skin contact.

The vapors cause local irritation to the respiratory tract and to the eyes. Prolonged contact or high concentration of the fuel blend vapors cause pulmonary edema in the respiratory system. UDMH vapor is mildly irritating to the skin and eyes and will penetrate the tissue to cause systemic toxicity. In this respect, hydrazine is less dangerous but will produce an alkali-like burn or necrosis of the skin. Short exposure to the vapor results in attack on the central nervous system causing hypernea and convulsions. Longer explosure may cause death.[2] The concentrations of vapors which are hazardous to the eyes are not necessarily high enough to cause attack on other areas. Prolonged eye contact with hydrazine vapors will cause the eyes to become swollen and inflamed and can cause temporary loss of sight. In some instances, the blindness lasts for about three days, but, within a week, full recovery usually occurs.

The allowable concentration (MAC) in air of N_2H_4 is 1 ppm and 0.5 ppm for UDMH for an 8-hour day.[19] Personnel suffering from over exposure to vapors should be immediately removed to an uncontaminated atmosphere and kept as quiet as possible while administering first aid.[44] Liquid hydrazine will cause permanent blindness if first aid is not rendered immediately.[12]

Patrick and Black[31] give detailed description of the pathological and toxic effects on monkeys and rats of small repeated doses of the fuel components. Weir et al[43] discussed the mechanism of acute toxic effects of UDMH. If the fuel blend should come in contact with the skin, the contaminated clothes should be removed immediately and the exposed area washed thoroughly with large quantities of water while medical attention is summoned. Eyes exposed to liquid A-50 should be immediately rinsed with clean water for 15 minutes during which time proper medical help, preferably an ophthalmologist, is summoned.

2. Nitrogen Tetroxide

a. Properties and Reactions

Nitrogen tetroxide is a heavy liquid which boils near room temperature (70.07° F). The liquid is an equilibrium mixture of about 85% N_2O_4 with 15% NO_2 at 68° F. The presence of the NO_2 gives the liquid its characteristic dark brown color, but as the temperature is lowered, the equilibrium favors less NO_2 and thus the solutions approach a pale yellow color.[27] N_2O_4 is normally handled as a gas. If the N_2O_4 falls within the specifications shown in Table 4-VIII where water content is 0.1% or less, storage in most steel containers is practicable.[30]

Nitrogen tetroxide is a very strong, corrosive oxidizing agent and extremely poisonous. It is hypergolic with UDMH, N_2H_4, aniline, furfuryl, alcohol, and many other combustible compounds.[1] With sufficient shock, N_2O_4 can be detonated with certain chloronated hydrocarbons and many other compounds not normally thought to be explosive.[23] N_2O_4 is not sensitive to mechanical shock or heat, but above 302° F free oxygen is dissociated. On cooling, the free oxygen recombines to form N_2O_4. It is nonflammable but will easily support combustion.[1]

N_2O_4 is soluble in water and reacts with water to form nitric and nitrous acids ($N_2O_4 + H_2O \longrightarrow HNO_3 + HNO_2$). The nitrous acid undergoes further decomposition ($3HNO_2 \longrightarrow HNO_3 + 2NO\uparrow + H_2O$). NO is sparingly soluble but may undergo oxidation ($2NO + O_2 \longrightarrow 2NO_2$).[34] A report by Coon and Streib[13] on the dissociation of N_2O_4 and its products indicates that the dissociation cannot be correctly calculated from pressure data at elevated temperature.

The properties of N_2O_4 are shown in Tables 4-VIII through 4-XIV and Figures 4-8 through 4-14.

b. Hazards and Toxicity

The effects of liquid N_2O_4 are similar to those of 70% HNO_3; brief exposure causes yellowing of the skin; severe burns result from longer contact. If the liquid is splashed into the eyes, blindness is likely to occur. If taken internally, severe burns result in death.(21)

The vapor phase above liquid N_2O_4 is primarily NO_2. Vapor contact with skin is less harmful than liquid for a given exposure time. The vapor will cause a stinging sensation to the exposed area. The most serious problem in handling N_2O_4 is probably vapor inhalation, and it is possible for harmful concentrations to be undetected by exposed personnel. Pulmonary edema or the reduction in the ability of the lungs to carry out oxygen exchange may then occur. The lag in time for symptoms to develop may complicate the effect of pulmonary edema because exposed personnel may continue with accustomed physical exertion.(35)

The threshold limit value (MAC) is given as 5 ppm for NO_2 and as 2.5 ppm for N_2O_4. Dr. Silverman(20) of the Harvard Medical School of Public Health, suggested that the MAC value can be exceeded safely by a factor of 5 for a 10-minute period. Dr. E. C. Wortz(45) also did similar work and concurred with Dr. Silverman's findings.

The initial symptoms, after exposure to N_2O_4, are irritation of the eyes and throat, cough, tightness of the chest and nausea. These first symptoms are slight but, several hours later, coughing, constriction of the chest, and very difficult breathing occurs. Cyanosis, a blue tinge to the mucous membranes of the mouth, eyelids, lips, and fingernails, may follow. A person at this stage is in great danger. Repeated exposure to the fumes may lead to ulceration of the mouth and nose and to decay of the teeth. Chronic irritation can occur to the entire respiratory tract complicated by bronchitis, bronchiectasis, or secondary pulmonary emphysema.(28)

Liquid N_2O_4 spills on the skin should immediately be washed with copious quantities of water. For N_2O_4 splashed into the eyes, immediate flushing with clean water is mandatory. If a choice should exist as to flushing the eyes or calling a physician, the eyes must be flushed first for at least 10 minutes, keeping the victim's eyes open. After this, call for assistance at the first opportunity but continue the eye washing. A person exposed to the vapors should be removed to an uncontaminated atmosphere and proper first aid administered.(35)

E. Propellant Storage and Handling

The high energy content and toxicity of the propellants require careful design and special precautions for storage and handling. The fuel and oxidizer must be isolated from each other and also from any incompatible substances or environment.

The fuel and oxidant are stored in closed systems under nitrogen pads. The fuel blend necessitates a pad to reduce fire and vapor explosion hazards.[28] The oxidizer requires a pad to maintain a positive pressure over the liquid to suppress the dissociation to NO_2. The N_2O_4 storage system should be provided with a water sprinkler system to serve as a coolant on warm days.[35] If the propellant tanks are exposed to temperatures below freezing, a heating system may be required. The propellants contract in volume on freezing, thus eliminating expansion problems associated with water.

The vessels and connecting lines of the storage facilities should be welded where possible and should comply with the ASME Boiler and Pressure Vessel code specifications.[3] The N_2O_4 vessels must withstand at least 150 psia, with rupture discs set for 75 psia, and an automatic relief valve set for a lower pressure. All vents and relief valves should pass through water scrubbers.[28]

The immediate and surrounding area of storage facilities should be free of all organics and kept as meticulously clean as possible. Cotton lint, sawdust, rags, or any other material of this nature will be spontaneously ignited by absorption of fuel vapors. The storage area should be diked in some manner to contain spills. All buildings and materials of support should be fireproof and designed for a corrosive atmosphere.[28]

All vessels and lines must be adequately grounded. Electric motors and electrical control systems should be installed under the NFPA No. 70[3] explosion-proof code to eliminate any possibility of vapor contact.

Pumps used in the system should be the self-priming type, preferably centrifugal. Any other pumps should be of a design to eliminate contamination of the propellant by moisture. The pump should be of the type needing no seal or one with a seal that is compatible with the propellant.[28]

Water outlets should be strategically located in the storage area and be of sufficient size to handle fires and spills. A wind direction marker and an evacuation signal horn are needed to aid in safe evacuation. Safety shower and eye wash baths should be conveniently located. The personnel should be thoroughly educated and familiarized with the hazards of the propellants and the problems they may create.[28] Self aid and first aid procedures must be established for all possible types of exposure.

Spills of propellants always present a very serious hazard. Decontamination of N_2O_4 spills is best accomplished by a water spray. The spray knocks down the vapors and contains them along with a liquid. No advantage results from using water containing additives. Decontamination of fuel blend spills was also affected by a fine water spray. The vapors should be rapidly diluted with water spray to diminish a possible fire hazard. If a fire does develop, dry chemicals and foam are most effective as extinguishers. Water is the best material for disposing of an A-50 spill since the contaminant can be flushed down the drain and the fire hazard is considerably reduced.[36]

F. Compatibility of Propellants with Materials of Construction

The materials of construction that are satisfactory for N_2H_4 service are also acceptable for UDMH.[19] Some materials such as iron, molybdenum, or copper oxides, should not be used since they catalyze the decomposition of N_2H_4. At 290° F, N_2H_4 violently decomposes whereas UDMH is stable up to 700° F in the presence of the above materials. Oxides of iron, lead, magnesium, and molybdenum may cause ignition of N_2H_4 vapors.

Most alloys are compatible with the fuel blend. The naturally occurring oxide surface that forms on aluminum protects it from corrosive attack. The surfaces should be carefully cleaned, after fabrication, to remove contaminants such as welding slag. Any such foreign substances contaminating the system may initiate corrosion. The aluminum alloys are highly resistant to corrosion in the pH range of A-50, and prolonged exposure does not affect the mechanical properties. Alloys such as 2014-T6, 5254-f, 6061-T6, and 356 tested at 160° F for 90 days in contact with A-50 containing up to 16% H_2O showed only a slight stain in the metal above the liquid line.[6]

Stainless steel is unaffected by A-50. However, most alloys must be acid-pickled prior to use in order to prevent stains and minor deposits. Molybdenum-bearing stainless steel alloys do not form deposits, but their use is not usually recommended.[19] Only 316, 17-4PH, and AM355 Cond-H alloys gave satisfactory results when exposed to the blend at 160° F for 90 days, showing only slight staining above the liquid line and having no deposits.[6]

Ferrous alloys can be used in systems where oxygen and moisture can be eliminated and if the temperature is maintained below 160°. However, the ferrous alloys are not recommended because the possible formation of iron oxide.[19]

Nickel alloys and certain cobalt alloys, such as Haynes Stellite 25, exhibit good resistance to the fuel at low moisture levels. Titanium alloys such as C120AV show excellent resistance to the fuel blend containing up to 16% water.

Magnesium alloys show poor resistance to corrosion. Alloys of copper show good resistance, but the possible adverse effect of their oxides limit their use.

Platings such as cadmium, silver, non-porous chromium, and nickel are satisfactory for fuel blend use. Gold-plated Berylco 25 is also satisfactory but discolors during contact.[19]

The fuel blend is a strong solvent as well as a powerful reducing agent. It will attack, dissolve, or react with many of the substances that normally constitute gaskets and seats. The soft parts must show resistance to attack and still retain a volume range of ± 0 to +25% and less than a 3% durability change. Also, the soft parts must have no effect on the propellant and show no change on visual examination.

In most instances, the preservation of sealing characteristics and resilience may be given more weight than changes in physical properties.[19]

Teflon® and Teflon® products are the most resistant to chemical attack by the fuel blend. But, in contrast to its good resistance, Teflon® as gasket material has several disadvantages. Probably the most serious of these is propellant absorption and subsequent slow degassing. This effect may appear as a slight leak around the seal or may delay decontamination of the part. Teflon® has limited reuse since it lacks resilience.[19]

Certain nylons and polyethylenes show satisfactory chemical resistance, but only for a limited time or temperature, such as 30 days or 60° F. Kel-F 300 is also restricted to use of 70 days at room temperature, or 30 days at 160° F, after which it becomes brittle.[6]

Of the elastomers, certain butyl rubbers showed the best resistance to chemical attack. Parker XB800-71 and B496-7 performed well in tests at 160° F for 30 days with less than 15% loss of tensile strength. Parco 823-70 and Precision Rubber 9257 and 9357 softened from 13 to 20% when tested at 70-80° F for 50 days. Other butyl rubbers exhibited lesser degrees of resistance to the fuel blend, but most showed especially good resistance to aging. Fluorosilicons and fluororubber generally showed poorer resistance to the fuel but better resistance to solvents and heat.[19]

The only lubricant or sealant which significantly resisted washing out was Microseal 100-1. UDMH proved to be very satisfactory for use in contact with O-rings.

Table 4-XVI illustrates the behavior of construction materials on prolonged contact with the fuel blend.

The metal for N_2O_4 service is more limited by the water content of the oxidizer than the fuel blend.

Carbon steels, aluminums, stainless steel, nickel, and Inconel are suitable for N_2O_4 service where the moisture content is 0.1 percent or less. Only stainless steel of the 300 series and titanium exhibit adequate corrosion resistance at high moisture content for long-term service. Metals such as brass, bronze, cadmium, copper, lead, magnesium, silver, and zinc or their alloys should be avoided for use with N_2O_4.[19]

Titanium and several of its alloys such as Ti 65A are satisfactory for use with N_2O_4.[19]

Cobalt alloys, Haynes Stellite No. 6K and 25, and certain nickel alloys are acceptable for use under anhydrous conditions. Only a few elastomers are compatible with N_2O_4. It can dissolve, degrade, decompose, or even completely destroy the substance. Certain components in the soft parts can be extracted, causing drastic changes

in physical properties. In fact, only one material, Teflon®, was found to resist attack sufficiently for long-term service.[19]

The inadequacies of suitable elastomers for N_2O_4 service can be further illustrated by recent research on this problem. Work with filled Teflons® and certain polyethylene-encapsulated elastomers has been successful only for short-term exposures.[22] Gamma radiation curing techniques have been tried with several elastomers to increase their resistance.[1] Very recently, a carboxy nitroso rubber has been developed as an elastomer highly resistant to N_2O_4. Tests on this rubber after immersion in N_2O_4 for 90 days at 165° F showed no change in mechanical properties.[17]

Teflons®, filled with graphite, molydisulfide, asbestos, or impregnated with Teflon® fibers, usually provide adequate services in N_2O_4 if moisture content is less than 0.10%.[22] Both Teflon® TFE and FEP soften at higher moisture concentrations.[19] Formula 53 (polyethylene with isobutylene) shows good strength resistance but undergoes swelling of about 19%.[39]

Only three lubricants-Molykote Z, Drilube 703, and Electrofilm 66C were found to be satisfactory.[22] Water glass graphite, Reddylube 100 and 200, and N_2O_4 sealant were satisfactory for thread sealant service.[19]

The behavior of construction materials in contact with N_2O_4 is given in Table XVII.

G. Detection and Analysis

The published literature includes many articles on the detection and analysis of N_2O_4 and the hydrazines. Detection of the presence of propellant materials is of prime interest in work areas where contamination of the atmosphere is possible. Analysis of the respective propellants for impurities such as moisture and particulate solids is important to the proper functioning of the propellant system.

1. Detection

The maximum allowable concentration in the atmosphere for an 8-hour day is 0.5 ppm for the fuel blend and 5 ppm for N_2O_4. The atmosphere in work areas exposed to possible contamination by the propellant components must be accurately monitored for propellant vapors in order to detect immediately an increase to greater than allowable concentration.

Vapor phase chromatography has been used for detection of propellants. An instrument equipped with a 1/8-inch by 3-foot glass column packed with 15% SE oil on Gas Chrom Z at 60° was used with a flame ionization detector. Successful detection of 0.5 ppm UDMH in air was accomplished. An electron capture detector used with the vapor phase chromatograph had similar sensitivity, but reaction to atmospheric oxygen or traces of other impurties yielded less reliable results.[33]

A very simple and inexpensive method for atmospheric detection of fuel vapor down to 0.5 ppm has been used. This method is colorimetric in nature and uses paradimethyl aminobenzaldehyde absorbed on paper as the coloring agent. Measured volumes of air are pumped through the paper. If fuel vapors are present in the air, the paper will turn yellow. The degree of color can be matched against standards and concentrations down to 0.5 ppm can be determined. This method has the limitation that concentrations of chlorine above 5 ppm and ammonia above 50 ppm interfere.(37)

More sophisticated detection instruments are available for air contaminants. The M.S.A. Billion-Aire instrument manufacturers claim detection down to the ppb range. It uses a relatively complex ionization chamber in which the contaminant is reacted to form a solid. This reaction constitutes a sensitization whereby the desired physical changes are correlated to concentration levels. Hydrazine is detected in the 0-50 ppb range, UDMH in the low ppm, and NO_2 in the 0-10 ppm range according to claims by the manufacturer.(38)

Other means of detection utilize air contaminant impingement on chemically treated tapes or into liquid scrubbing solutions. This type of detection departs from rapid, simple atmospheric monitoring in that the information read-out occurs after analysis by conventional methods.

2. Analysis

Simple methods may be needed to determine the purity of the propellants. Weight percent N_2O_4 can be determined in the following manner:

> A 1.5 gram sample of N_2O_4 is carefully collected in a sealed tube and accurately weighed. One hundred milliliters of 3% H_2O_2 are added to a 500-milliliter flask in a nitrogen atmosphere. The sealed ampoule of N_2O_4 is carefully inserted into the flask and broken below the liquid surface. The solution is diluted to 240 milliliters and chilled to freezing with constant shaking, then allowed to come to room temperature. The solution is next titrated with 0.5 N NaOH along with a blank, and appropriate calculation made.(10)

The nitrosyl chloride content of the N_2O_4 can also be simply determined.

> A portion of the 250-milliliter solution prepared as mentioned above is titrated for chloride ion by the standard $AgNO_3$ titration method.

A non-volatile ash determination can be made as follows:

> A weighed sample collected in the manner described above is placed in a prepared 100-milliliter platinum evaporating dish.

> After evaporation, the dish is heated in a muffle furnace for 30 minutes at 2,000° F. The dish is cooled, desiccated, carefully reweighed, and the percent non-volatile ash is calculated.[10]

The composition of the fuel blend can also be determined:

> A difference in reaction rates for acetylation of hydrazines can be used to determine the weight percent of the constituent in the blend. Acetylation of hydrazine occurs very rapidly while the UDMH reaction proceeds slowly. Two titrations are made. The first determines the total basicity of N_2H_4. The second measures UDMH after N_2H_4 has reacted with acetic anhydride. The amount of water and impurities can be determined by subtracting the sum of these two values from 100.[10]

Gas chromatography is the most convenient method for analysis of water content present in the range of specification given for fuel blend.

> A column of Fluoropak-80 coated with 20% Ucon Oil 550X gave very reproducible results. Water content in hydrazine in concentrations from 0.5 to 2.0 weight percent was accurately determined.[15]

The Karl Fisher method of water detection is accurate to very low concentrations. However, this method cannot be applied to detection of water in the oxidizer.[10]

To determine moisture content in a propellant tank after cleaning, an instrument such as the dew-pointer can be used. This instrument is valuable in detecting trace amounts of moisture and other vapor contaminants.

For the detection of particulate matter, various filters can be used to entrap the matter. The size and number per unit area can be determined by microscopic examination or the total level may be determined by weight gain during passage of a measured volume of gas. Elaborate electronic counting instruments are also available to quickly obtain the same information.

Many other methods of analysis are readily available in the published literature. A useful catalog of infrared spectra covering rocket fuels and products of combustion in vapor and liquid combination has been prepared. This type of analysis is useful in any application where a wide variety of products are to be identified and measured.[32]

TABLE 4-I

PROPELLANT SPECIFICATION - 50/50 FUEL BLEND*

Chemical Requirements	Specification (Wt. %)
UDMH	47.0 (min.)
N_2H_4	51.0 ± 0.8
Total N_2H_4 and UDMH	98.2 (min.)
H_2O and Other Soluble Impurities	1.8 (max.)

(Reference 7)

*The above specifications define the fuel Aerozine-50 and apply in all instances of reference.

TABLE 4-II

PHYSICAL PROPERTIES

50/50 Fuel Blend

Molecular Weight (Avg.)	45.0
Melting Point*	18.8°F.
Boiling Point	158.2°F.
Physical State	Colorless Liquid
Density of Liquid at 77°F.	56.1 lb./ft.^{3}
Viscosity of Liquid at 77°F.	54.9 x 10^{-5} lb./ft-sec.
Vapor Pressure at 77°F.	2.75 psia.
Critical Temperature (calc.)	634°F.
Critical Pressure (calc.)	1696 psia.
Heat of Vaporization (calc.)	425.8 BTU/lb.
Heat of Formation at 77°F. (calc.)	527.6 BTU/lb.
Specific Heat at 77°F. (calc.)	0.694 BTU/lb-°F.
Thermal Conductivity at 77°F. (calc.)	0.151 BTU/ft-hr-°F.

(Reference 1)

Hydrazine

Molecular Weight	32
Melting Point	35°F.
Boiling Point	236°F.
Density at 68°F.	8.48 lb/gal.
Critical Pressure	2120 psig.
Critical Temperature	716°F.
Flash Point (open cup)	100-126°F.

(Reference 9)

Unsymmetrical Dimethyl Hydrazine

Molecular Weight	60
Melting Point	71°F.
Boiling Point	146°F.
Density at 68°F.	6.6 lb/gal.
Critical Temperature	480°F.
Critical Pressure	865 psig.
Flash Point (closed cup)	3°F.

(Reference 9)

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*Mixtures complying to specifications in Table 4-I.

TABLE 4-III

DISTILLATION RANGE OF THE 50/50 FUEL BLEND

Blend Composition by Weight %	
UDMH	48.7
N_2H_4	50.4
H_2O + impurities	0.9

Temperature (°F)	Volume % (Distilled)	Distillate Analyses*
149.0	First Drop Distilled	-
158.0	10	86.0% UDMH, 8.0% N_2H_4
161.6	20	85.0% UDMH, 9.0% N_2H_4
167.0	30	-
170.6	40	-
194.0	50	79.0% UDMH, 15.0% N_2H_4
233.6	60	-
235.4	70	-
235.4	80	100% N_2H_4
239.0	90	95% N_2H_4

(Reference 6)

*Analysis done spectrally with calibration curves for UDMH and N_2H_4 concentration range of 45 to 55% by weight.

TABLE 4-IV

VAPOR PRESSURE OF 50/50 FUEL BLEND AT 46% ULLAGE

Temperature (°F)	Vapor Pressure (Psia)	Reference No.
14.0	0.55	1
23.0	0.71	1
32.0	0.92	1
68.0	2.09	1
77.0	2.75	1
85.3	3.08	7
86.0	3.42	1
104.0	5.00	1
108.9	5.30	7
122.0	7.30	1
135.3	9.29	7
140.0	10.50	1
159.8	15.10	1

TABLE 4-V

SOLUBILITY OF VARIOUS GASES IN 50/50 FUEL BLEND

Pressurizing Gas	Temperature (°F)	Solubility (Wt %)	Final Gas Pressure (Psia)
Nitrogen	70.0	<0.01	86.0
	32.0	<0.01	79.4
Helium	71.5	0.012 ± 0.008	63.6
	33.0	<0.008	60.7
Ammonia	57.5	0.26 ± 0.01	38.0
	70.0	0.25 ± 0.01	44.4

(References 6 and 8)

TABLE 4-VI

HEAT CAPACITY OF 50/50 FUEL BLEND

(Calculated by Aerojet-General)

Temperature (°F)	Heat Capacity (BTU/Lb-°F)
21	0.680
35	0.684
63	0.692
81	0.696
99	0.702
135	0.709
153	0.715
250	0.743
350	0.780
420	0.814

(Reference 7)

TABLE 4-VII

FLASH AND FIRE POINTS OF 50/50 FUEL BLEND WITH VARIOUS WATER DILUTIONS

(Using a Modified Cleveland Open-Cup Tester)

H_2O in Fuel Blend (Vol. %)	Flash Point (°F.)	Fire Point (°F.)
Undiluted	38	38
10	40	40
20	35	35
50	110	125
60	160	160
65	180	200
75	>212	>212

(Reference 7)

TABLE 4-VIII

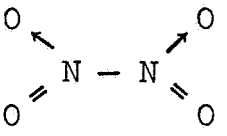
PROPELLANT SPECIFICATION* - N_2O_4

Chemical Requirements	Specification (Wt. %)
N_2O_4 Assay	99.5 (min)
H_2O Equivalent	0.1 (max)
Chloride as NOCl	0.06 (max)
Non-Volatile Ash	0.01 (max)

*Taken from Mil-P-26539 specifications (USAF) 18 July 1960

TABLE 4-IX

PHYSICAL PROPERTIES OF N_2O_4

Empirical Formula	$N_2O_4 \rightleftharpoons 2NO_2$
Structural Formula	
Molecular Weight	92.016
Physical State	Red-brown liquid
Melting Point	11.84°F.
Boiling Point	70.07°F.
Heat Formation at 77°F. (Liquid)	-87.62 BTU/lb.
Vapor Pressure at 77°F.	17.7 psia.
Viscosity at 77°F.	0.0002796 lb/ft-sec. 0.410 centipoise
Density at 77°F.	89.34 lb/ft^3
Heat Capacity at 70°F.	0.370 BTU/lb-°F.
Critical Temperature	316.8°F.
Critical Pressure	1469 psia.
Thermal Conductivity at 40°F. and 200 psia.	0.0812 BTU/ft-hr-°F.
Heat Vaporization	178 BTU/lb.
Heat of Fusion	68.4 BTU/lb.

(Reference 27)

TABLE 4-X

EQUILIBRIUM VALUES - PERCENT DISSOCIATION OF N_2O_4

$N_2O_4 \leftrightarrows 2NO_2$

Temperature (°F)	Pressure (psia)		
	7.4	14.7	29.4
68	19.5	15.8	7.2
104	38.7	31.0	15.1
140	66.0	50.4	28.2
176	85.0	73.8	46.7
212	93.7	88.0	66.5

(Reference 27)

TABLE 4-XI

VAPOR PRESSURE OF N_2O_4

Temperature (°F)	Vapor Pressure (psia)	Temperature (°F)	Vapor Pressure (psia)
11.8	2.70	180	163.29
14	2.90	190	196.35
32	5.08	200	235.01
50	8.56	210	281.56
68	13.92	220	332.8
70	14.78	230	393.2
80	18.98	240	463.3
90	24.21	250	543.9
100	30.69	260	636.3
110	38.62	270	732.6
120	48.24	280	864.1
130	59.98	290	1000.5
140	74.12	300	1160.1
150	91.06	310	1336.5[a]
160	111.24	316.8[b]	1469.0[a]
170	135.14		

a - Value extrapolated.

b - Critical pressure estimated from measured critical temperature.

(References 1 and 27)

TABLE 4-XII

DENSITY OF LIQUID N_2O_4
(Under its Own Vapor Pressure)

Temperature (°F)	Specific Gravity	Density (lb/ft³)	Density (lb/gal)
11.8	1.515	94.54	12.62
32.0	1.490	93.05	12.44
50.0	1.470	91.77	12.27
68.0	1.447	90.34	12.08
77.0	1.431	89.34	11.94
95.0	1.412	88.15	11.76
104.0	1.400	87.40	11.66
113.0	1.388	86.61	11.56
118.4	1.379	86.05	11.49
122.0	1.375	85.80	11.45
129.2	1.363	85.05	11.35

(References 1 and 27)

TABLE 4-XIII

VISCOSITY OF N_2O_4 IN THE LIQUID PHASE

	Temperature (°F)								
	40	70	100	130	160	190	220	250	280
		Bubble Pressure (psia)							
		14.8	30.7	60.0	111.2	196.4	332.8	543.9	864.1
Pressure (psia)				Viscosity (centipoise)					
Bubble Point	0.4990	0.4132	0.3420	0.2784	0.2235	0.1752	0.1325	0.0924	0.0570
200	0.5021	0.4155	0.3441	0.2800	0.2250	0.1753			
400	0.5055	0.4180	0.3470	0.2820	0.2281	0.1804	0.1350		
600	0.5090	0.4208	0.3495	0.2840	0.2310	0.1850	0.1420	0.0948	
800	0.5121	0.4232	0.3520	0.2861	0.2334	0.1896	0.1482	0.1028	
1000	0.5150	0.4260	0.3544	0.2880	0.2355	0.1939	0.1539	0.1100	0.0630
1250	0.5190	0.4297	0.3566	0.2906	0.2380	0.1975	0.1599	0.1179	0.0713
1500	0.5230	0.4330	0.3587	0.2919	0.2400	0.2010	0.1646	0.1252	0.0798
1750	0.5270	0.4366	0.3608	0.2949	0.2420	0.2040	0.1686	0.1319	0.0881
2000	0.5310	0.4400	0.3628	0.2965	0.2440	0.2083	0.1720	0.1370	0.0940
2200	0.5345	0.4433	0.3649	0.2990	0.2459	0.2060	0.1742	0.1400	0.0990
2500	0.5382	0.4470	0.3670	0.3010	0.2480	0.2098	0.1764	0.1430	0.1045
2750	0.5422	0.4502	0.3691	0.3024	0.2496	0.2110	0.1785	0.1444	0.1090
3000	0.5465	0.4535	0.3713	0.3042	0.2510	0.2127	0.1800	0.1470	0.1120
3500		0.4593	0.3753	0.2070	0.2540	0.2151	0.1822	0.1510	0.1170
4000		0.4655	0.3792	0.3095	0.2568	0.2183	0.1850	0.1532	0.1210
4500		0.4714	0.3830	0.3118	0.2600	0.2200	0.1880	0.1555	0.1249
5000		0.4782	0.3869	0.3145	0.2625	0.2229	0.1900	0.1579	0.1280

(Reference 27)

TABLE 4-XIV

HEAT CAPACITY OF LIQUID N_2O_4

Temperature (°F)	Heat Capacity (BTU/Lb.-°F.)
20.5	0.3564
27.0	0.3578
36.1	0.3598
45.6	0.3624
56.8	0.3652
64.8	0.3667

(Reference 14)

TABLE 4-XV

SOLUBILITY OF NITROGEN AND HELIUM IN LIQUID N_2O_4

Pressurizing Gas	Temperature (°F)	Solubility (Wt.%)	Final Gas Pressure (psia)
Nitrogen	70	0.20±0.01	63.7
	32	0.14±0.01	64.2
Helium	73	0.04±0.01	54.3
	32	0.02±0.01	55.4

(Reference 8)

TABLE 4-XVI

COMPATIBILITY OF CONSTRUCTION MATERIALS
WITH 50/50 FUEL BLEND

Material	Temp. (°F)	Exposure Time	Remarks
Birch Wood	75	2 hr 30 min	Wood grain split
Concrete			
Bare	75	13 hr	No visual effect
Coated w/water glass	75	1 hr 30 min	Water glass crystallized and powdered off
Coated w/water glass and floor enamel (Esco Brand 41138)	75	1 hr 15 min	Paint blistered
Coated w/water glass and Chex-Wear floor enamel	75	6 min	Paint blistered
Coated with Rockflux	75	10 hr 30 min	No visual effect
Mild Steel Coated With			
Tygon K Paint	75	1 hr	Paint blistered
Catalac improved paint	75	1 hr 30 min	Grainy appearance; lifted when totally immersed
Co-polymer P-200G	75	3 min	Paint was removed
Sauereisen 47 (4 coatings)	75	7 hr	First coating was removed in 1 hr; blistered but did not penetrate 4 coatings
CA 9747 Primer Paint	75	10 min	Blistered and discolored
Corrosite Clear 581	75	1 hr 15 min	Blistered

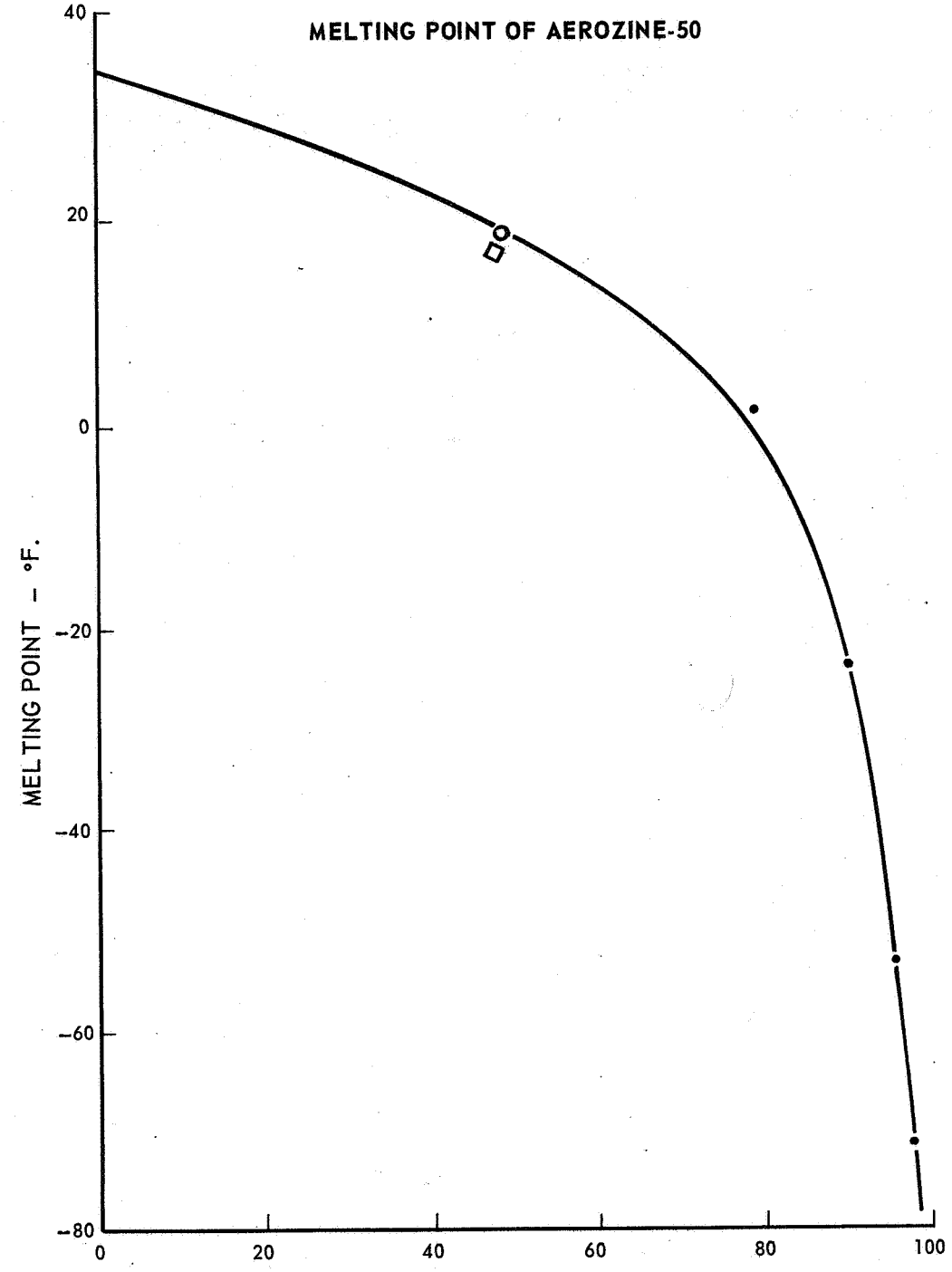
TABLE 4-XVII

COMPATIBILITY OF CONSTRUCTION MATERIALS WITH N_2O_4

Material	Temp. (°F.)	Exposure Time	Remarks
Birch Wood	75	30 min	Surface darkened; attacked at H_2O-N_2O_4 interface
Concrete			
Bare	75	1 hr 42 min	Concrete attacked
Coated w/water glass	75	1 hr	No apparent reaction; affords protection
Coated w/water glass and floor enamel (Esco Brand 41138)	75	30 min	Reaction at H_2O-N_2O_4 interface after 6 minutes; stripped to water glass.
Coated w/water glass and Chex-Wear floor enamel	75	3 min	Only paint removed
Coated w/Rockflux	75	1 hr 15 min	N_2O_4 absorbed; adhesion weakened; material turned white.
Mild Steel Coated with			
Tygon K paint	75	20 min	Paint blistered
Catalac, improved	75	10 min	Paint blistered; lifted when totally immersed
Copolymer P-200G	75	2 min	Dissolved immediately
Sauereisen 47 (4 coatings)	75	10 min	Dissolved
CA9747 Primer Paint	75	2 min	Reaction and discolored immediately
Corrosite Clear 581	75	30 min	Blistered

Figure 4-1

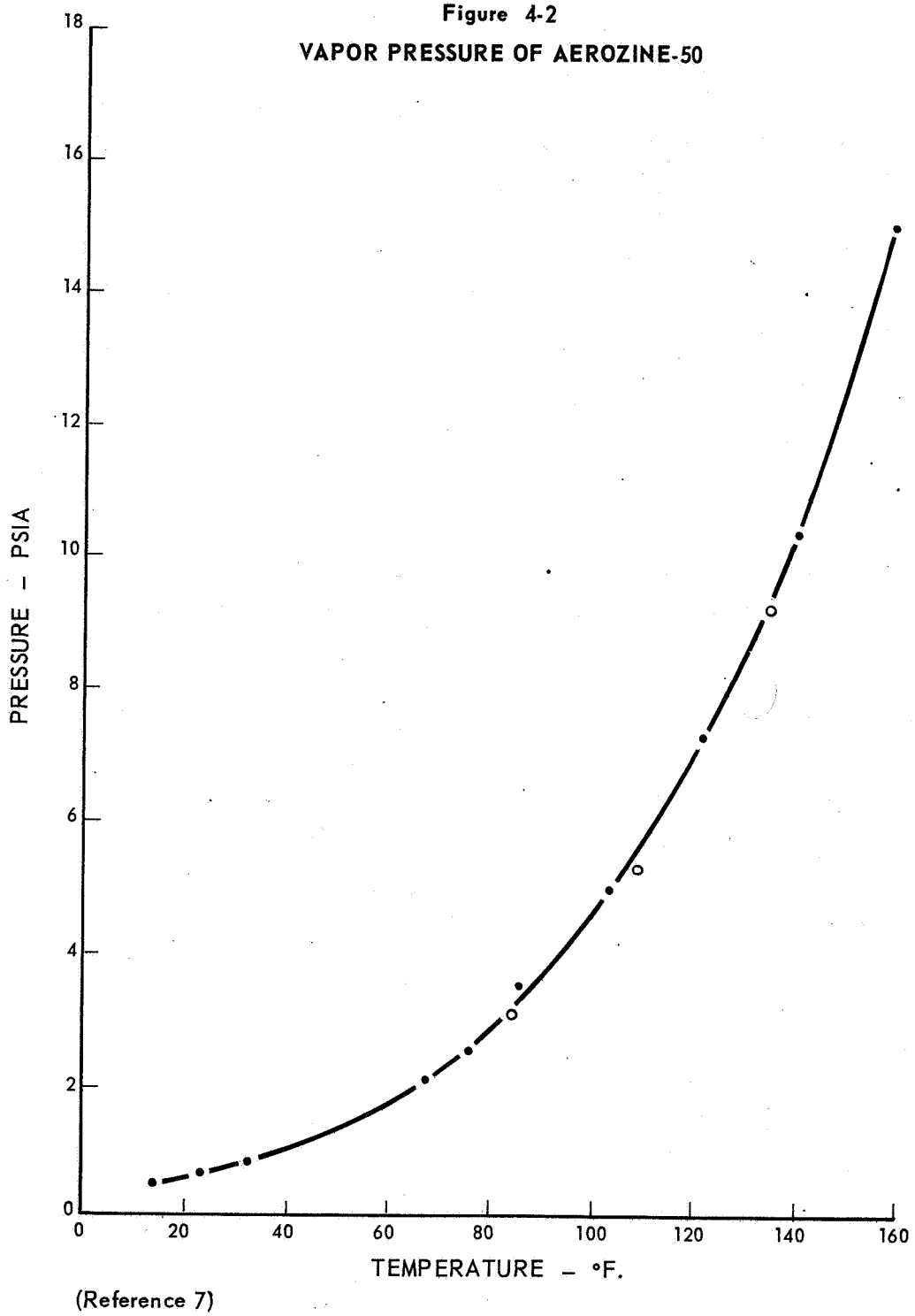
MELTING POINT OF AEROZINE-50



(Reference 7)

Figure 4-2

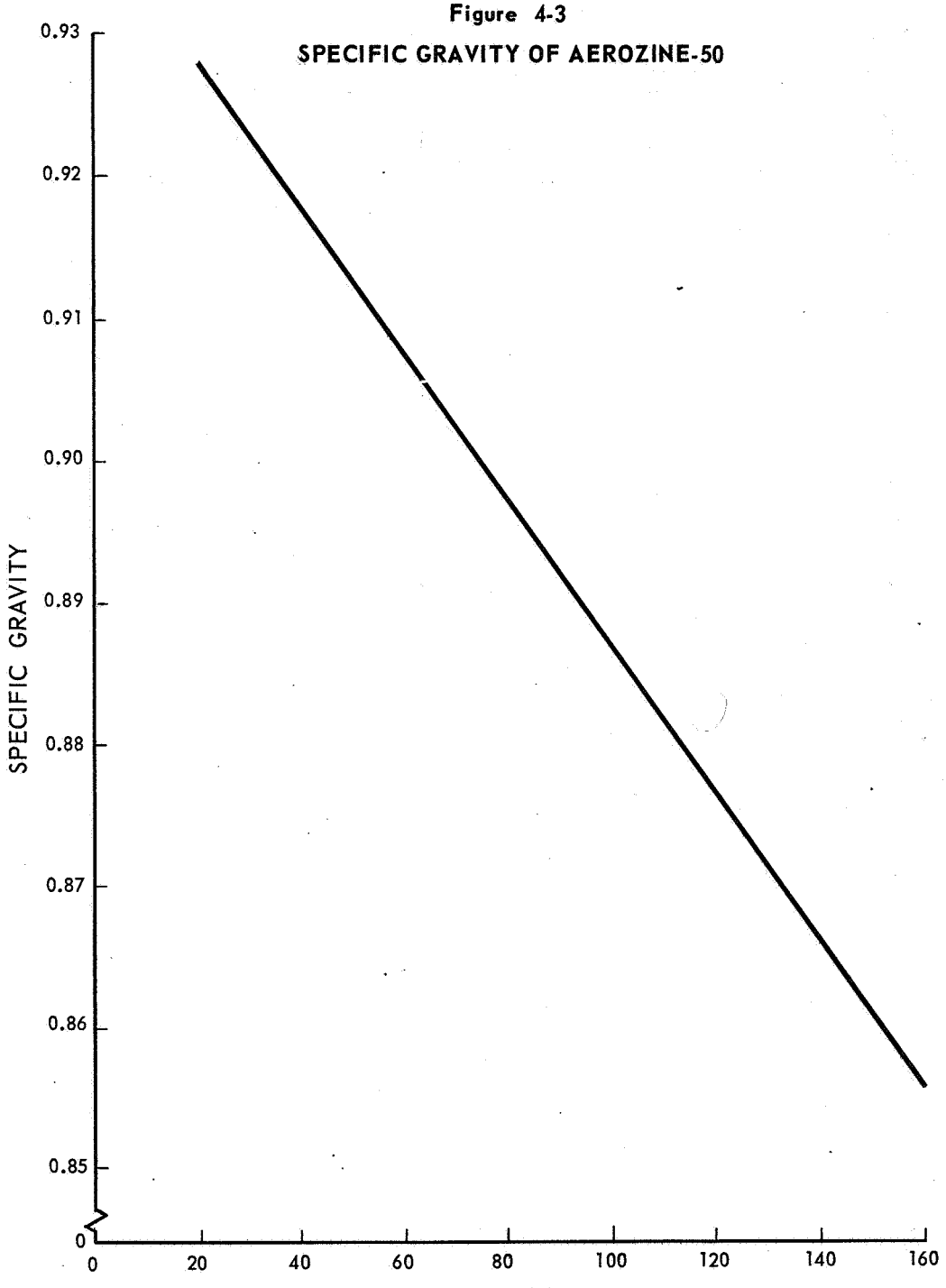
VAPOR PRESSURE OF AEROZINE-50



(Reference 7)

Figure 4-3

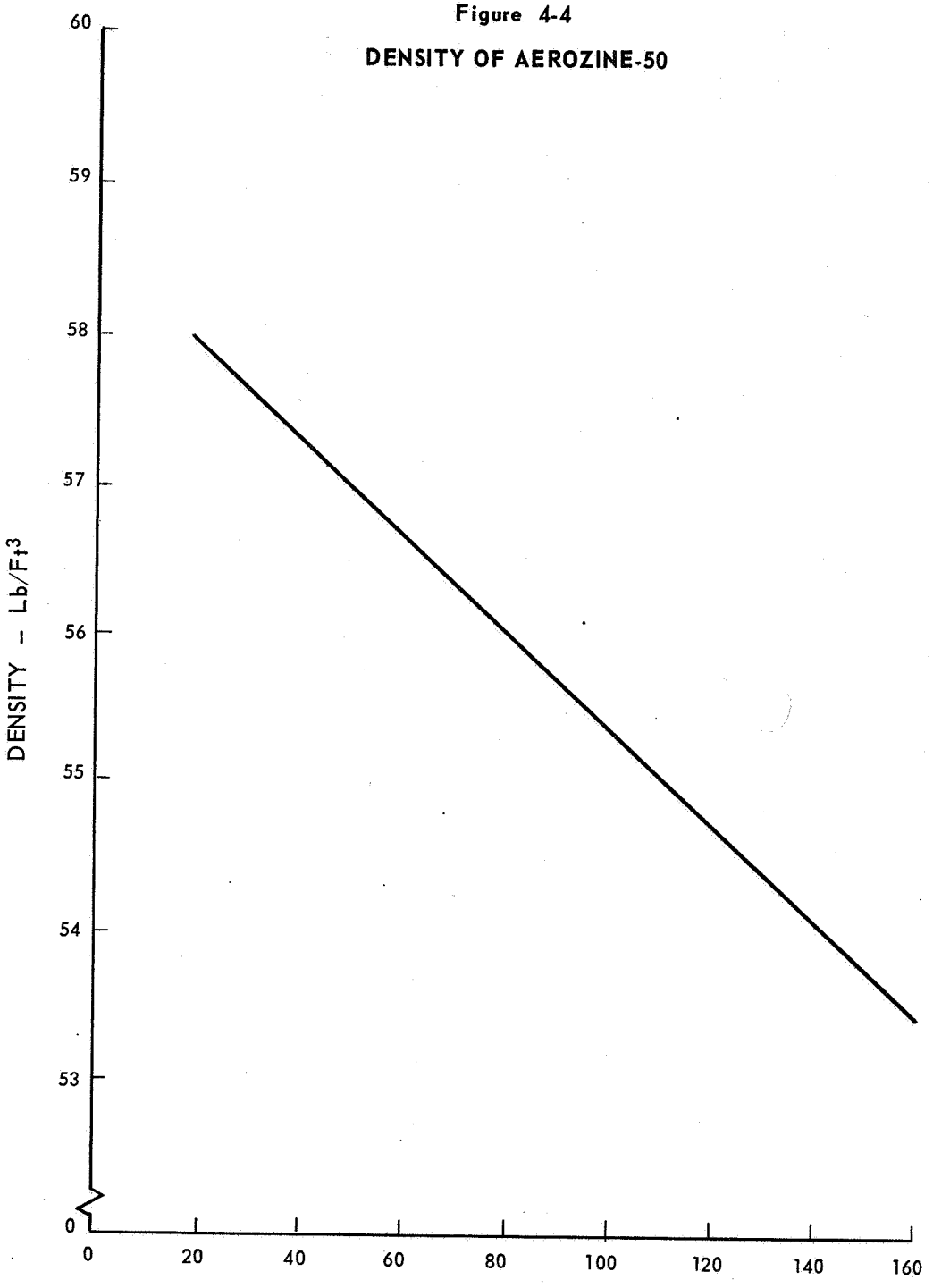
SPECIFIC GRAVITY OF AEROZINE-50



(Reference 1)

Figure 4-4

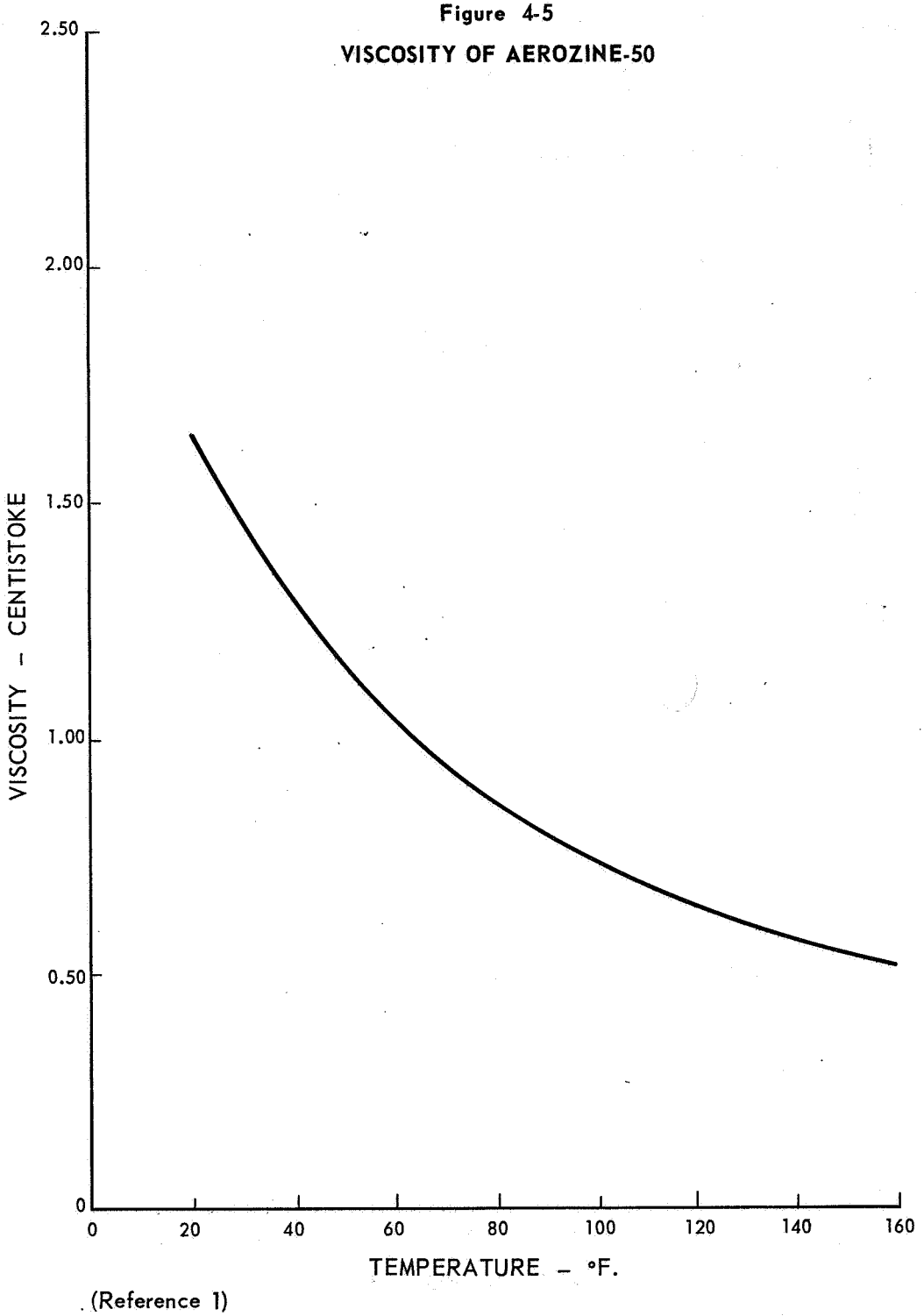
DENSITY OF AEROZINE-50



(Reference 1)

Figure 4-5

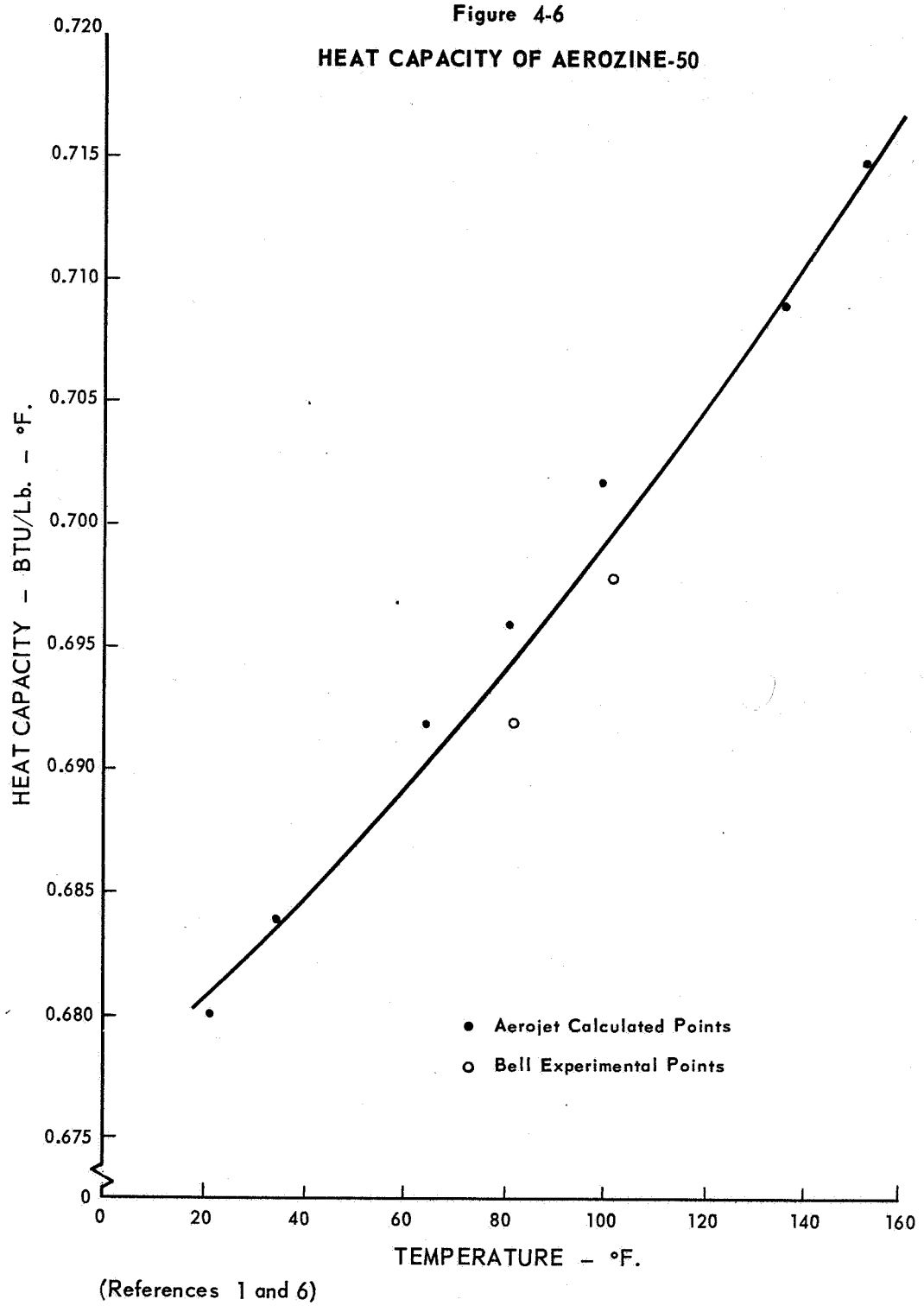
VISCOSITY OF AEROZINE-50



(Reference 1)

Figure 4-6

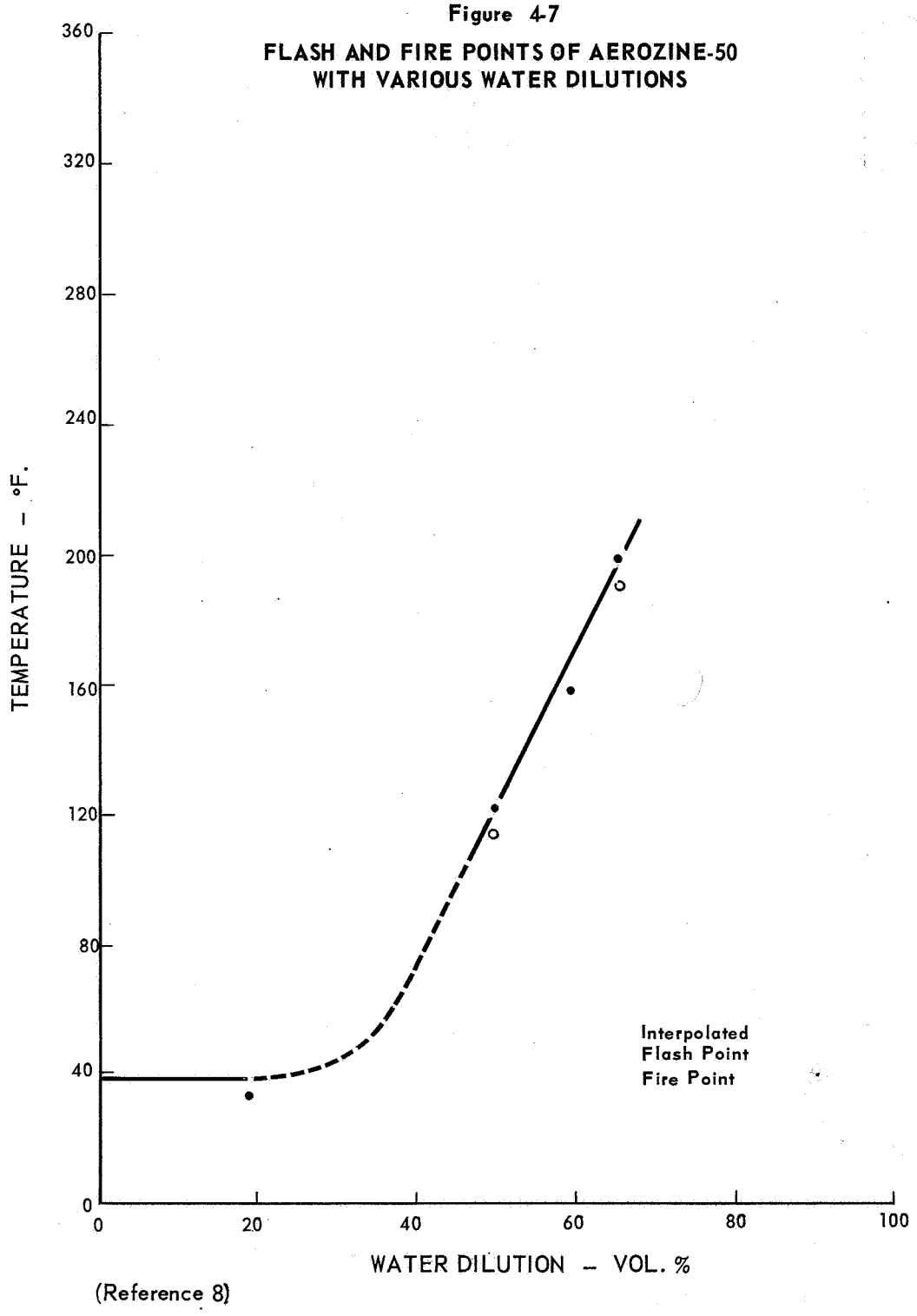
HEAT CAPACITY OF AEROZINE-50



(References 1 and 6)

Figure 4-7

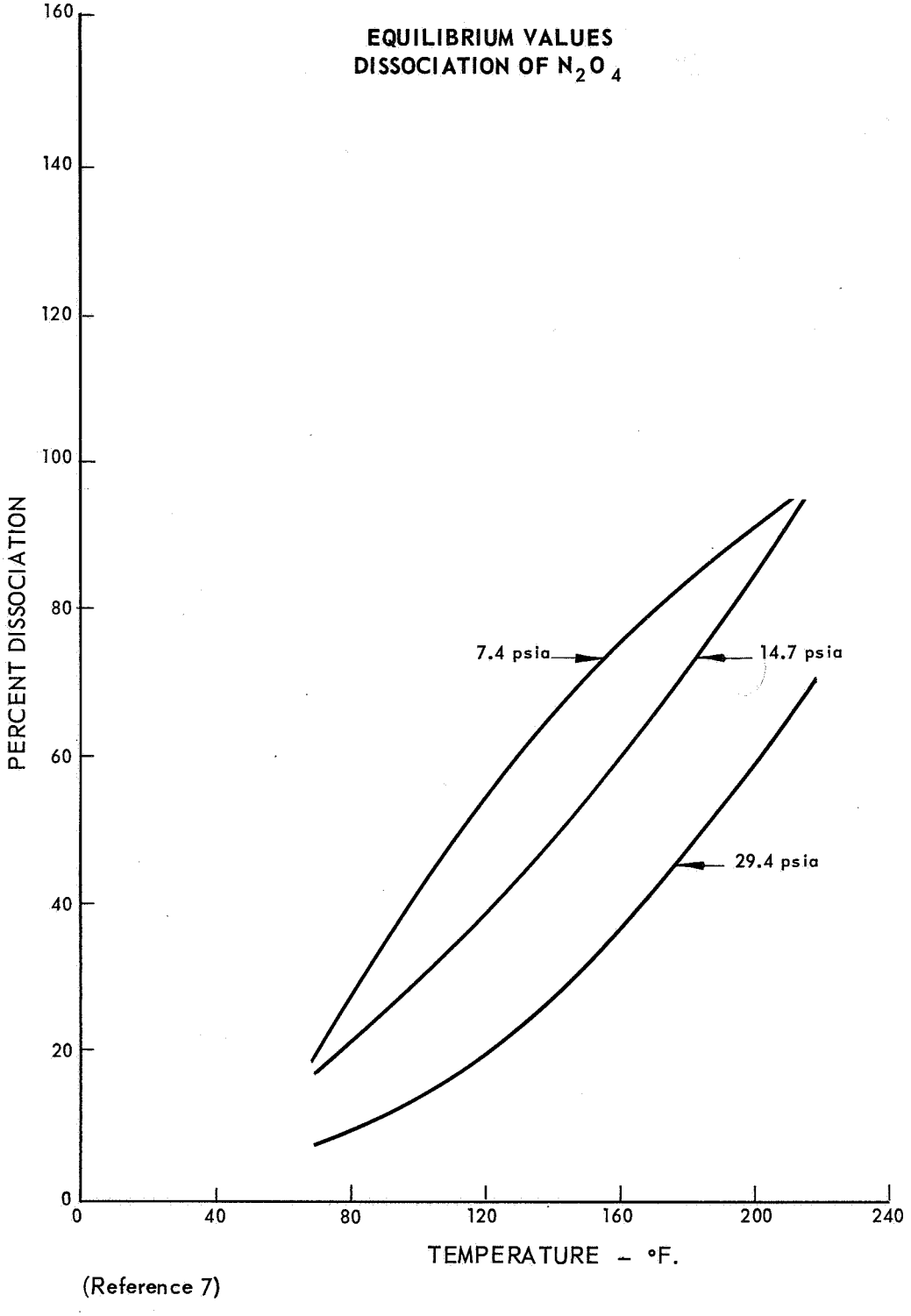
FLASH AND FIRE POINTS OF AEROZINE-50
WITH VARIOUS WATER DILUTIONS



(Reference 8)

Figure 4-8

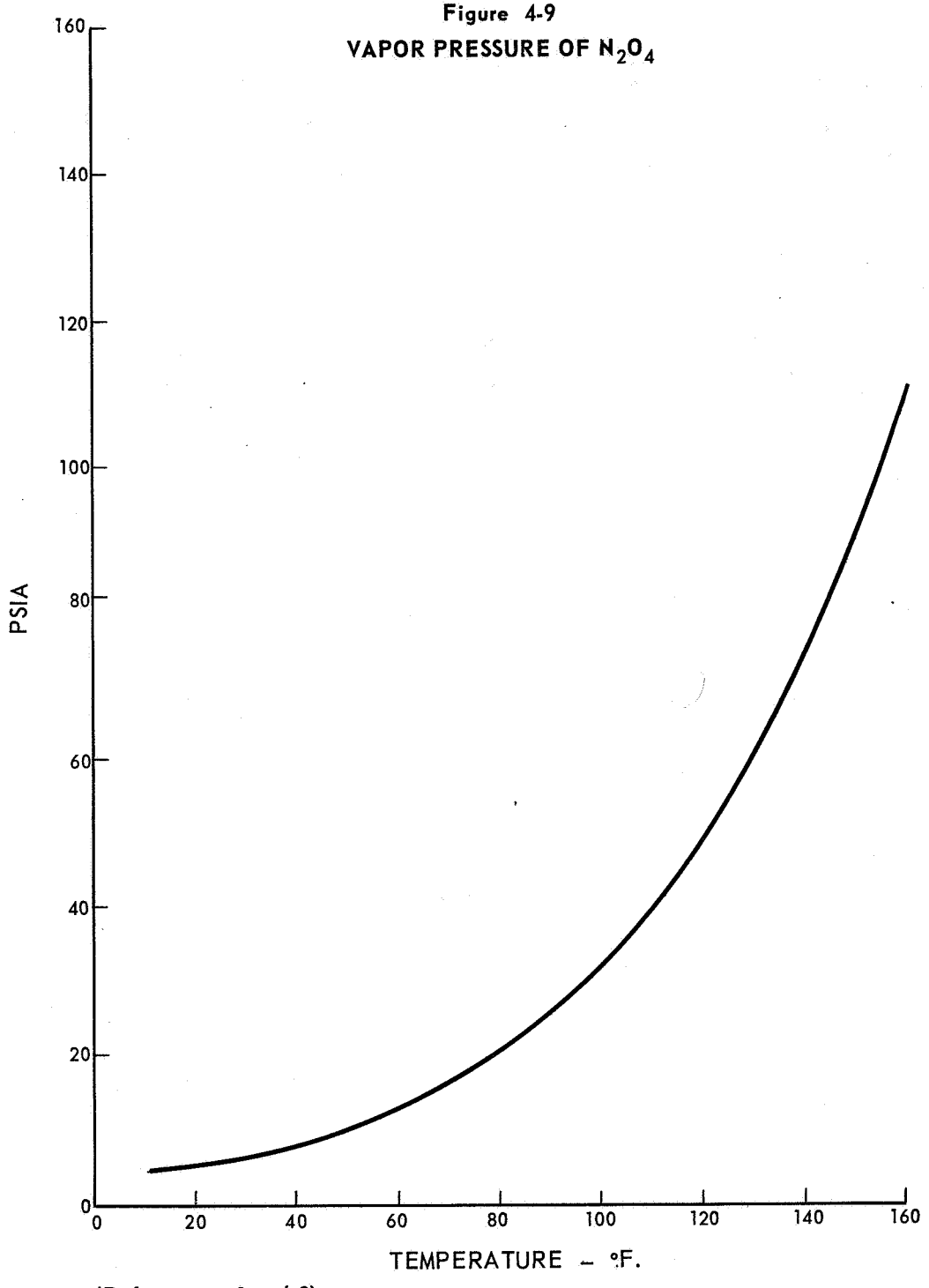
EQUILIBRIUM VALUES
DISSOCIATION OF N_2O_4



(Reference 7)

Figure 4-9

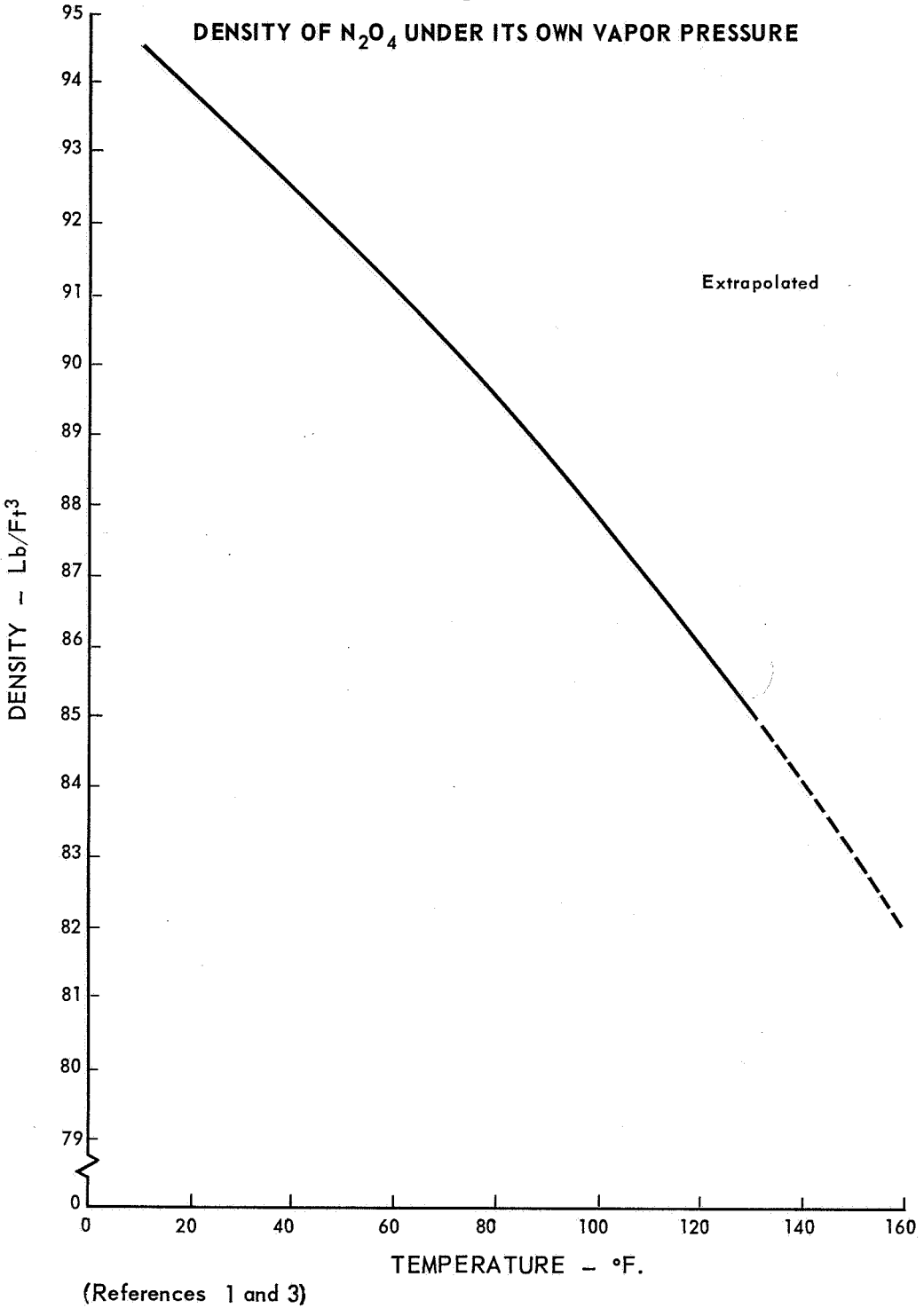
VAPOR PRESSURE OF N_2O_4



(References 1 and 3)

Figure 4-10

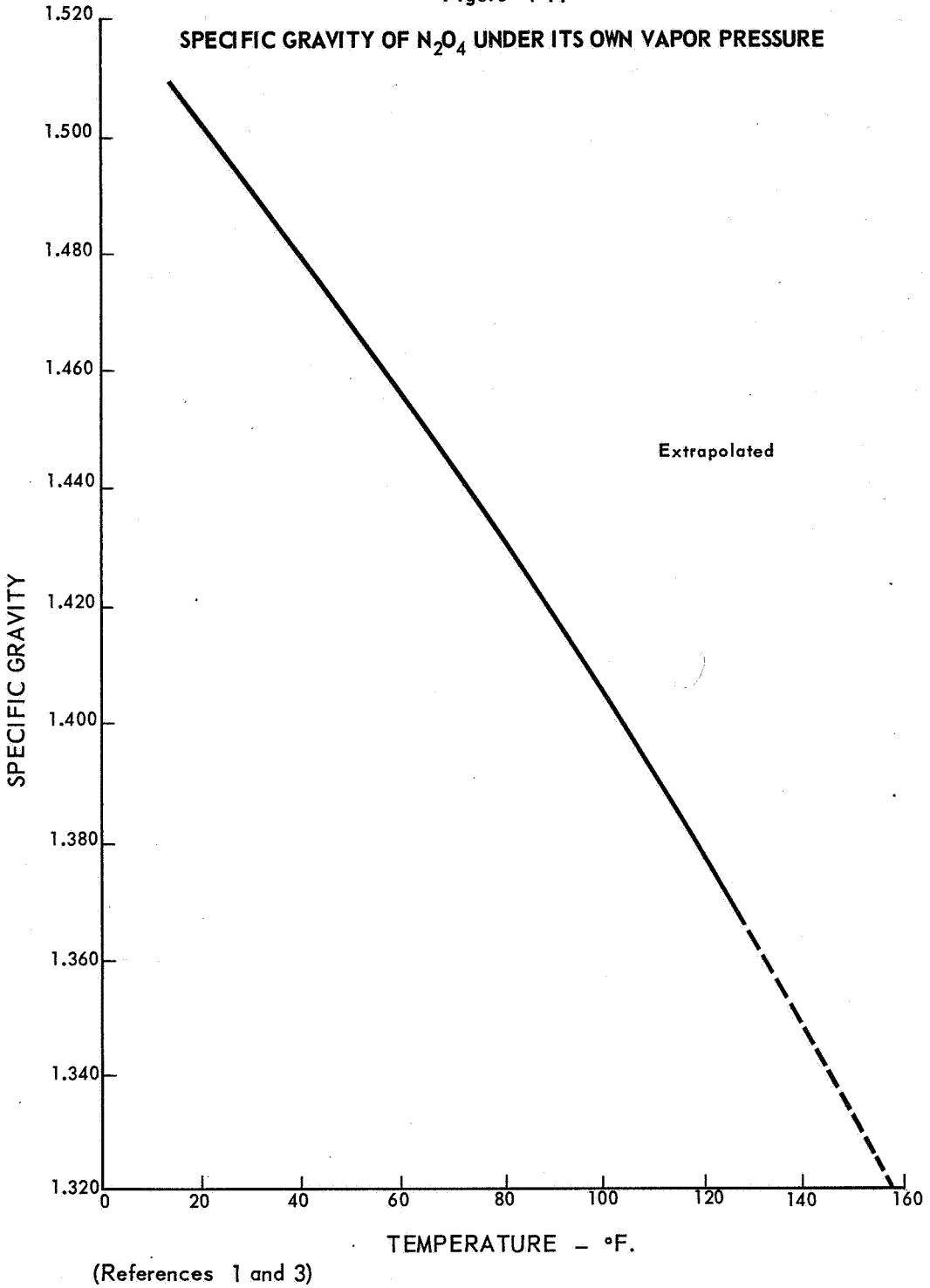
DENSITY OF N_2O_4 UNDER ITS OWN VAPOR PRESSURE



(References 1 and 3)

Figure 4-11

SPECIFIC GRAVITY OF N_2O_4 UNDER ITS OWN VAPOR PRESSURE



(References 1 and 3)

Figure 4-12

EFFECTS OF TEMPERATURE ON VISCOSITY IN THE LIQUID PHASE, N_2O_4

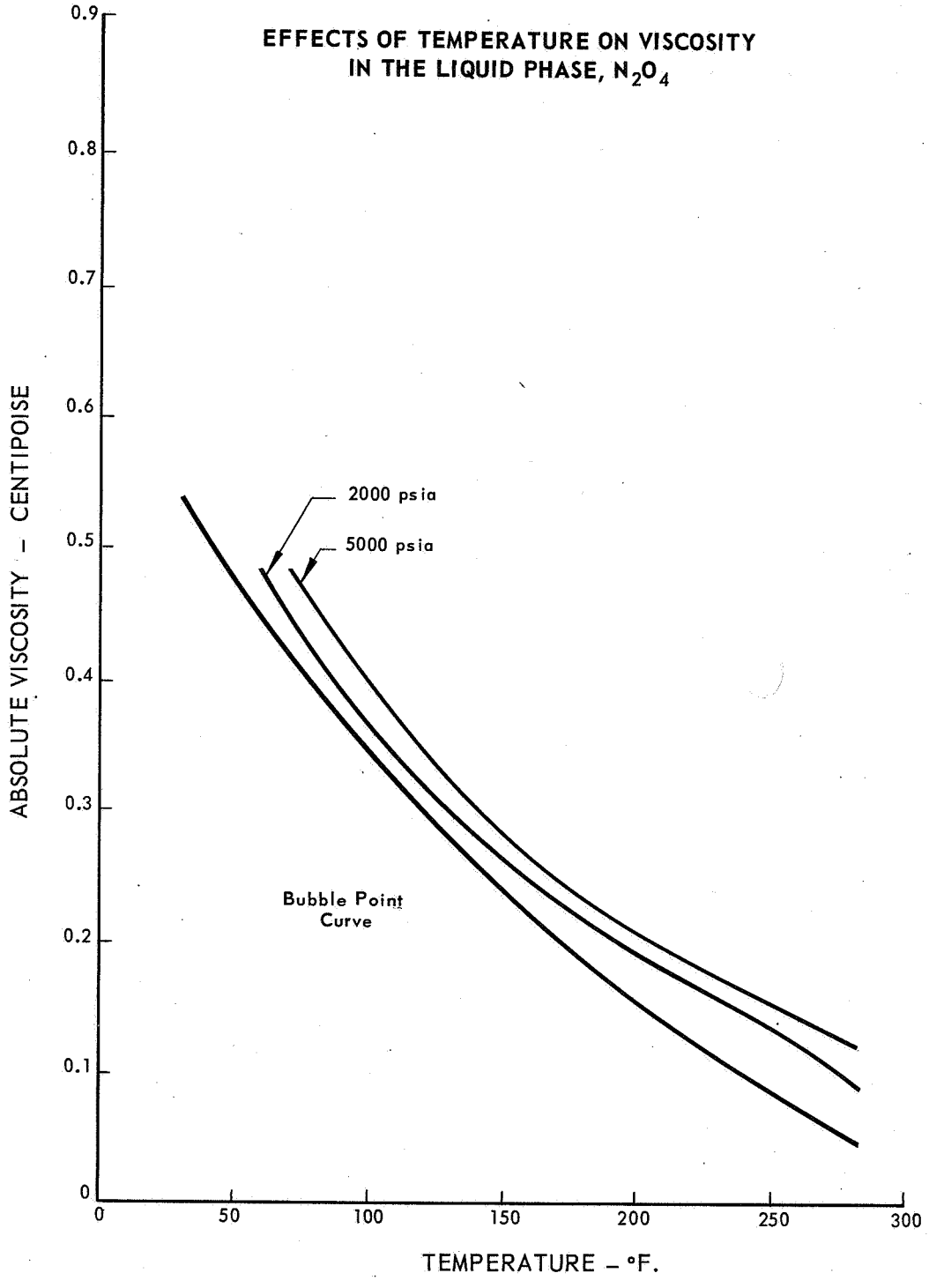
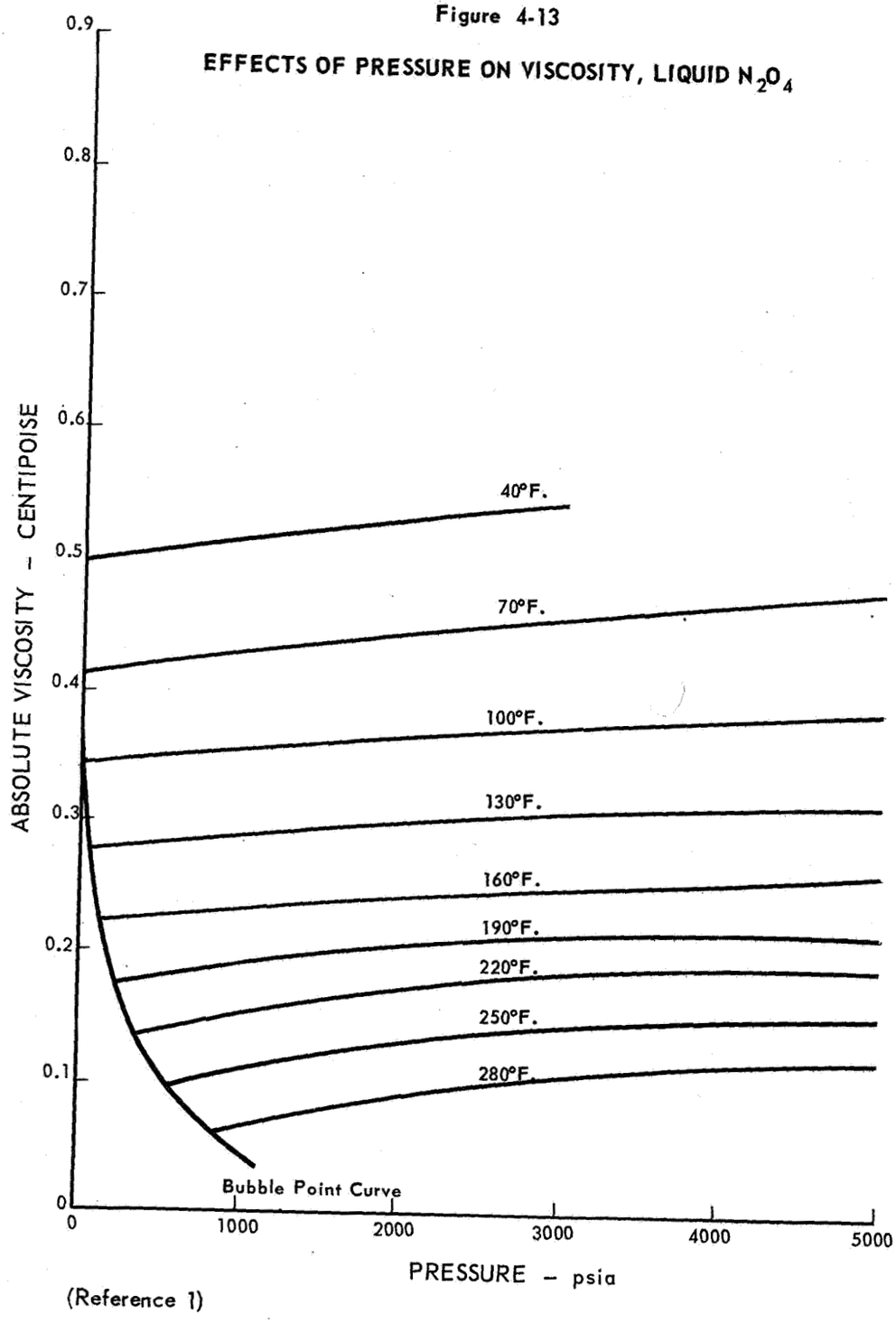


Figure 4-13

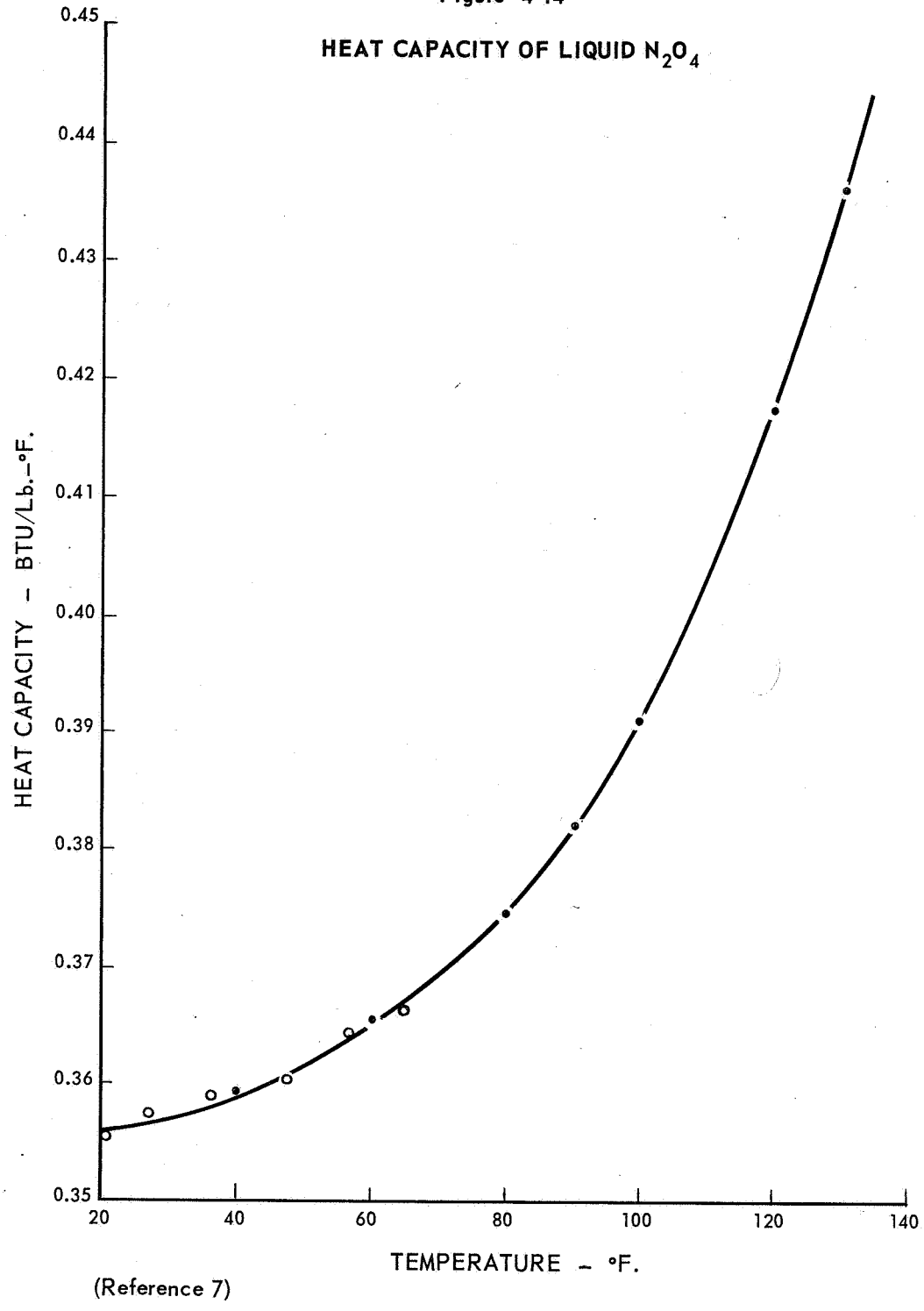
EFFECTS OF PRESSURE ON VISCOSITY, LIQUID N_2O_4



(Reference 1)

Figure 4-14

HEAT CAPACITY OF LIQUID N_2O_4



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K. Appendix

FINAL REPORT

Search of Technical Literature

TO: G. C. Mattson

FROM: Lewis F. Hatch

The following abstract journals were searched for the ten-year period 1955-1964: Chemical Abstracts, Zentralblatt. All of the pertinent abstracts found in the German abstract journal were also in Chemical Abstracts. The topics covered were hydrazine, unsymmetrical dimethyl-hydrazine and nitrogen tetroxide. The subheadings were physical properties and spectra, chemical properties, decomposition and decomposition products and analysis for the parent compounds and their decomposition products. Additional keywords were air pollution, atmospheric pollution, rockets, fuels and propellants.

The following government publications were not searched because they were not available and because they are abstracted by Chemical Abstracts: Governmentwide Index, International Aerospace Abstracts, Scientific and Technical Aerospace Reports, Technical Abstract Bulletin, U. S. Government Research Reports. The Rice University Library was searched for information which might have been absent from The University of Texas Library. None was found.

Xerox copies were made of about thirty (30) of the most interesting abstracts and of about ten (10) of the most interesting articles. These copies were sent to Jerry LaCoume to make the information available within the shortest possible time. We have brief abstracts of all the abstracts which are listed in this report. They can be made available if desired.

The literature gave no evidence of reaction between either hydrazine, UDMH, or nitrogen tetroxide and fluoro-compounds of the Freon® type.

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*Xerox copy of abstract sent to LaCoume

#Xerox copy of article sent to LaCoume

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UNSYMMETRICAL DIMETHYLHYDRAZINE (UDMH)

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HYDRAZINE-UDMH MIXTURES

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PHASE II

Summary

The object of Phase II was to evaluate the methods recommended in Phase I. Phase II work was carried out in a test unit consisting of pumps, solvent storage tanks, heat exchangers, a vent gas scrubber, a filter, adsorption and drying columns, a titanium test vessel, the necessary piping and control valves, and instrumentation. The titanium test vessel is cylindrical, with hemispherical heads, and is approximately 1/20th the size of an Apollo service module propellant tank.

Twelve tests were made in which the system was first contaminated with Aerozine-50, then cleaned by liquid flushing or by vapor-phase flushing. Cleaning solvents used were methanol and normal propanol.

Ten tests were made in which the system was first contaminated with N_2O_4, then cleaned by liquid flushing or by vapor-phase flushing. Cleaning solvents used were Freon® MF and Freon® TF.

One test was made in which the pressure was cycled from 45 to 5 psig two times during a vapor-phase cleaning test using Freon® MF.

Economic analyses were made which compared the cost of liquid flushing (present method) with vapor-phase flushing (proposed method).

Conclusions

1. Vapor-phase flushing is superior to liquid flushing. Its advantages are:

   a. Vapor-phase flushing is more effective.

   b. Vapor-phase flushing requires less time by a factor of five.

   c. The solvent required is reduced by a factor of at least two, maybe five.

   d. The volume of purge gas is reduced by a factor of five.

   e. The associated equipment to decontaminate the service module of the Apollo would not be complex if the vapor-phase flushing was accepted.

2. Pulsating-pressure cycles, while vapor-phase cleaning, was found to be an improvement over constant-pressure vapor-phase cleaning.

3. The estimates show that the cost of cleaning by the "Single-Flush" (present method) is approximately $11,600 per day compared with $610 per day for "Vapor-Phase Cleaning" (proposed method).

XI. TEST UNIT

The work in this phase was performed in a test unit which consisted of a test vessel, pumps, solvent storage tanks, heat exchangers, a vent gas scrubber, a filter, adsorption and drying columns, the necessary piping, control valves, and instruments. The titanium test vessel is cylindrical with hemispherical heads and is about 1/20th the size of an Apollo service module propellant tank.

Figure 5-1 is a block diagram of the integrated unit. The components shown are described in Table 5-I. The instruments are described in Table 5-II. Figure 5-2 is a perspective drawing of the test unit. A scale drawing, showing specifications of the test vessel is given in Figure 5-3. This vessel was fabricated from titanium metal and is about 1/20th the size of the tanks in the Apollo service module. Figure 5-4 is a diagram of the exit gas sampling station.

Figures 5-5 through 5-7 are photographs of the unit. The structural framing consists of two racks spaced about four feet apart on which the tanks, heat exchangers, and piping are mounted. The two pumps are mounted in the catwalk between the two support structures. The components are identified in the figures by letters and numbers which correspond to the symbols in Tables 5-I and 5-II.

XII. PROCEDURE

Initial tests were made to simulate the procedure used at Cape Kennedy so as to establish a bench mark for comparison with subsequent tests. A brief description of the procedure used at Cape Kennedy is given. A solvent (methanol for the fuel side, or Freon® MF for the oxidizer side) is pumped to the contaminated system. The solvent is allowed to remain in the tank for a short period of time; then it is pumped out. The system is then dried with heated GN_2. Near the end of the drying cycle, samples of the exit gas are analyzed for contaminant using Teledyne Systems Company's toxic vapor detector. The contaminant concentration in the exit gas should not exceed 5 ppm to meet the specifications set by the Safety Department at the Cape. A Safety Department engineer carries out the test. It is assumed that, if the contaminant concentration exceeds this limit, the cleaning procedure will be repeated or the drying cycle will be continued. The rate of the GN_2 purge at the time the exit gas was sampled was not defined. Therefore, if the GN_2 rate was high, the 5 ppm specification would not be difficult to meet.

About a month before actual test runs on Phase II work were started, a number of specimens of the elastomers were weighed and soaked in Aerozine-50 or N_2O_4, depending on the nature of the elastomer. We expected that the elastomers in the service module of the Apollo would have contacted the propellant for at least this period of time. The specimens were again weighed just prior to insertion in the test vessel and then following the test run. The test vessel was unflanged for installation of the test specimens. These were secured by tying them with a chromel wire to the riser inside the vessel. After placing the specimens and securing the flange, approximately ten gallons of the propellant were charged into the test vessel where it remained overnight. Then it was transferred back to the receiving container. It was found more convenient to use the receiving container than to use the propellant storage tank originally provided. After the propellant was transferred, the test vessel was purged for about five minutes with GN_2. Then, approximately eighteen gallons of the solvent under test were pumped to the test vessel. The solvent was allowed to remain in the test vessel one hour. It was then transferred to the contaminated solvent storage tank. A composite sample of the solvent was analyzed for contaminant content. The drying cycle started five minutes after the solvent was emptied out of the test vessel. The GN_2 rate was set at 2.68 cubic feet per minute. This was one test vessel volume per minute. The nitrogen comes out of the heat exchanger at about 135° C, but temperature falls to about ambient by the time it enters the test vessel.

In vapor-phase decontamination tests, the solvent was vaporized in the heat exchanger and pressure was maintained in the test chamber by means of a pressure controller. Only about eight gallons of solvent were used in vapor-phase decontamination. This is less than one-half than used in the ambient liquid flush procedure. The solvent was pumped to the heat exchanger at a rate ranging from one-third to one-half gallon per minute. The pressure of the test vessel was set at 10 psig in the Aerozine-50 decontamination runs and at 45 psig in the N_2O_4 decontamination tests. At these pressures, the boiling point of methanol was increased from 64 to 82° C and the boiling point of Freon® 11 was increased from 24 to 64° C. The temperature controller was set at 100° C but the exit vapors from the exchanger never reached this temperature. Only a slight amount of superheating was observed. The temperature of the vessel, as measured by a thermocouple in the exit line,

quickly reached the boiling temperature of the solvent due to the latent heat of vaporization. Heated GN_2, having no similar phase change is not able to heat the test vessel. After completing the vapor-phase cleaning, the drying cycle starts. The GN_2 rate was set at one tank volume per minute which was the same as the test made at ambient conditions.

The exit gas in both decontamination methods was monitored for contaminant concentration and dew point. The toxic vapor detector was intended to monitor the exit gas for contaminant. It seemed to work satisfactorily for the first few runs, but the results were obviously incorrect after use in about six runs. Consequently, provisions were made to take off a sample stream from the exit gas. This was passed through water scrubbers to remove the contaminants by means of two spargers which were used alternately. This permitted the exit gas to be monitored continuously. The volume of gas to the spargers was also measured, and the sample time was noted. The amount of contaminant absorbed by the water was determined by wet analysis. The contaminant in the exit gas stream was then calculated and reported as ppm. The relative dryness of the exit gas stream was determined by dew point using an instrument made by Alnor Company. This instrument gave consistent and dependable results.

Job procedures were detailed for major operations routinely performed. These procedures include contamination of the test vessel with Aerozine-50 and N_2O_4, liquid and vapor-phase flushing with solvents, drying the system with GN_2 purge, and sampling of the exit gas stream.

The instructions for the valve setting for specific operation, including the order of changing, are given. The valves and locations are listed in Table 5-III.

Operation Number	Purpose and Procedure
1	Leak Testing of Test Vessel D-6 Open Valves E_1-30, E_1-31, D_6-34, D_6-36, SPL-6, SPL-7, and N-23. All other valves are either closed or out of the affected circuit. Finally, open FC-1 and read PR-1. When pressure reaches desired test value (usually 40 psig), close FC-1 and N-23. The pressure in D-6 will remain constant if there are no leaks in the system. If the pressure falls, make tests for leaks, eliminate same, and repeat the pressure test.
2	Preparation of D-6 for Filling With Aerozine-50 Open Valves E_2-54, E_2-52, E_2-51, E_2-50, and D_3-47. Now, carefully open D_6-37 slightly to bleed pressure from D-6 through scrubber. When pressure is reduced to match the hydrostatic head in the scrubber, transfer of Aerozine-50 from its drum is feasible.

Operation Number	Purpose and Procedure
3	Transfer of Aerozine-50 from Its Storage Drum (Mounted and Balanced on Platform Scales) to D-6

a. Connect H-9 hose to fitting above Valve A-62 and to fitting on nitrogen cylinder regulator.

b. With A-62 closed, set regulator output pressure at 5 psig.

c. Close Valve D_6-34. Other valves remaining open are D_6-36, D_6-37, D_3-47, E_2-50, E_2-51, E_2-52, and E_2-54.

d. Open Valves SPL-8, A-60, A-61, and A-62.

e. Aerozine-50 should now transfer into D-6. The progress of the transfer should be followed by keeping the scales approximately balanced.

f. When the gross weight has fallen by eighty pounds, stop the transfer (Operation No. 4).

4 Stop Transfer of Aerozine-50 to D-6

Close Valves A-60, A-61, SPL-8, A-62, and D_6-36 in order. Other valves remaining open are D_3-47, E_2-50, E_2-51, E_2-52, and E_2-54.

5 Transfer of Aerozine-50 from D-6 to Aerozine-50 Supply Drum

a. Disconnect H-9 hose from nitrogen cylinder and connect to fitting above D_6-41 to permit drum to vent through scrubber.

b. Open Valves E_1-30, E_1-31, D_6-34, D_6-36, SPL-8, A-60, A-61, A-62, D_6-41, D_3-47, E_2-50, E_2-51, E_2-52, E_2-54, and N-23. Opening of the above valves should be performed in the order given.

c. Set FC-1 at scale reading of 10% until transfer is complete. When the transfer is complete, the Aerozine-50 drum should weigh about one pound less than before transfer to D-6. Also, nitrogen gas coming out of D-6 can be heard bubbling inside of the Aerozine-50 drum. Upon completion of transfer, allow transfer line to purge for thirty seconds, then proceed with Operation 6.

6 Stop Transfer of Aerozine-50 to Supply Drum

Close Valves SPL-8, A-60, A-61, A-62 and D_6-41. Other valves remaining open are N-23, E_1-30, E_1-31, D_6-34, D_6-36, D_3-47, E_2-50, E_2-51, E_2-52, and E_2-54.

NOTE: Operation No. 7 should follow immediately upon completion of Operation No. 6.

Operation Number	Purpose and Procedure
7	Clearing Residual Aerozine-50 from Process Lines, Step 1 Open Valve D_6-38 and purge for thirty seconds through D_3-47, E_2-50, E_2-51, E_2-52, and E_2-54 to scrubber.
8	Clearing Residual Aerozine-50 from Process Lines, Step 2 a. Open Valve E_3-35. b. Close Valve D_6-36. Other valves remaining open are: D_2-19, N-23, E_1-30, E_1-31, D_6-34, E_1-35, D_6-38, D_3-47, E_2-50, E_2-51, E_2-53, and E_2-54. NOTE: Purge in this manner for thirty seconds, then proceed with Operation 9.
9	Clearing Residual Aerozine-50 from Process Lines, Step 3 a. Close Valve E_1-35, D_6-38. b. Open Valve D_6-37. Other valves remaining open are: D_2-19, E_1-30, E_1-31, D_6-34, D_6-37, D_3-47, E_2-50, E_2-51, E_2-52, E_2-53, and E_2-54. Purge in this manner for two minutes. NOTE: Operation 10 should follow immediately upon completion of two minute purge in Operation 9.
10	Shut Off GN_2 Purge Close N-23, D_2-21, FC-1, and E_2-53. Other valves remaining open are: D_2-19, E_1-30, E_1-31, D_6-34, D_6-37, D_3-47, E_2-50, E_2-51, E_2-52, and E_2-54.
11	Preparation for Liquid Solvent Flush a. Open Valve D_2-21. b. Check to be sure Valve E_1-32 is closed. Other valves remaining open are: D_2-19, E_1-30, E_1-31, E_1-35, D_6-36, D_6-37, D_6-40, D_3-47, E_2-50, E_2-51, E_2-52, and E_2-54. c. Start Pump P-2 and set FC-1 on scale reading to get desired rate of flow. (See curve on panel.) d. Operate for a timed period to get required quantity of solvent into D-6. NOTE: Usual Operation: Scale Reading = 4 for 1.5 gpm. Time = 12 minutes for 18 gallons.

Operation Number	Purpose and Procedure
12	Preparation for Vapor-Phase Solvent Flush

a. Open Valves D_1-1, E_2-55, D_6-38, W-48, and E_2-49.

b. Close Valves E_1-35, D_6-37, and E_2-54. Other valves remaining open are: D_2-19, D_2-21, E_1-30, E_1-31, D_6-34, D_6-36, D_3-47, E_2-50, E_2-51, and E_2-52.

c. Set TRC-1 at desired temperature.

d. Set FRC-1 at desired flow.

e. Start Pump P-2.

f. Operate for timed interval to get desired vapor volume throughput.

NOTE: Usual operation is:
FRC-1 scale reading of 1.25 = 0.5 gpm.
TRC-1 at temp. 10^{o} -15^{o} above bp of solvent.
Time: 16 minutes for eight gallons liquid feed.

g. When sufficient liquid has been pumped, shut down the pump.

13 Preparation of D-6 for Solvent Soak (Follows Operation 11)

Close Valves D_1-1, D_2-21, E_1-35, and D_6-36. Other valves remaining open are: D_2-19, E_1-30, E_1-31, D_6-34, D_6-38, D_3-47, E_2-50, E_2-51, E_2-52, and E_2-55.

14 Preparation for Transfer of Liquid Solvent From D-6 to D-1 (Follows Operation 13)

a. Open Valves D_1-1, N-23, D_6-36. Other valves remaining open are: D_2-19, E_1-30, E_1-31, D_6-34, D_6-38, D_3-47, E_2-50, E_2-51, E_2-52, and E_2-55.

b. Prepare sample bottles and have near Sample Valve E_2-49.

c. Set FC-1 at 20% scale reading until transfer is complete. This will become evident when Sample Valve E_2-49 runs dry.

15 Clearing Process Lines of Solvent, Step 1

a. Set TRC-1 instrument to control at 140^{o} C.

b. Open Valve E_2-54.

Operation Number	Purpose and Procedure
15 (Cont'd)	c. Close Valves D_1-1, D_6-37, and E_2-55. Other valves remaining open are: D_2-19, N-23, E_1-30, E_1-31, D_6-34, D_6-36, D_6-38, D_3-47, E_2-50, E_2-51, E_2-52, and E_2-54.
	d. Adjust FC-1 to continue 20% scale reading.
	e. Purge in this manner for two minutes.
16	Clearing Process Lines of Solvent, Step 2
	a. Open Valve E_1-35.
	b. Close Valve D_6-36. Other valves remaining open are: D_2-19, N-23, E_1-30, E_1-31, D_6-34, D_6-38, D_3-47, E_2-50, E_2-51, E_2-52, and E_2-54.
	c. TRC-1 control instrument should continue to operate at 140° C.
	d. Change FC-1 to 50% scale reading.
	e. Purge in this manner for sixty seconds.
17	Clearing Process Lines of Solvent, Step 3
	a. Open Valve D_6-37.
	b. Close Valves D_6-38 and E_1-35. Other valves remaining open are: D_2-19, N-23, E_1-30, E_1-31, D_6-34, D_3-47, E_2-50, E_2-51, E_2-52, and E_2-54.
	c. TRC-1 control instrument should continue at 140° C.
	d. FC-1 should continue at 60% scale reading.
	e. Purge in this manner for two minutes.
18	Heated GN_2 Purging
	a. Set TRC-1 instrument to continue control at 140° C.
	b. Open Valve D_6-36.
	c. Close Valve D_6-37. Other valves remaining open are: D_2-19, N-23, E_1-30, E_1-31, D_6-34, D_3-47, E_2-50, E_2-51, E_2-52, and E_2-54.
	d. Purge in this manner until contaminant in exit gas from D-6 is at desired level.

Operation Number	Purpose and Procedure
19	Clearing Sample Lines of Liquid in Preparation for Monitoring a. Set regulator on nitrogen cylinder at five or six pounds above pressure in D-6 vessel. b. Purge with cylinder nitrogen through SPL-1, SPL-2, SPL-5, SPL-6, SPL-7, and D_6-40 for fifteen minutes. Other valves remaining open are: D_2-19, N-23, E_1-30, E_1-31, D_6-34, D_3-47, E_2-50, E_2-51, E_2-52, and E_2-54.
20	Sampling Exit Gas Stream From D-6 a. Close Valve SPL-1. b. Sample exit gas from D-6 via Valves SPL-2, SPL-5, SPL-6, and SPL-7 at the instrument and sparger outlet valves SPL-11, SPL-4, and SPL-3.
21	Preparation of D-6 for Filling with N_2O_4 Open Valves E_2-54, E_2-52, E_2-51, E_2-50, and D_3-47. Now, carefully open D_6-37 slightly to bleed pressure from D-6 through scrubber. When pressure is reduced to match the hydrostatic head in the scrubber, transfer N_2O_4 from cylinder. (Operation 22)
22	Transfer of N_2O_4 From Storage Cylinder to D-6* a. Close Valve D_6-34. Other valves remaining open are D_6-36, D_6-37, D_3-47, E_2-50, E_2-51, E_2-52, and E_2-54. b. Set PC-5 at 5 psig (to prevent N_2O_4 dissociation). c. Open Valves SPL-8, N_2O_4-66, N_2O_4-68, and N_2O_4-69. N_2O_4 should now transfer into D-6. The progress of the transfer should be followed by keeping the scales approximately balanced. d. When the gross weight has fallen by twenty pounds, stop the transfer (Operation No. 23).
23	Stop Transfer of N_2O_4 to D-6 Close Valves SPL-8, N_2O_4-66, N_2O_4-68, N_2O_4-69, and D_6-36 in order. Other valves remaining open are D_3-47, E_2-50, E_2-51, E_2-52, and E_2-54.

*Mounted and balanced on platform scales.

Operation Number	Purpose and Procedure
24	Transfer of N_2O_4 from D-6 to N_2O_4 Supply Cylinder* a. Open Valves E_1-30, E_1-31, D_6-34, D_6-36, SPL-8 N_2O_4-66, N_2O_4-68, N_2O_4-69, D_6-41, D_3-47, E_2-50, E_2-51, E_2-52, E_2-54, and N-23 in order. b. Set FC-1 at scale reading of 20% and let pressure come up into D-6 until it reaches forty pounds. Close W-23. When the transfer is complete, the cylinder should weigh about one pound less than before transfer to D-6. Upon completion of transfer, allow transfer line to purge for thirty seconds, then proceed with Operation 25.
25	Stop Transfer of N_2O_4 to Supply Cylinder* Close Valves SPL-8, N_2O_4-66, N_2O_4-68, N_2O_4-69, and D_6-41. Other valves remaining open are D_1-30, E_1-31, D_6-36, D_3-47, E_2-50, E_2-51, E_2-52, and E_2-54. Vent excess pressure in D-6 through PC-5 slowly.
26	Preparation for Liquid Solvent Flush a. Open Valves D_2-21 and T_2-71. b. Check to be sure Valve E_1-32 is closed. Other valves remaining open are: D_2-19, E_1-30, E_1-31, E_1-35, D_6-36, D_6-37, D_6-40, D_3-47, E_2-50, E_2-51, E_2-52, and E_2-54. c. Set GN_2 regulator on nitrogen cylinder for desired pressure on solvent storage in T-2. d. Open T_2-70 to regulate flow of solvent at desired rate and operate for a timed period to get required quantity of solvent into D-6. NOTE: To obtain smooth flow, the solvent was pressured into D-6 and the rate of flow was measured by a Fischer-Porter No. 5 Rotometer. Usual Operation: Scale Reading = 44% for 1.5 gpm. Time = 12 minutes for 18 gallons
27	Preparation for Vapor-Phase Solvent Flush a. Open Valves D_1-1, D_2-55, D_6-38, W-48, and E_2-49. b. Close Valves E_1-35, D_6-37, and $E_2$54. Other valves remaining open are: T_2-71, E_1-30, E_1-31, D_6-34, D_6-36, D_3-47, E_2-50, E_2-51, and E_2-52.

*Mounted and balanced on platform scales.

Operation Number	Purpose and Procedure
27 (Cont'd)	c. Set TRC-1 at desired temperature.
	d. Adjust T_2-70 for desired flow. Operate for timed interval to get desired vapor volume throughput.
	NOTE: Usual operation is: FRC-1 scale reading of 15% = 0.5 gpm. TRC-1 at temp. 10^{o} -15^{o} above bp of solvent. Time: 16 minutes for 8 gallons liquid feed.
	e. When sufficient liquid has been transferred, close T_2-70.
28	Preparation of D-6 for Solvent Soak (Follows Operation 26) Close Valves D_1-1, D_2-21, E_1-35, and D_6-36. Other valves remaining open are D_2-19, E_1-30, E_1-31, D_6-34, D_6-38, D_3-47, E_2-50, E_2-51, E_2-52, and E_2-55.

The above operations are the most important being performed routinely. The procedures given were developed to insure safety of operation and to improve reproducibility of test results.

XIII. DATA

The data from all test runs are given. These data were transferred from original laboratory "Data Books." All tests are included, no exceptions. Interpretation of the significant data follows in the next section.

PHASE II TEST UNIT OPERATION

Run No. 1 Aborted

Purpose: To Decontaminate the System Containing Aerozine-50

Method: 3 Liquid Methanol Flushes

Temperature in Test Vessel	-	Ambient	°C
Pressure in Test Vessel	-	Ambient	psig
Volume of Solvent Used	-	18	gals
Transfer Rate	-	1.5	gpm
Retention Time	-	1	hours

(Data Not Tabulated)

GN_2 DRYING DATA

Time From Start Min	GN_2 Rate		Temperatures: °C		Dew Point Exit Test Vessel °F	Test Vessel Exit Gas A-50 Content PPM		Pressure In Test Vessel PSIG
	Test Vessel Volumes Per Min	Cubic Feet GN_2 Cuml.	Exit Heat Exchanger (E-1)	Exit Test Vessel D-6		Olfactron	By Titration	

Contaminant Removed From Elastomers = %

Remarks: Run was discontinued because residual CCl_4 was present in system from previous cleaning operations.

PHASE II TEST UNIT OPERATION

Run No. 2

Purpose: To Decontaminate the System Containing Aerozine-50

Method: Liquid Methanol Flush

Temperature in Test Vessel	-	Ambient	°C
Pressure in Test Vessel	-		psig
Volume of Solvent Used	-	18	gals
Transfer Rate	-	1.5	gpm
Retention Time	-	1	hours

GN_2 DRYING DATA

Time From Start Min	GN_2 Rate		Temperatures: °C		Dew Point Exit Test Vessel °F	Test Vessel Exit Gas A-50 Content PPM		Pressure In Test Vessel PSIG
	Test Vessel Volumes Per Min	Cubic Feet GN_2 Cuml.	Exit Heat Exchanger (E-1)	Exit Test Vessel D-6		Olfactron	By Titration	
75	1	200	138	15	25	>50	--	2
105	1	280	137	15	-4	>50	--	2
120	1	320	136	16	--	45	--	2
135	1	360	136	17	-18	--	--	2
150	1	400	137	18	--	20	--	2
165	1	440	136	18	-25	--	--	2
180	1	480	135	18	-43	18	--	2
210	1	560	135	18	-46	11	--	2

Contaminant Removed From Elastomers = 66%

Remarks: The methanol used in this test was passed through Dowex-50 resin, thereby picking up (H^+) that made it impossible to calculate the Aerozine-50 content in the methanol.

PHASE II TEST UNIT OPERATION

Run No. 3

Purpose: To Decontaminate the System Containing Aerozine-50

Method: 2 Liquid Methanol Flushes

Temperature in Test Vessel	-	Ambient	°C
Pressure in Test Vessel	-		psig
Volume of Solvent Used	-	18	gals
Transfer Rate	-	1.5	gpm
Retention Time	-	1	hours

GN_2 DRYING DATA

Time From Start Min	GN_2 Rate		Temperatures: °C		Dew Point Exit Test Vessel °F	Test Vessel Exit Gas A-50 Content PPM		Pressure In Test Vessel PSIG
	Test Vessel Volumes Per Min	Cubic Feet GN_2 Cuml.	Exit Heat Exchanger (E-1)	Exit Test Vessel D-6		Olfactron	By Titration	
60	1	160	136		38	>50	--	2
90	1	240	136		19	>50	--	2
120	1	370	136		6	>50	--	2
150	1	400	136		-3	>50	--	2
180	1	480	136		-27	>50	--	2
210	1	560	136		-31	>50	--	2
240	1	640	136		-34	44	--	2
270	1	720	136		-38	>50	--	2
285	1	760	136		-39	35	--	2
300	1	800	136		-58	25	--	2
	OVERNIGHT SIT UNDER 28 PSIG							
45	1	120	134		-81	12.5	--	2
105	1	280	134		-143	10.0	--	2

Contaminant Removed From Elastomers = 57 %

Remarks: The drying time seemed to be excessive.

PHASE II TEST UNIT OPERATION

Run No. 4

Purpose: To Decontaminate the System Containing Aerozine-50

Method: Vapor Methanol Flush

Temperature in Test Vessel	-	78	°C
Pressure in Test Vessel	-	12	psig
Volume of Solvent Used	-	8	gals
Transfer Rate	-	0.5	gpm
Retention Time	-	0	hours

GN_2 DRYING DATA

Time From Start Min	GN_2 Rate		Temperatures: °C		Dew Point Exit Test Vessel °F	Test Vessel Exit Gas A-50 Content PPM		Pressure In Test Vessel PSIG
	Test Vessel Volumes Per Min	Cubic Feet GN_2 Cuml.	Exit Heat Exchanger (E-1)	Exit Test Vessel D-6		Olfactron	By Titration	
19	1	51	134	64	-6	28	--	2
29	1	77	134	40	-20	17	--	2
44	1	117	132	26	-30	10	--	2
59	1	157	132	24	-34	8	--	2
74	1	197	128	22	-38	5.5	--	2
89	1	237	126	21	-38	5.0	--	2
104	1	277	122	20	-38	5.0	--	2
119	1	317	138		-53	<5.0	--	2

Contaminant Removed From Elastomers = 63 %

Remarks: Very good compared to the liquid flush test.

PHASE II TEST UNIT OPERATION

Run No. 5

Purpose: To Decontaminate the System Containing Aerozine-50

Method: Liquid Methanol Flush

Temperature in Test Vessel	-	Ambient °C
Pressure in Test Vessel	-	psig
Volume of Solvent Used	-	18 gals
Transfer Rate	-	1.5 gpm
Retention Time	-	1 hours

GN_2 DRYING DATA

Time From Start Min	GN_2 Rate		Temperatures: °C		Dew Point Exit Test Vessel °F	Test Vessel Exit Gas A-50 Content PPM		Pressure In Test Vessel PSIG
	Test Vessel Volumes Per Min	Cubic Feet GN_2 Cuml.	Exit Heat Exchanger (E-1)	Exit Test Vessel D-6		Olfactron	By Titration	
15	1	40	133	15	3	>50	--	2
40	1	107	137	15	-10	>50	--	2
70	1	187	138	16	-7	>50	--	2
90	1	240	137	18	-15	>50	--	2
135	1	360	132	19	-22	>50	--	2
165	1	440	135	20	-24	>50	--	2
180	1	480	135	20	-18	>50	--	2
240	1	640	135	20	-17	>50	--	2
300	1	800	136	20	-17	>50	--	2
360	1	960	135	20	-26	>50	--	2
420	1	1120	135	20	-37	>50	--	2
450	1	1200	134	20	-48	12	--	2
510	1	1360	134	20	-96	1	--	2

Contaminant Removed From Elastomers = 55 %

Remarks:

PHASE II TEST UNIT OPERATION

Run No. 6

Purpose: To Decontaminate the System Containing Aerozine-50

Method: Vapor Methanol Flush

Temperature in Test Vessel	-	78	°C
Pressure in Test Vessel	-	17	psig
Volume of Solvent Used	-	8	gals
Transfer Rate	-	0.5	gpm
Retention Time	-	0	hours

GN_2 DRYING DATA

Time From Start Min	GN_2 Rate		Temperatures: °C		Dew Point Exit Test Vessel °F	Test Vessel Exit Gas A-50 Content PPM		Pressure In Test Vessel PSIG
	Test Vessel Volumes Per Min	Cubic Feet GN_2 Cuml.	Exit Heat Exchanger (E-1)	Exit Test Vessel D-6		Olfactron	By Titration	
10	1	27	134	43			--	2
15	1	40	138	36	70		--	2
20	1	53	138	34		38	--	2
23	1	61	136	31	24	14	--	2
26	1	69	136	30	17	10	--	2
33	1	88	135	28		8	--	2
45	1	120	--	--	8	8	--	2
48	1	128	134	24	7	7.5	--	2
61	1	163	134	22	-6	0	--	2
71	1	189	134	21	-6.5	0	--	2
93	1	248	135	20	-7	0	--	2

Contaminant Removed From Elastomers = 69 %

Remarks:

PHASE II TEST UNIT OPERATION

Run No. 7 Aborted

Purpose: To Decontaminate the System Containing Aerozine-50

Method: Liquid Methanol Flush

Temperature in Test Vessel	-	Ambient	°C
Pressure in Test Vessel	-		psig
Volume of Solvent Used	-	18	gals
Transfer Rate	-	1.5	gpm
Retention Time	-	1	hours

(Data Not Recorded)

GN_2 DRYING DATA

Time From Start Min	GN_2 Rate		Temperatures: °C		Dew Point Exit Test Vessel °F	Test Vessel Exit Gas A-50 Content PPM		Pressure In Test Vessel PSIG
	Test Vessel Volumes Per Min	Cubic Feet GN_2 Cuml.	Exit Heat Exchanger (E-1)	Exit Test Vessel D-6		Olfactron	By Titration	

Contaminant Removed From Elastomers = %

Remarks: Run was discontinued because sample lines were fouled with liquid methanol. Instrument readings, therefore, were not reliable.

PHASE II TEST UNIT OPERATION

Run No. 8 Aborted

Purpose: To Decontaminate the System Containing Aerozine-50

Method: Liquid Methanol Flush

Temperature in Test Vessel	-	Ambient	°C
Pressure in Test Vessel	-		psig
Volume of Solvent Used	-	18	gals
Transfer Rate	-	1.5	gpm
Retention Time	-	1	hours

(Data Not Recorded)

GN_2 DRYING DATA

Time From Start Min	GN_2 Rate		Temperatures: °C		Dew Point Exit Test Vessel °F	Test Vessel Exit Gas A-50 Content PPM		Pressure In Test Vessel PSIG
	Test Vessel Volumes Per Min	Cubic Feet GN_2 Cuml.	Exit Heat Exchanger (E-1)	Exit Test Vessel D-6		Olfactron	By Titration	

Contaminant Removed From Elastomers = %

Remarks: Liquid Methanol was inadvertently admitted to instrument lines. Instruments had to be cleaned and dried. Run was scrubbed because of instrument errors resulting.

PHASE II TEST UNIT OPERATION

Run No. 9

Purpose: To Decontaminate the System Containing Aerozine-50

Method: Liquid Methanol Flush

Temperature in Test Vessel	-	Ambient	°C
Pressure in Test Vessel	-		psig
Volume of Solvent Used	-	18	gals
Transfer Rate	-	1.5	gpm
Retention Time	-	1	hours

GN_2 DRYING DATA

Time From Start Min	GN_2 Rate		Temperatures: °C		Dew Point Exit Test Vessel °F	Test Vessel Exit Gas A-50 Content PPM		Pressure In Test Vessel PSIG
	Test Vessel Volumes Per Min	Cubic Feet GN_2 Cuml.	Exit Heat Exchanger (E-1)	Exit Test Vessel D-6		Olfactron	By Titration	
10	1	27	128	15	41			2
30	1	80	130	14	41		500	2
45	1	120	129	14	38		552	2
60	1	160	133	14	32		462	2
75	1	200	134	15	17		357	2
90	1	240	128	14	3		46	2
120	1	320	133	15	-2		77	2
165	1	440	128	17	-10		92	2
225	1	600	126	18	-2		14	2
285	1	760	130	17	-15		9	2
400	1	1066	128	20				2
	SHUT	OFF 30 MIN.	PRESSURED	TO 10 PSIG				
430	1		130	12	-25		132	2

Contaminant Removed From Elastomers = 38 %

Remarks:

PHASE II TEST UNIT OPERATION

Run No. 10

Purpose: To Decontaminate the System Containing Aerozine-50

Method: Liquid N-Propyl Alcohol

Temperature in Test Vessel	-	Ambient	°C
Pressure in Test Vessel	-		psig
Volume of Solvent Used	-	18	gals
Transfer Rate	-	1.5	gpm
Retention Time	-	1	hours

GN_2 DRYING DATA

Time From Start Min	GN_2 Rate		Temperatures: °C		Dew Point Exit Test Vessel °F	Test Vessel Exit Gas A-50 Content PPM		Pressure In Test Vessel PSIG
	Test Vessel Volumes Per Min	Cubic Feet GN_2 Cuml.	Exit Heat Exchanger (E-1)	Exit Test Vessel D-6		Olfactron	By Titration	
15	1	40	130	18		--		4
30	1	80	130	17	68	--	485	4
60	1	160	130	17	30	--	196	4
90	1	240	130	17	17	--	129	4
135	1	360	130	17	11	--	56	4
195	1	520	130	19	12	--	25	4
255	1	680	130	19	2	--	14	4
315	1	840	135	20	5	--	12	4
375	1	1000	135	20	7	--	26	4
435	1	1160	132	20	-1	--	17	4
495	1	1320	130	20	-1	--	8	4
555	1	1480	129	19	-3	--	<5	4
595	1	1587	125	19	-6	--	<5	4

Contaminant Removed From Elastomers = 51 %

Remarks: Time required to dry the system was excessive.

PHASE II TEST UNIT OPERATION

Run No. 11 Aborted

Purpose: To Decontaminate the System Containing Aerozine-50

Method: Vapor Methanol Flush

Temperature in Test Vessel	-	80 °C
Pressure in Test Vessel	-	14 psig
Volume of Solvent Used	-	8 gals
Transfer Rate	-	0.5 gpm
Retention Time	-	0 hours

(Data Not Recorded)

GN_2 DRYING DATA

Time From Start Min	GN_2 Rate		Temperatures: °C		Dew Point Exit Test Vessel °F	Test Vessel Exit Gas A-50 Content PPM		Pressure In Test Vessel PSIG
	Test Vessel Volumes Per Min	Cubic Feet GN_2 Cuml.	Exit Heat Exchanger (E-1)	Exit Test Vessel D-6		Olfactron	By Titration	

Contaminant Removed From Elastomers = %

Remarks: N-Propanol from previous test intervened.

PHASE II TEST UNIT OPERATION

Run No. 11A

Purpose: To Establish a Drying Curve for Methanol Vapor Phase Test

Method: Vapor Methanol Flush

Temperature in Test Vessel	-	76 °C
Pressure in Test Vessel	-	10 psig
Volume of Solvent Used	-	8 gals
Transfer Rate	-	0.5 gpm
Retention Time	-	0 hours

GN_2 DRYING DATA

Time From Start Min	GN_2 Rate		Temperatures: °C		Dew Point Exit Test Vessel °F	Test Vessel Exit Gas Content PPM		Pressure In Test Vessel PSIG
	Test Vessel Volumes Per Min	Cubic Feet GN_2 Cuml.	Exit Heat Exchanger (E-1)	Exit Test Vessel D-6		Olfactron	By Titration	
20	1	53	130	28	-15	--	--	10
30	1	80	132	24	-21	--	--	10
45	1	120	132	20	-27	--	--	10
51	1	136	126	17	-30	--	--	10
85	1	227	125	16	-33	--	--	10
100	1	267	125	16	-30	--	--	10
110	1	293	125	16	-33	--	--	10

Contaminant Removed From Elastomers = %

Remarks: No contaminants involved.

PHASE II TEST UNIT OPERATION

Run No. 11B

Purpose: To Determine a Drying Curve for Methanol After Liquid Flush

Method:

Temperature in Test Vessel - Ambient °C
Pressure in Test Vessel - psig
Volume of Solvent Used - 18 gals
Transfer Rate - 1.5 gpm
Retention Time - 0.25 hours

GN_2 DRYING DATA

Time From Start Min	GN_2 Rate		Temperatures: °C		Dew Point Exit Test Vessel °F	Test Vessel Exit Gas Content PPM		Pressure In Test Vessel PSIG
	Test Vessel Volumes Per Min	Cubic Feet GN_2 Cuml.	Exit Heat Exchanger (E-1)	Exit Test Vessel D-6		Olfactron	By Titration	
15	1	40	120	15	30	--	--	10
30	1	80	134	12	16	--	--	10
45	1	120	132	12	3	--	--	10
60	1	160	132	12	0	--	--	10
75	1	200	130	12	-4	--	--	10
90	1	240	130	12	-6	--	--	10
120	1	320	132	13	-9	--	--	10
150	1	400	130	14	-12	--	--	10
180	1	480	120	16	-13	--	--	10
210	1	560	128	17	-15	--	--	10
240	1	640	132	17	-15	--	--	10
270	1	720	130	17	-15	--	--	10
300	1	800	130	17	-16	--	--	10

Contaminant Removed From Elastomers = %

Remarks:

PHASE II TEST UNIT OPERATION

Run No. 12

Purpose: To Study Drying of the System After Vapor Phase Freon® TF Flush

Method: Vapor Phase Freon® TF Flush

Temperature in Test Vessel	-	64	°C
Pressure in Test Vessel	-	10	psig
Volume of Solvent Used	-	20	gals
Transfer Rate	-	0.5	gpm
Retention Time	-	0	hours

GN_2 DRYING DATA

Time From Start Min	GN_2 Rate		Temperatures: °C		Dew Point Exit Test Vessel °F	Test Vessel Exit Gas Content PPM		Pressure In Test Vessel PSIG
	Test Vessel Volumes Per Min	Cubic Feet GN_2 Cuml.	Exit Heat Exchanger (E-1)	Exit Test Vessel D-6		Olfactron	By Titration	
15	1	40	110	42	--			10
30	1	80	130	32	-23			10
45	1	120	130	27	-39			10
60	1	160	130	25	-39			10

Contaminant Removed From Elastomers = %

Remarks: No contaminants involved.

PHASE II TEST UNIT OPERATION

Run No. 13

Purpose: To Study Drying of the System Following Liquid Freon® TF Flush

Method: Liquid Freon® TF Flush

Temperature in Test Vessel - Ambient °C
Pressure in Test Vessel - 5 psig
Volume of Solvent Used - 14.5 gals
Transfer Rate - 1.5 gpm
Retention Time - 0.25 hours

GN_2 DRYING DATA

Time From Start Min	GN_2 Rate		Temperatures: °C		Dew Point Exit Test Vessel °F	Test Vessel Exit Gas Content PPM		Pressure In Test Vessel PSIG
	Test Vessel Volumes Per Min	Cubic Feet GN_2 Cuml.	Exit Heat Exchanger (E-1)	Exit Test Vessel D-6		Olfactron	By Titration	
15	1	40	136	15	-49			5
30	1	80	134	16	-45			5
45	1	120	138	17	-45			5
60	1	160	138	18	-31			5
75	1	200	138	18	-68			5

Contaminant Removed From Elastomers = %

Remarks: No contaminants involved.

PHASE II TEST UNIT OPERATION

Run No. 14

Purpose: To Decontaminate the System Containing N_2O_4

Method: Liquid Freon® TF Flush

Temperature in Test Vessel	-	Ambient	°C
Pressure in Test Vessel	-	4	psig
Volume of Solvent Used	-	18	gals
Transfer Rate	-	1.5	gpm
Retention Time	-	1	hours

GN_2 DRYING DATA

Time From Start Min	GN_2 Rate		Temperatures: °C		Dew Point Exit Test Vessel °F	Test Vessel Exit Gas N_2O_4 Content PPM		Pressure In Test Vessel PSIG
	Test Vessel Volumes Per Min	Cubic Feet GN_2 Cuml.	Exit Heat Exchanger (E-1)	Exit Test Vessel D-6		Olfactron	By Titration	
15	1	40	136	14	-41		--	4
30	1	80	138	15	-48		--	4
45	1	120	136	17	-51		--	4
60	1	160	136	19	-53		14	4
90	1	240	136	20	-57		12	4
120	1	320	136	20	-57		7	4

Contaminant Removed From Elastomers = 79 %

Remarks:

PHASE II TEST UNIT OPERATION

Run No. 15

Purpose: To Decontaminate the System Containing N_2O_4

Method: Vapor Phase Freon® TF Flush

Temperature in Test Vessel	-	60 °C
Pressure in Test Vessel	-	6 psig
Volume of Solvent Used	-	8 gals
Transfer Rate	-	0.5 gpm
Retention Time	-	0 hours

GN_2 DRYING DATA

Time From Start Min	GN_2 Rate		Temperatures: °C		Dew Point Exit Test Vessel °F	Test Vessel Exit Gas N_2O_4 Content PPM		Pressure In Test Vessel PSIG
	Test Vessel Volumes Per Min	Cubic Feet GN_2 Cuml.	Exit Heat Exchanger (E-1)	Exit Test Vessel D-6		Olfactron	By Titration	
15	1	40	139	42	-51		1013	5
30	1	80	140	28	-54		680	5
45	1	120	135	25	-56		420	5
60	1	160	138	24	-58		190	5
75	1	200	133	20	-59		190	5
90	1	240	135	21	-61		120	5
120	1	320	135	20	-65		120	5
150	1	380	136	20	-66		70	5
180	1	460	137	20	-64		80	5
210	1	540	138	19	-67		50	5
240	1	620	137	18	-72		50	5

Contaminant Removed From Elastomers = 78 %

Remarks: N_2O_4 leaked into the system during the drying cycle.

PHASE II TEST UNIT OPERATION

Run No. 16

Purpose: To Decontaminate the System Containing N_2O_4

Method: Liquid Freon® TF Flush

Temperature in Test Vessel - Ambient °C
Pressure in Test Vessel - 4 psig
Volume of Solvent Used - 18 gals
Transfer Rate - 1.5 gpm
Retention Time - 1 hours

GN_2 DRYING DATA

Time From Start Min	GN_2 Rate		Temperatures: °C		Dew Point Exit Test Vessel °F	Test Vessel Exit Gas N_2O_4 Content PPM		Pressure In Test Vessel PSIG
	Test Vessel Volumes Per Min	Cubic Feet GN_2 Cuml.	Exit Heat Exchanger (E-1)	Exit Test Vessel D-6		Olfactron	By Titration	
15	1	40	136	12	-22		--	4
30	1	80	138	12	-50		160	4
45	1	120	138	14	-56		11	4
75	1	200	138	17	-53		14	4
105	1	240	138	17	-68		8	4

Contaminant Removed From Elastomers = 80%

Remarks:

PHASE II TEST UNIT OPERATION

Run No. 17

Purpose: To Decontaminate the System Containing N_2O_4

Method: Vapor Phase Freon® TF Flush

Temperature in Test Vessel	-	80	°C
Pressure in Test Vessel	-	26	psig
Volume of Solvent Used	-	8	gals
Transfer Rate	-	0.33	gpm
Retention Time	-	0	hours

GN_2 DRYING DATA

Time From Start Min	GN_2 Rate		Temperatures: °C		Dew Point Exit Test Vessel °F	Test Vessel Exit Gas N_2O_4 Content PPM		Pressure In Test Vessel PSIG
	Test Vessel Volumes Per Min	Cubic Feet GN_2 Cuml.	Exit Heat Exchanger (E-1)	Exit Test Vessel D-6		Olfactron	By Titration	
15	1	40	132	42	-44		--	4
30	1	80	136	32	-51		66	4
45	1	120	136	28	-54		12	4
75	1	200	136	25	-67		14	4
105	1	240	136	22	-72		--	4

Contaminant Removed From Elastomers = 64 %

Remarks:

PHASE II TEST UNIT OPERATION

Run No. 18

Purpose: To Decontaminate the System Containing N_2O_4

Method: Liquid Freon® MF Flush

Temperature in Test Vessel - Ambient °C
Pressure in Test Vessel - 5 psig
Volume of Solvent Used - 18 gals
Transfer Rate - 1.5 gpm
Retention Time - 1 hours

GN_2 DRYING DATA

Time From Start Min	GN_2 Rate		Temperatures: °C		Dew Point Exit Test Vessel °F	Test Vessel Exit Gas N_2O_4 Content PPM		Pressure In Test Vessel PSIG
	Test Vessel Volumes Per Min	Cubic Feet GN_2 Cuml.	Exit Heat Exchanger (E-1)	Exit Test Vessel D-6		Olfactron	By Titration	
15	1	40	134	10	-48		--	5
30	1	80	135	15	-54		72	5
45	1	120	134	17	-76		40	5
60	1	160	135	18	-84		23	5
90	1	240	132	18	-91		10	5
120	1	320	134	18	-95		8	5

Contaminant Removed From Elastomers = 72 %

Remarks:

PHASE II TEST UNIT OPERATION

Run No. 19

Purpose: To Decontaminate the System Containing N_2O_4

Method: Vapor Phase Freon® MF Flush

Temperature in Test Vessel	-	64	°C
Pressure in Test Vessel	-	40	psig
Volume of Solvent Used	-	8	gals
Transfer Rate	-	0.33	gpm
Retention Time	-	0	hours

GN_2 DRYING DATA

Time From Start Min	GN_2 Rate		Temperatures: °C		Dew Point Exit Test Vessel °F	Test Vessel Exit Gas N_2O_4 Content PPM		Pressure In Test Vessel PSIG
	Test Vessel Volumes Per Min	Cubic Feet GN_2 Cuml.	Exit Heat Exchanger (E-1)	Exit Test Vessel D-6		Olfactron	By Titration	
15	1	40	132	35	-31		3302	5
30	1	80	130	26	-72		179	5
45	1	120	129	24	-75		356	5
60	1	160	129	22	-75		285	5
75	1	200	130	21	-75		150	5
90	1	240	130	20	-91		317	5
120	1	320	129	20	-94		272	5
165	1	440	130	20	-99		233	5
	NO PURGE FOR 64 HOURS							
15			130	18	60		248	5
30			134	18	62		6	5
60			134	18	62		0	5

Contaminant Removed From Elastomers = 91%

Remarks:

PHASE II TEST UNIT OPERATION

Run No. 20

Purpose: To Decontaminate the System Containing N_2O_4

Method: Vapor Phase Freon® MF Flush with Pressure Cycles

Temperature in Test Vessel	-	60 °C
Pressure in Test Vessel	-	45 psig
Volume of Solvent Used	-	8 gals
Transfer Rate	-	0.33 gpm
Retention Time	-	0 hours

GN_2 DRYING DATA

Time From Start Min	GN_2 Rate		Temperatures: °C		Dew Point Exit Test Vessel °F	Test Vessel Exit Gas N_2O_4 Content PPM		Pressure In Test Vessel PSIG
	Test Vessel Volumes Per Min	Cubic Feet GN_2 Cuml.	Exit Heat Exchanger (E-1)	Exit Test Vessel D-6		Olfactron	By Titration	
15	1	40	137	35	-62		5	5
30	1	80	137	26	-70		2	5
60	1	160	137	21	-95		0	5
0	1				-38		15	5
15	1				-105			5

Contaminant Removed From Elastomers = 74%

Remarks:

PHASE II TEST UNIT OPERATION

Run No. 21

Purpose: To Decontaminate the System Containing N_2O_4

Method: Pulsating Vapor Freon® Flush

Temperature in Test Vessel	-	68	°C
Pressure in Test Vessel	-	41	psig
Volume of Solvent Used	-	8	gals
Transfer Rate	-	0.33	gpm
Retention Time	-	0	hours

GN_2 DRYING DATA

Time From Start Min	GN_2 Rate		Temperatures: °C		Dew Point Exit Test Vessel °F	Test Vessel Exit Gas N_2O_4 Content PPM		Pressure In Test Vessel PSIG
	Test Vessel Volumes Per Min	Cubic Feet GN_2 Cuml.	Exit Heat Exchanger (E-1)	Exit Test Vessel D-6		Olfactron	By Titration	
15	1	40	138	38	-61			5
30	1	80	137	29	-68		10	5
60	1	160	137	22	-92			5
90	1	240	138	21	-100		5	5
	NO PURGE OVERNIGHT		20 PSIG					5
0	0			18	-57			5
15		40		19			20	5

Contaminant Removed From Elastomers = 78 %

Remarks:

PHASE II TEST UNIT OPERATION

Run No. 22

Purpose: To Decontaminate the System Containing N_2O_4

Method: Liquid Freon® MF Flush

Temperature in Test Vessel	-	Ambient	°C
Pressure in Test Vessel	-		psig
Volume of Solvent Used	-	18	gals
Transfer Rate	-	1.5	gpm
Retention Time	-	1	hours

GN_2 DRYING DATA

Time From Start Min	GN_2 Rate		Temperatures: °C		Dew Point Exit Test Vessel °F	Test Vessel Exit Gas N_2O_4 Content PPM		Pressure In Test Vessel PSIG
	Test Vessel Volumes Per Min	Cubic Feet GN_2 Cuml.	Exit Heat Exchanger (E-1)	Exit Test Vessel D-6		Olfactron	By Titration	
15	1	40	135	14	-33	37	--	5
30	1	80	136	15	-43	27	337	5
45	1	120	136	17	-47	19	20	5
60	1	160	136	18	-47	15	31	5
75	1	200	134	18	-52	6	49	5
90	1	240	134	18	-47	7	18	5
120	1	320	134	19	-53	5	11	5
150	1	400	135	19	-58	6	12	5

Contaminant Removed From Elastomers = 70%

Remarks:

XIV. INTERPRETATION OF DATA

The results obtained from the operation of the unit show the proposed method (vapor-phase flushing) is superior to the method (liquid flush) now used. The improvement is shown by the results presented in Figures 5-8, 5-9, and 5-10.

Figure 5-8 shows the Aerozine-50 in the exit GN_2 purge after flushing the system with liquid methanol and after flushing the system with methanol vapors. The Aerozine-50 concentration in parts per million is plotted against time on semi-log paper. The data points were generated in different runs. The curves show vapor-phase flushing saves time and materials. The time required to clean the contaminated systems by vapor-phase, including flushing and drying, ranges from one to one and one-half hours compared to seven or eight hours for liquid flushing. The solvent saved, as demonstrated in this study, is about one-half, but this amount can be reduced substantially. The GN_2 required for drying the hot vessel after vapor-phase cleaning is one-fifth the amount used in liquid flushing.

Drying the test vessel after flushing is part of the decontamination procedure. Dew point is an accepted measure of the dryness. The procedure used monitors the dew point of the exit gas. The curves in Figure 5-9 show the dew point of the exit gas versus time after flushing the system by two methods, liquid and vapor-phase flush. Inspection of the curve shows the vapor-phase flush is superior to liquid flush since less purging is required and the dew point was lower than achieved by the liquid flushing. It should be pointed out that the vapor-phase flush preceded the liquid flushing test, and no contaminants were involved.

The decontamination of N_2O_4 from the system using Freon® 11 as the flushing solvent is shown in Figure 5-10. Inspection of the curve shows that the vapor-phase flushing is the superior method although the slopes of the curve are almost identical. The reason for the similarity of the curves is as follows: The pressure of the test vessel was maintained at 45 psig during the flushing cycle which raises the temperature of the walls of the vessel to approximately 64° C. Since the vessel was not insulated, there was continuous condensing of the vapors on the walls of the vessel. When the pressure was released, the condensate on the walls evaporated and cooled the vessel to the boiling point of Freon® 11 at 5 psig which is approximately 30° C. Therefore, the purging cycle was carried out, not with the vessel hot, but at, or near, the same temperature as in the liquid phase flushing test, thus, the reason for the similarity of the curves. However, the contaminant concentration was less at the start of the purge cycle in the vapor-phase test.

Inspection of the test vessel after completing a run usually showed the presence of red fumes, even when the contaminant level was quite low. Since about 20% of the N_2O_4 disassociates into NO_2 at 80° F, the fumes were NO_2. At the start of the solvent flushing cycle, the test tank was full of NO_2 gas. The solubility of NO_2 in the Freon® 11 would obey Henry's and Raoults' gas laws. After draining the solvent from the test tank, the gas remaining would probably be primarily NO_2. The noncondensed vapors in vapor-phase cleaning sweep out some of the NO_2 fumes. Hence, another reason

for the lower contaminant level in the vapor-phase test. Continuous GN_2 purge requires considerable time to remove the NO_2 fumes to an acceptable level. The slopes of the curves illustrate this fact.

Pulsing of the pressure in the system during vapor-phase flushing to create turbulence appeared to be a solution to the problem of sweeping out trapped NO_2 fumes. In one run the pressure was allowed to build up to 45 psig and was then quickly reduced to 5 psig. Two pressure cycles were used during this run. During the release of pressure the volume of vapors leaving the test vessel increased by at least three-fold. Also, condensed Freon® 11 on the walls of the vessel flashed off to add to the volume of exit vapors. The results of this run are shown by two data points in Figure 5-10.

It can be seen that the contaminant level in the exit gas from the first sample at thirty minutes was approximately 5 ppm. The next sample, fifteen minutes later, contained 2 ppm of N_2O_4. It is apparent from this test that pulsating pressure cycles during vapor-phase cleaning is the best decontamination method.

XV. ECONOMIC ANALYSIS

The contract stated, "if one or more candidate methods effectively cleans the oxidizer system and the fuel system and is superior to the present "Tri-Flush" method, the contractor shall perform an evaluation cost comparison of the selected method(s)." Since the "Tri-Flush" method was abandoned in favor of the "Single-Flush" method about the time this contract was awarded to The Dow Chemical Company, the economics of the "Single-Flush" method will be compared with the economics of the proposed "Vapor-Phase Cleaning" method. The procedures used in "Single-Flush" and in "Vapor-Phase Cleaning" have already been described.

The following assumptions were made regarding "Single-Flush" cleaning costs:

1. Four thousand gallons of methanol at 35 cents per gallon and four thousand gallons of Freon® MF at $2.40 per gallon are used for one cleaning operation.

2. The cleaning solvents are transported from central storage to the cleaning sites by tank trucks.

3. Contaminated solvents are transported by tank truck to a waste disposal point; solvent is not reclaimed.

Assumptions made regarding "Vapor-Phase Cleaning" costs:

1. Equipment for decontamination, solvent storage, and solvent reclamation can be mounted on a single trailer.

2. This unit is delivered to the cleaning site ready to operate.

3. The decontamination procedure consists of vaporizing the solvent, passing the vapors through the system to be cleaned, liquefaction of vapors, and reclamation of contaminated solvent.

4. Solvent inventories delivered to the site are about one thousand gallons of methanol and one thousand gallons of Freon® MF; losses of solvent are assumed to be about 10% per cleaning operation.

Cost estimates for the "Single-Flush" (present method) and the "Vapor-Phase" (proposed method) cleaning procedures are tabulated.

The estimates show that the cost of cleaning by the "Single-Flush" method is approximately $11,600 per day compared with about $600 per day for the "Vapor-Phase Cleaning" method.

This is based on one cleaning of the Apollo service module in one day.

Single-Flush Cost of Cleaning Method			Dollars/Day
Raw Materials			
Freon® - (12.1 Lbs./Gal.) 4,000 Gallons @20¢/Lb.			$ 9,680
N_2 - 552 Pounds @ 30¢/Lb.			166
MeOH - 4,000 Gallons @ 35¢/Gallon			1,400
Labor with Overhead			
1-1/2 Drivers (Freon®) @ $4.00/Hr. x 8 Hr./Day			48
2 Ops. (Freon®) @ $5.80/Hr. x 8 Hr./Day			93
1 Ops. (MeOH) @ $5.80/Hr. x 8 Hr./Day			46
1 Driver (MeOH) @ $4.00/Hr. x 8 Hr./Day			32
Capital			
Tanks, Storage 4 @ $4,500	=	$18,000	
Pumps, 4 @ $500	=	2,000	
Tractor (Freon®) 1 @ $15,000	=	15,000	
Tractor (MeOH) 1 @ $15,000	=	15,000	
Trailers (Freon®) 2 @ $10,000	=	20,000	
Trailers (N_2) 2 @ $10,000	=	20,000	
Trailers (MeOH) 2 @ $10,000	=	20,000	
		$110,000	
5 Years, 365 days @ 2 x Capital			120
Disposal 4,000 Gallons @ 2¢/Gal.			80
TOTAL DAILY COST			$11,665

Vapor-Phase Flush Cost of Cleaning Method			
Raw Materials			
Freon® Makeup - 100 Gallons @ 20¢/Lb.			$242
MeOH Makeup - 100 Gallons @ 35¢/Gal.			35
N_2 Makeup - 138 Lbs. @ 30¢/Lb.			41
Labor with Overhead			
1 Driver @ $4.00/Hr. x 8 Hr./Day			32
3 Ops. @ $5.80/Hr. x 8 Hr./Day			139
Capital			
1 Nitrogen Trailer @ $10,000	=	$10,000	
1 Tractor @ $15,000	=	15,000	
1 Recovery Trailer @ $85,000	=	85,000	
		$110,000	
5 Years, 365 Days @ 2 x Capital			121
TOTAL DAILY COST			$610

TABLE 5-I

EQUIPMENT LIST AND DESCRIPTION FOR TEST UNIT

Symbol	Name	Description
D-1	Dirty Solvent Storage Tank	Stainless Steel Tank; Capacity - 50 Gallons.
D-2	Clean Solvent Storage Tank	Stainless Steel Tank; Capacity - Approximately 95 Gallons.
D-3	Propellant Storage Tank	Monel Metal Tank; Capacity - Approximately 16 Gallons.
D-5	Fume Scrubber	Pyrex Glass, 4" Dia. x 6' Long. Packed with 1/2" burl saddles. Packing depth about 30".
E-1, E-2	Heat Exchangers	Type SSCF Exchangers, No. 303. Two-pass, 11 square feet of surface area.
T-1	Contaminant Adsorption Column	12" ID x 3' 8" bend line to bend line (4' 6" approx. overall length), stainless steel. Approx. capacity - 22 Gallons.
T-2	Drying Column	12" ID x 6' 8" bend line to bend line (7' 6" overall length) stainless steel. Approx. capacity - 40 Gallons.
F-1	Filter	Cuno Model 181 Filter, 316 stainless steel, with 1" NPT connections equipped with Cuno 10-micron 316 stainless steel Poro-Klean cartridge No. 501SS-1-24A-5A-C1.
SV	Safety Relief Valve	3/4" x 1" Crosby JMB pressure relief safety valve. Six such valves were used on the various vessels in accordance with Dow Safety Standards.
D-6	Test Vessel	Titanium Vessel, 12-3/4" ID x 28-5/8" tangent to tangent. Top section above flange only is titanium; lower portion is stainless steel flanged (four bolts). A stainless steel stand pipe is inside the tank to allow venting through a connection in the lower part while filling with liquid.
P-1 P-2	Pumps	Gould stainless steel, 3/4" x 1", centrifugal pump, equipped with mechanical seals, driven by 3500 rpm, 5 hp electric motor.

TABLE 5-II
TEST UNIT - INSTRUMENTS

Symbol	Description
FRC-1	Foxboro No. 13A D/P Cell 150", 0.250" Integral orifice. V-4 Valve 1/2" line size. 1/4" Trim. All stainless steel. Red pen on recorder.
FC-1	*Brooks No. 6 Rotometer, tant. float.
FRC-2	Foxboro No. 13A D/P Cell 150", 0.250" Integral orifice. V-4 Valve 1/2" line size. 1/4" Trim. All stainless steel. *Red pen on recorder.
TRC-1	*Foxboro Dynalog, 0-200° C, Red pen. Foxboro V4, 3/8" Trim, Iron body.
TR-1	*Red pen, Fox Dynalog.
PR-1	*Blue pen, Fox Dynalog.
PC-1	*Foxboro 41A, 0-100 Lb. Foxboro V4 Valve, 3/8" Trim, All SS.
CR-1	*L. and N. Recorder for Analyzer Record, 0-10 MV.
PI-1	*Nitrogen bottle, Pressure 0-400 Lbs.
PI-2	*D-1 Tank Pressure 30" 0-30 Lbs.
PI-3	*D-2 Tank Pressure 0-100 Lbs.
PI-4	*D-3 Tank Pressure 30" 0-30 Lbs.
LI-1, LI-2	*Barton Model 200 Differential Pressure Indicator, 0-100".
Contaminant Detector	Toxic Vapor Detector No. 6055A, manufactured by Teledyne, Inc., Teledyne Systems Company.
Dew Point Detector	Alnor Dewpointer, Model 7000L.

*Mounted on panel board.

TABLE 5-III
LISTING OF VALVES IN TEST UNIT

Valve No.	Function or Location
D_1-1	1" out of D-1 to Vent.
D_1-2	1" out of D-1 bottom to P-1 suction.
D_1-3	1" out of D-1 and bottom. Drain or fill.
D_1-4	1" P-1 recycle line on D-1.
D_1-5	1" in P-1 forwarding line to D_1-6.
D_1-6	Flow control diaphragm valve.
D_1-7	1" in line out of D_1-6.
D_1-8	1" bypassing D_1-6.
D_1-9	1" bypassing T-1.
T_1-10	1" in forwarding line to T-2.
T_1-11	1" drains T-1.
T_2-12	1" at bottom of T-2.
T_2-13	1" drain of T-2.
T_2-14	1" in forwarding line to D-2.
D_2-15	1" drain valve out of 4" flange.
D_2-16	1" bottom of D-2 in line to P-2 suction.
D_2-17	1" below D_2-16 for use in draining or filling.
D_2-18	1" P-2 recycle on D-2.
P_2-19	1" in forwarding line D-2 to D_2-19.
D_2-19	1" ahead of D_2-20 control valve.
D_2-20	Controls rate of flow of solvent into E-1.
D_2-21	1" following D_2-20 control valve.
D_2-22	1" bypassing D_2-20 control valve.
N-23	1" on N_2 purge supply.
STM-24	1" steam to system

Table 5-III (Continued)

Valve No.	Function or Location
STM-25	1" steam to control valve.
STM-26	Control; steam; diaphragm valve.
STM-27	1" steam to process (with pressure reducer).
E_1-30	1" in process line to filter.
E_1-31	1" in process line out of filter.
E_1-32	1" bypass around filter.
E_1-33	1" left end of lower header.
D_6-34	1" in upper header under D_6 between union and check valve.
E_1-35	1" in line to D-6 liquid leg from E-3.
D_6-36	1" in upper header under D-6 nearest D-6.
D_6-37	1" in lower header to right of downcomer connecting upper and lower headers.
D_6-38	1" in D-6 liquid leg above lower header.
D_6-39	Number reserved for future use.
D_6-40	1" riser from lower header to Moore transducer.
D_6-41	1" riser from lower header to transfer lines.
D_3-42	Number reserved for future use.
D_3-43	Number reserved for future use.
D_3-44	Number reserved for future use.
D_3-45	1" valve at right end of lower header into 3/8" vent.
D_3-46	1" valve at junction of 3/8" header with scrubber.
D_3-47	1" process line into E-2.
W-48	1" water into condenser E-2
E_2-49	1/4" needle valve out of E-2 for sampling.
E_2-50	1" in line from E-2 to D-1 below diaphragm valve.

Table 5-III (Continued)

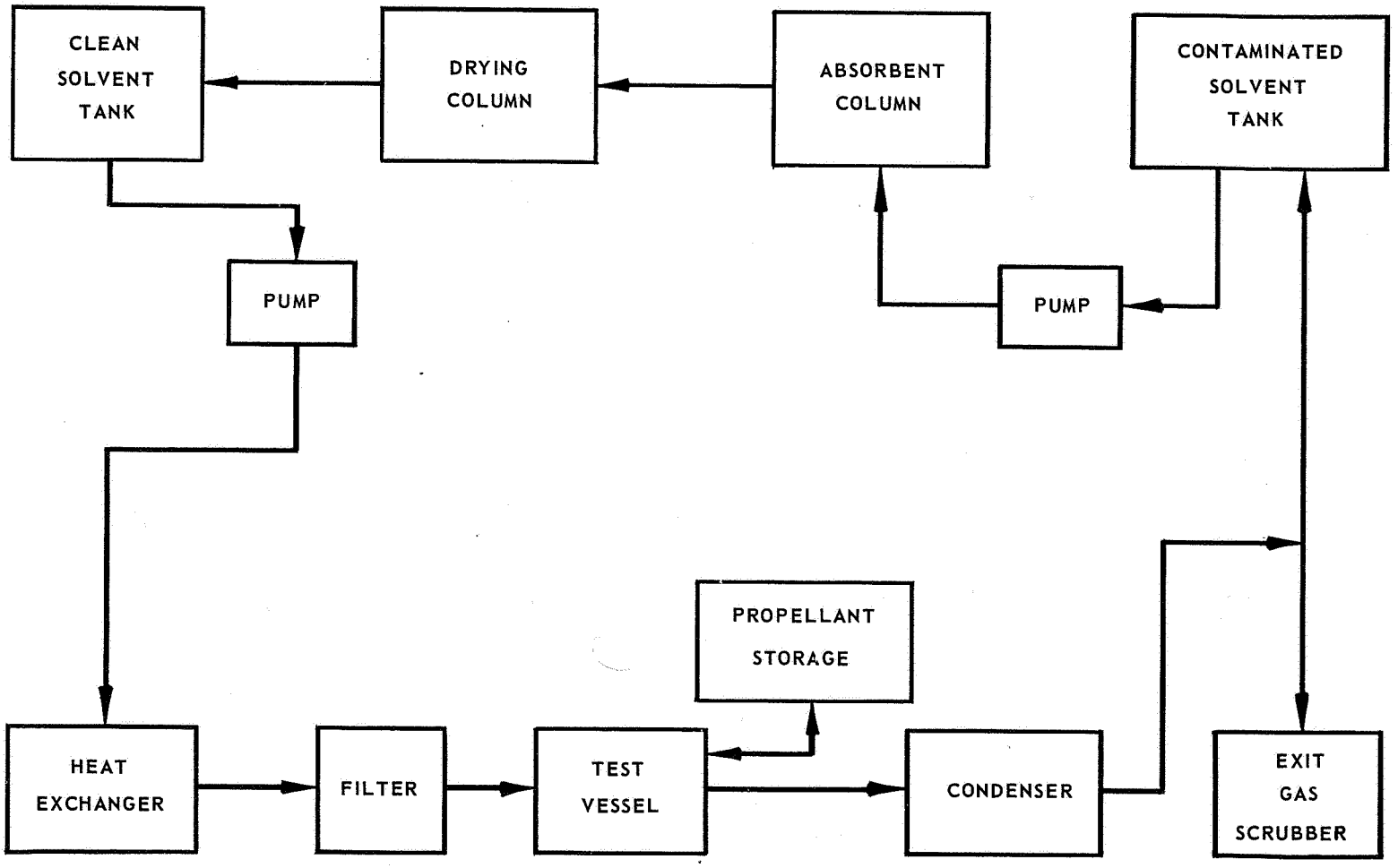
Valve No.	Function or Location
E_2-51	Back pressure diaphragm control valve.
E_2-52	1" in line from E-2 to D-1 above diaphragm valve.
E_2-53	1" in bypassing E_2-51.
E_2-54	1" in line from E-2 to scrubber.
E_2-55	1" in line from E-2 to D-1.
W-56	1" main water supply cutoff at rig.
W-57	1/2" in screen flush line.
W-58	1" in line supplying scrubber.
S-59	1/4" ball valve.
A-60	A-50 drum: 1/4" ball valve in 3/8" SS tubing transfer line nearest drum.
A-61	A-50 transfer line. 1/4" ball valve midway to D-6.
A-62	N_2 pad control when transferring from drum to D-6. Vent opening when transferring from D-6 to drum: 1/4" Hoke valve at drum.
A-63	Number reserved for future use.
A-64	Number reserved for future use.
A-65	Number reserved for future use.
N_2O_4-66	Valve in 1/4" tubing near D-6.
N_2O_4-67	Valve above cylinder to vent transfer line.
N_2O_4-68	First valve out of N_2O_4 cylinder.
N_2O_4-69	N_2O_4 liquid cylinder valve.
T_2-70	3/8" needle valve below F-P No. 5 Rotometer.
T_2-71	1/4" ball valve above F-P No. 5 Rotometer.
SPL-1	1/4" ball valve controlling cylinder N_2 purge line.
SPL-2	1/4" ball valve controlling sample gas to Alnor.

Table 5-III (Continued)

Valve No.	Function or Location
SPL-3	1/4" Hoek valve controlling sample gas or N_2 to Alnor.
SPL-4	1/4" Hoek valve controlling sample gas or N_2 to Olfactron.
SPL-5	1/4" ball valve just behind small gauge in sample system.
SPL-6	1/4" ball valve nearest to D-6 in sample line system.
SPL-7	1/4" Hoek valve near Moore transducer.
SPL-8	1/4" ball valve near D-6 in N_2O_4 transfer line.
SPL-9	1/4" Hoke valve in line from D-6 nitrogen supply to 3/8" SS tubing header.

Figure 5-1

BLOCK DIAGRAM OF TEST UNIT



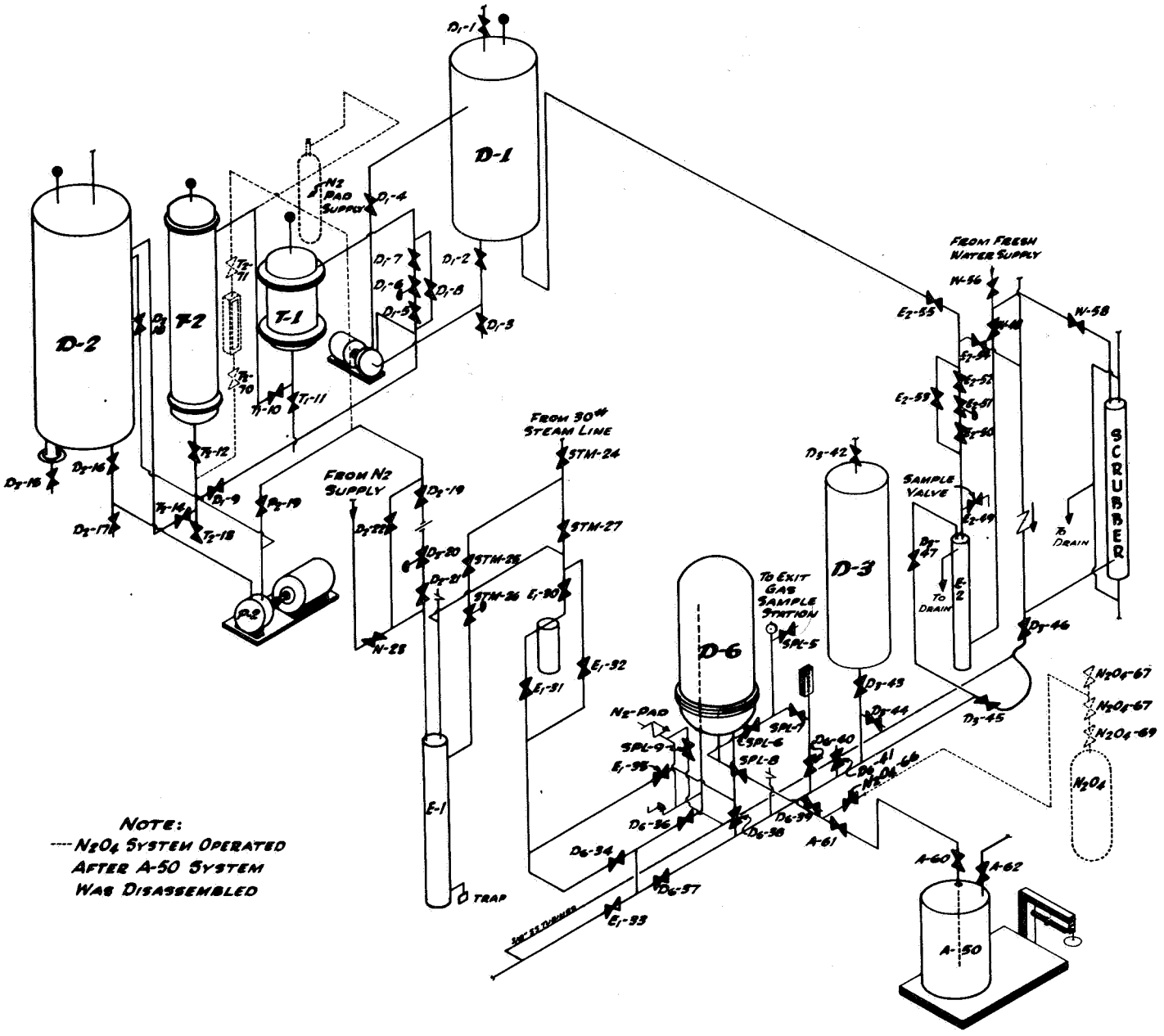
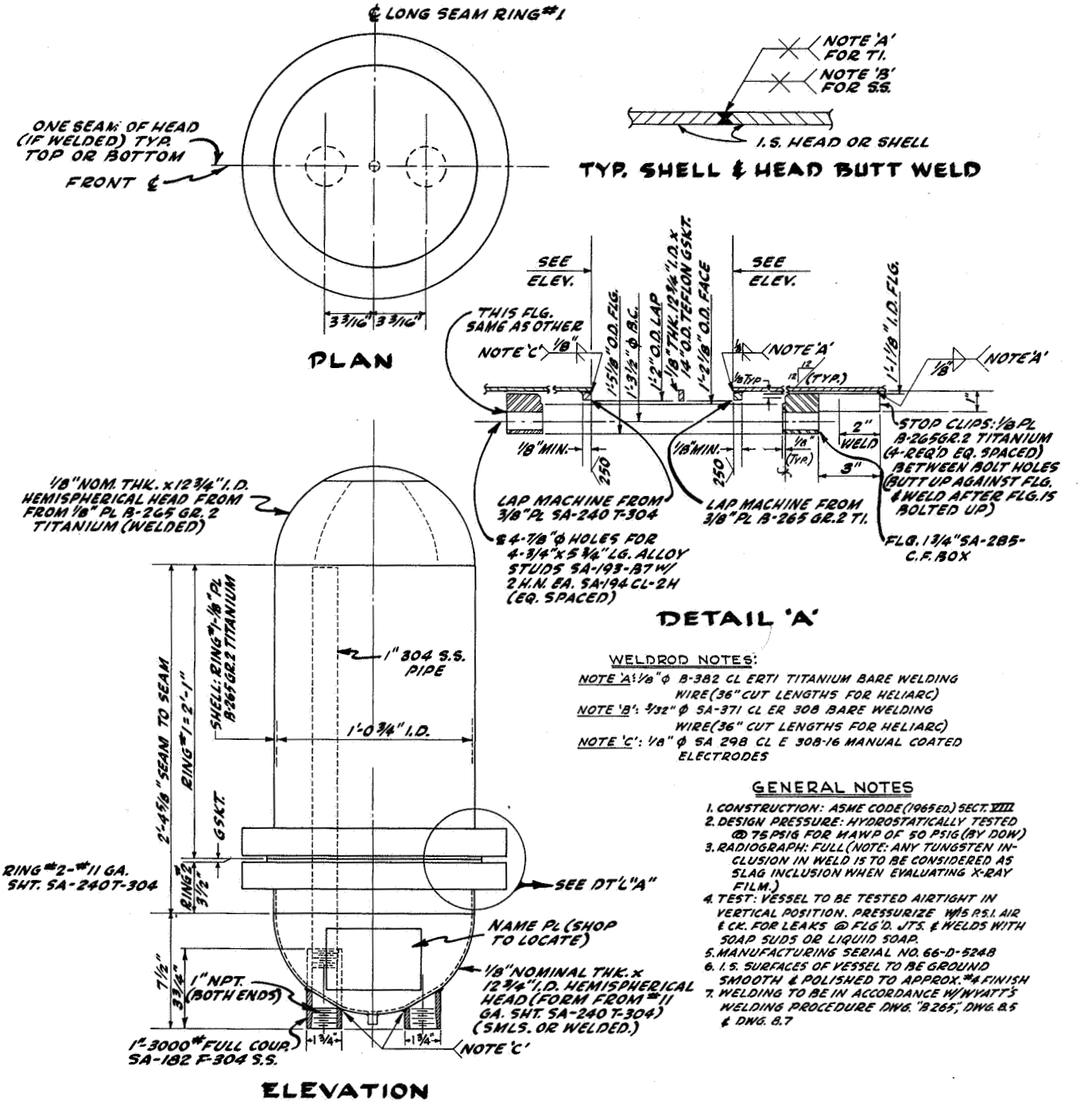


FIGURE 5-2

PERSPECTIVE DRAWING OF TEST UNIT



WELDROD NOTES:

NOTE 'A': 1/8" ϕ B-382 CL ERTI TITANIUM BARE WELDING WIRE (36" CUT LENGTHS FOR HELIARC)

NOTE 'B': 5/32" ϕ SA-371 CL ER 308 BARE WELDING WIRE (36" CUT LENGTHS FOR HELIARC)

NOTE 'C': 1/8" ϕ SA 298 CL E 308-16 MANUAL COATED ELECTRODES

GENERAL NOTES

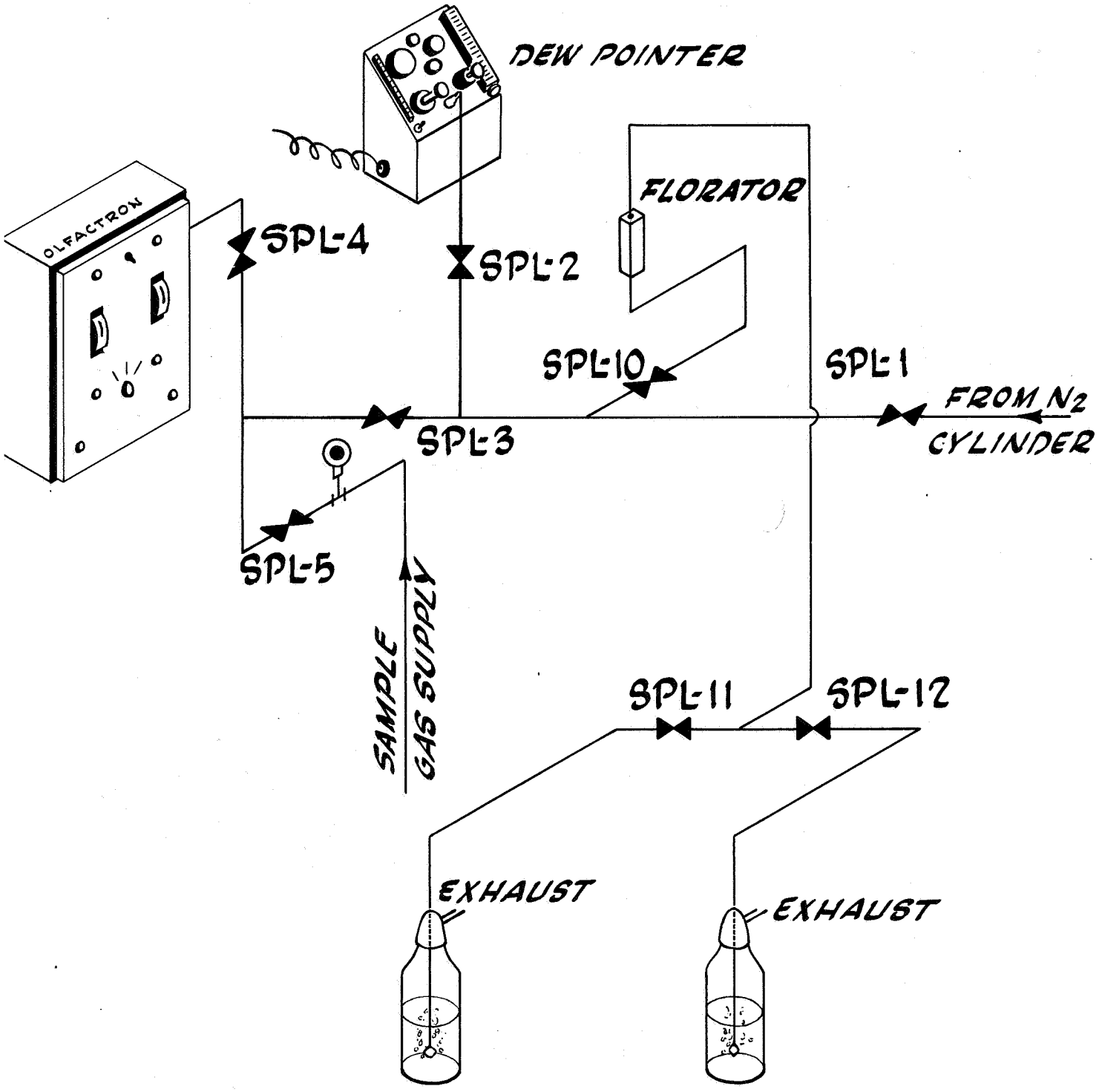
1. CONSTRUCTION: ASME CODE (1965 ED.) SECT. VIII
2. DESIGN PRESSURE: HYDROSTATICALLY TESTED @ 75 PSIG FOR MAWP OF 50 PSIG (BY DOW)
3. RADIOGRAPH: FULL (NOTE: ANY TUNGSTEN INCLUSION IN WELD IS TO BE CONSIDERED AS SLAG INCLUSION WHEN EVALUATING X-RAY FILM.)
4. TEST: VESSEL TO BE TESTED AIRTIGHT IN VERTICAL POSITION. PRESSURIZE W/5 P.S.I. AIR & CK. FOR LEAKS @ FLG'D. JTS. & WELDS WITH SOAP SUDS OR LIQUID SOAP.
5. MANUFACTURING SERIAL NO. 66-D-5248
6. I.S. SURFACES OF VESSEL TO BE GROUND SMOOTH & POLISHED TO APPROX. #4 FINISH
7. WELDING TO BE IN ACCORDANCE W/WYATT'S WELDING PROCEDURE DWG. "B 265", DWG. B.5 & DWG. B.7

FIGURE 5-3

TEST VESSEL AND SPECIFICATIONS

Figure 5-4

EXIT GAS SAMPLING STATION



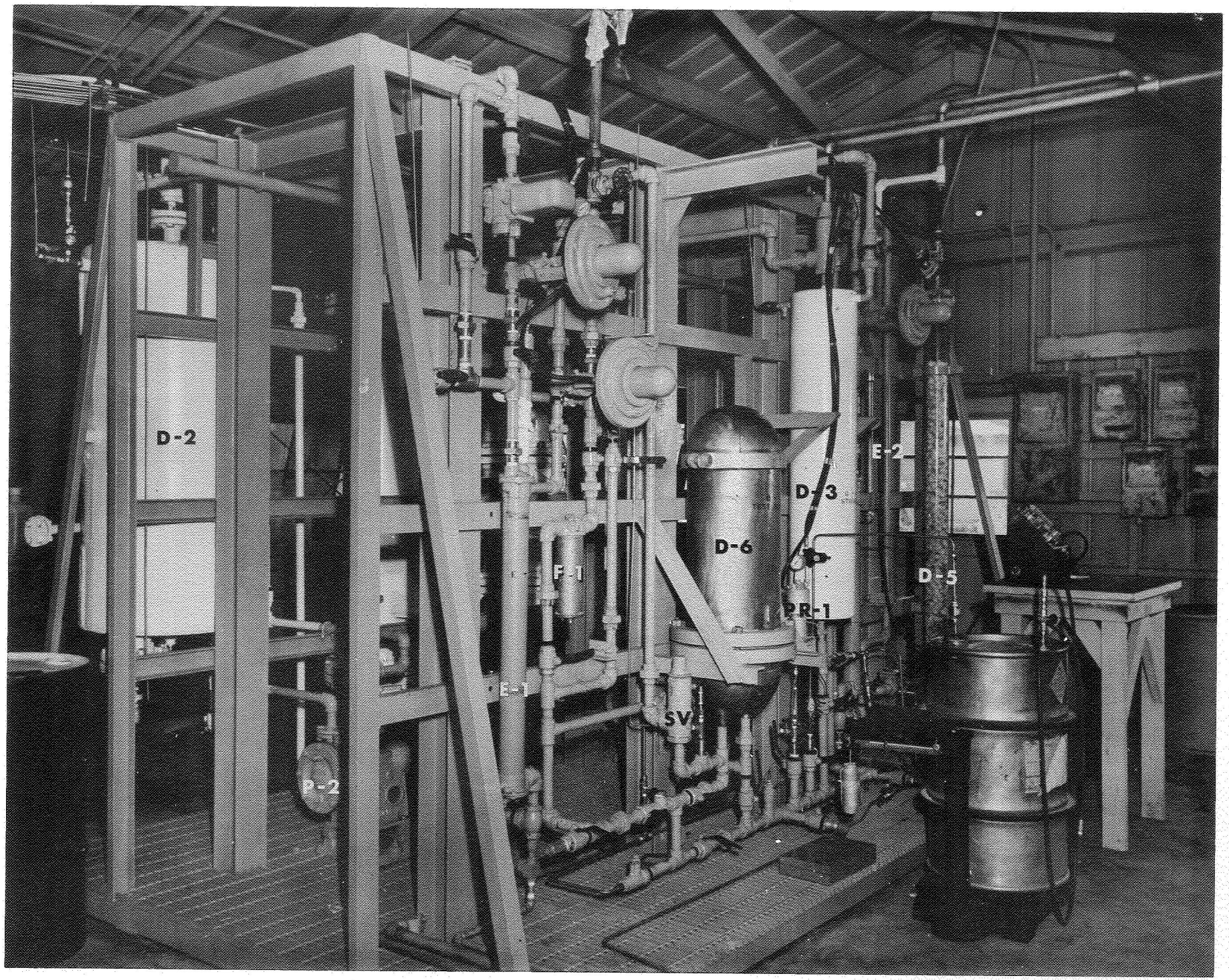
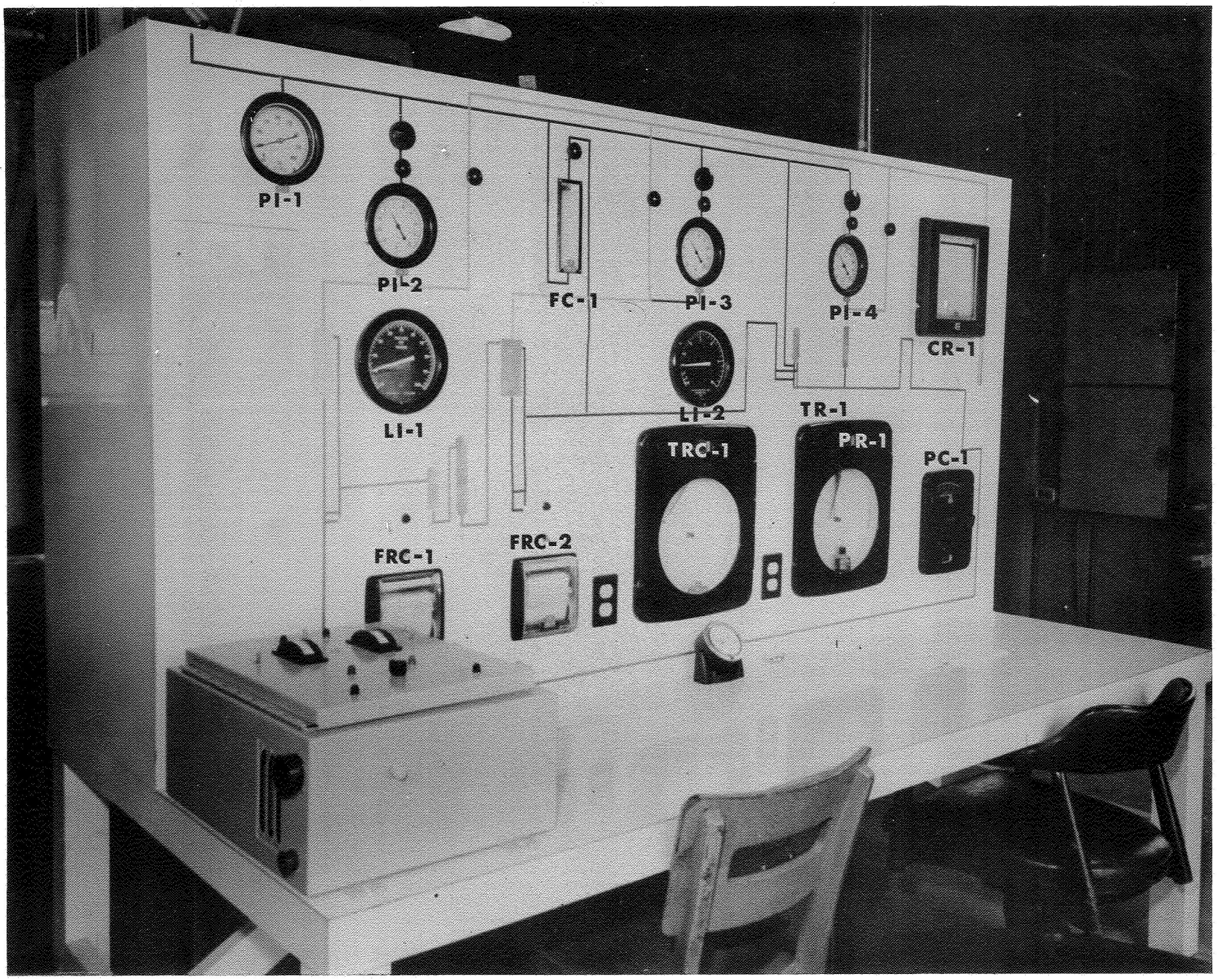


Figure 5-5


PI-1
PI-2
FC-1
PI-3
PI-4
CR-1
LI-1
LI-2
TR-1
TRC-1
PR-1
PC-1
FRC-1
FRC-2

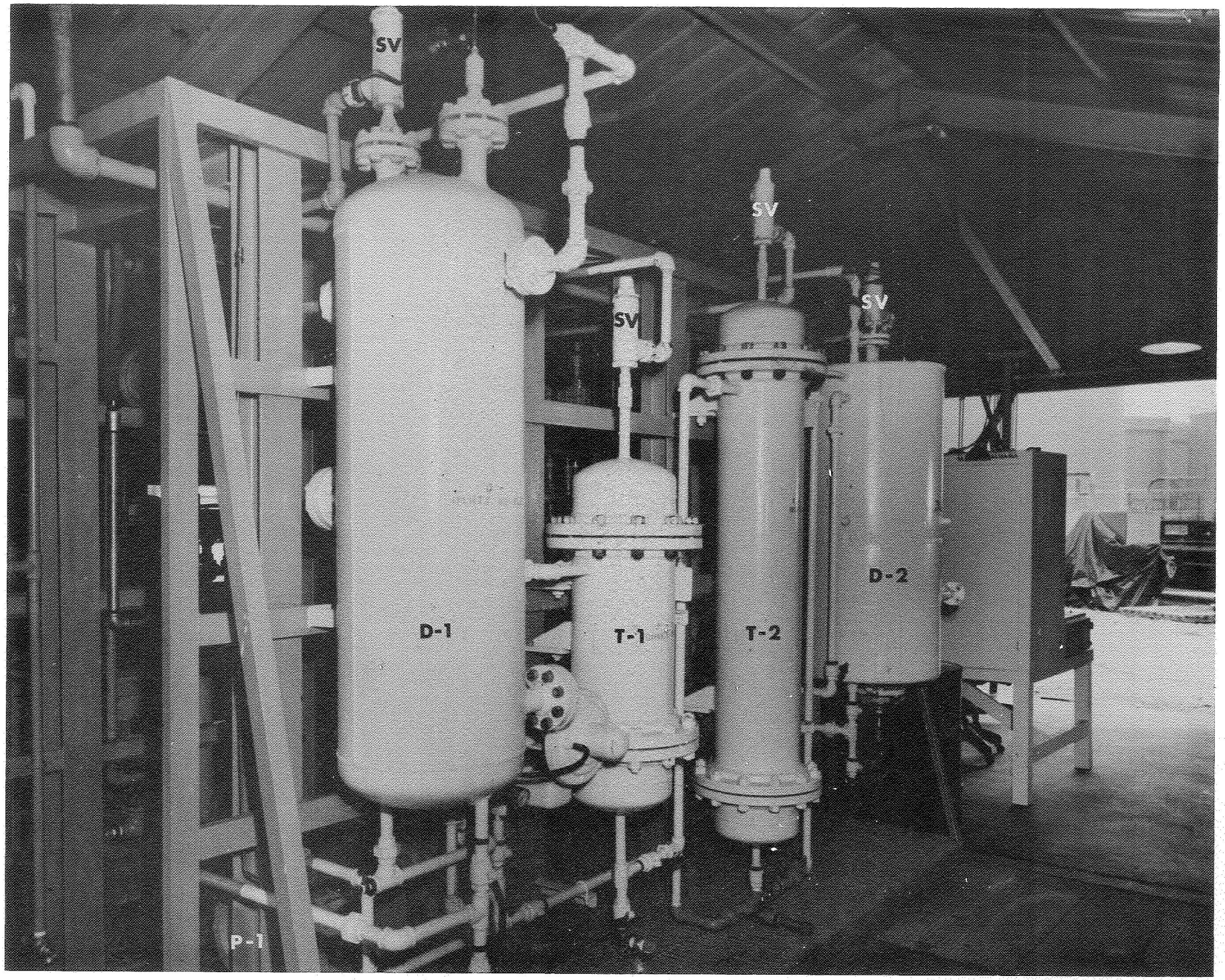


Figure 5-7

Figure 5-8

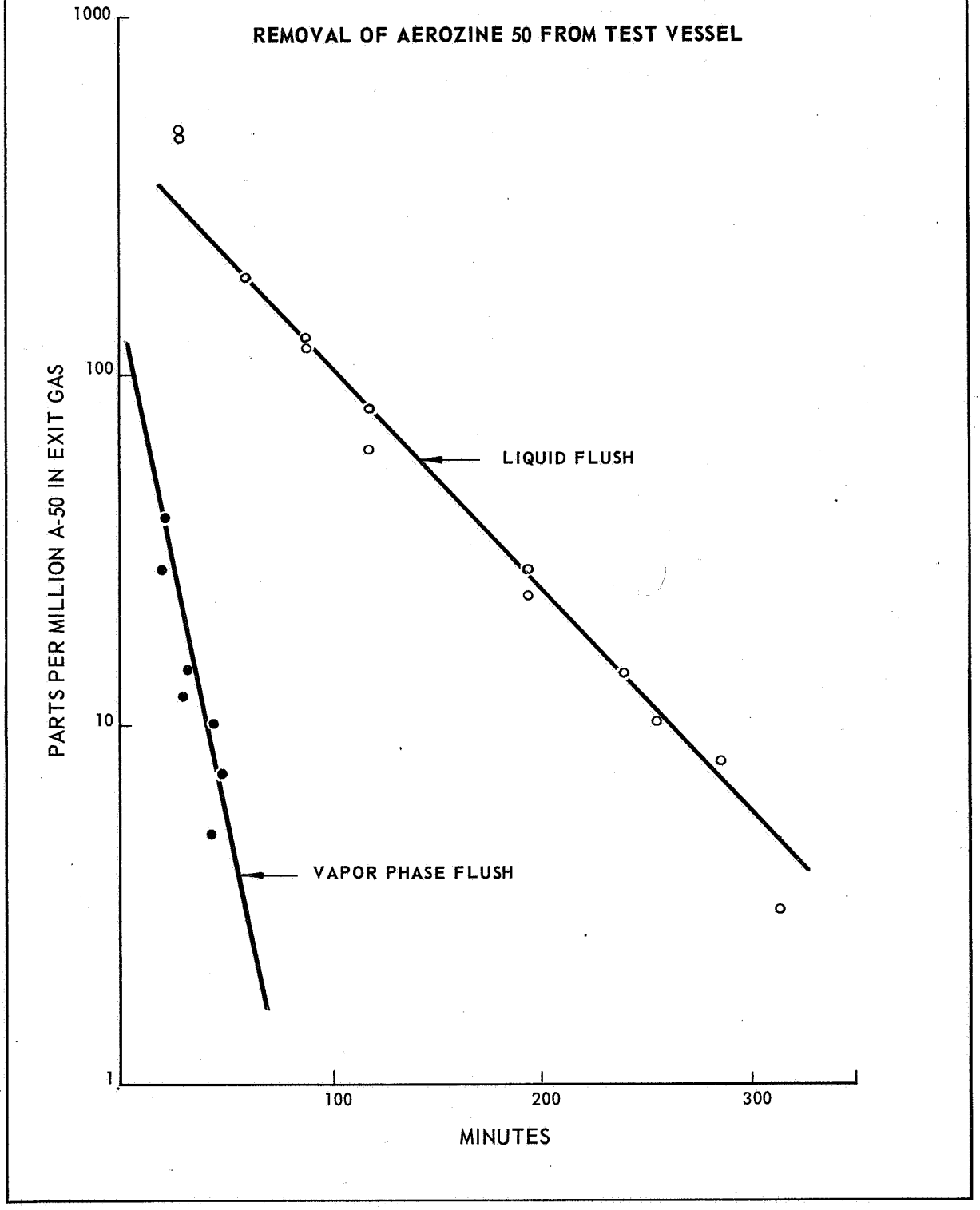

REMOVAL OF AEROZINE 50 FROM TEST VESSEL
8
1000
100
10
1
PARTS PER MILLION A-50 IN EXIT GAS
LIQUID FLUSH
VAPOR PHASE FLUSH
100
200
300
MINUTES

Figure 5-9

REMOVAL OF METHANOL FROM TEST VESSEL

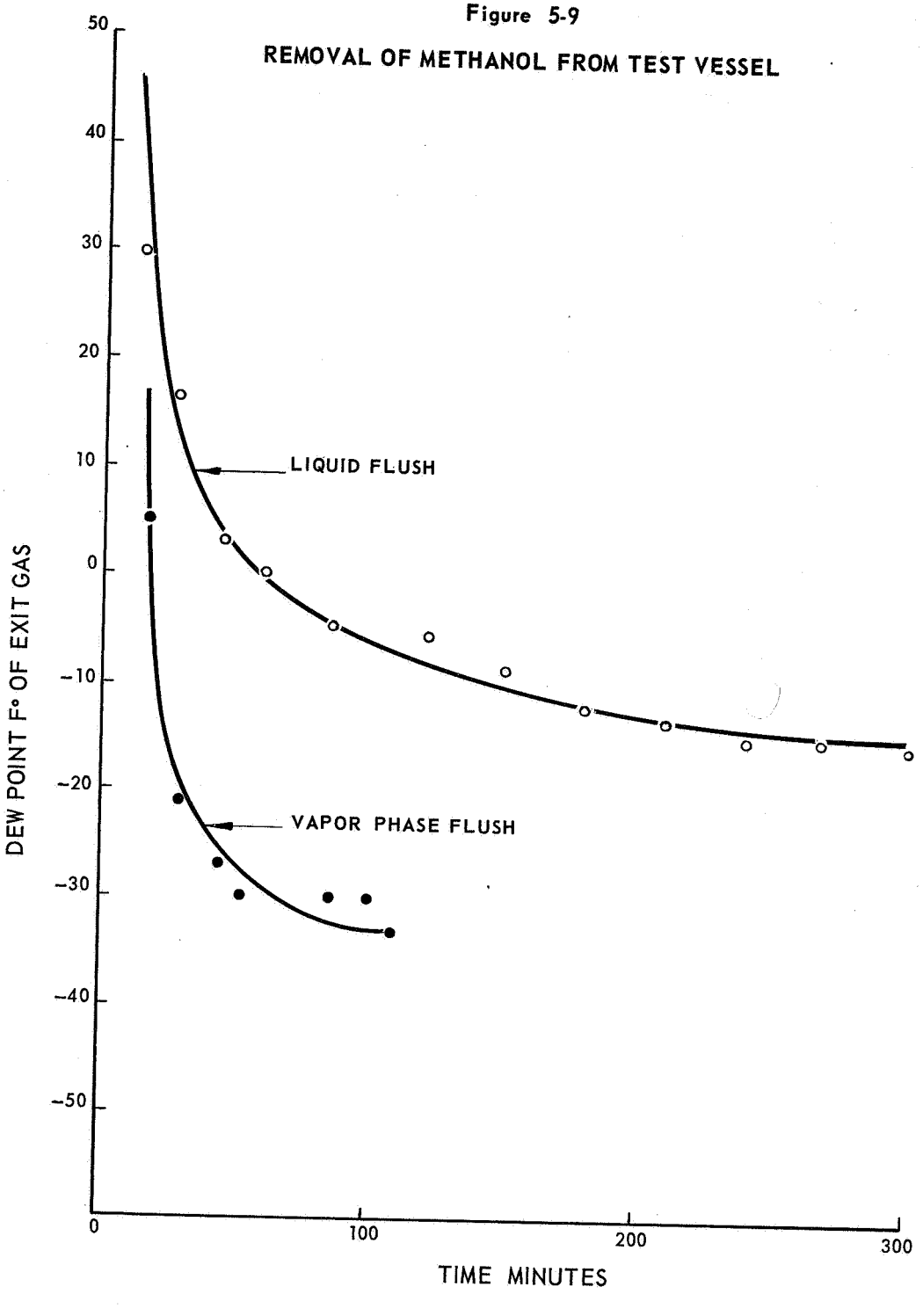


Figure 5-10

REMOVAL OF N_2O_4 FROM TEST VESSEL USING FREON® MF