GPO PRICE $

CFSTI PRICE(S) $

Hard copy (HC) 2.50

Microfiche (MF) .75

ff 653 July 65

FINAL REPORT

For

INVESTIGATION OF THE EXPLOSION HAZARD OF CONTAMINATED DIFFUSION PUMP FLUIDS

(1 July 1965 - 1 June 1966)

IITRI Project No. K6090
Contract No. NAS5-9632

Prepared By

Jerry Farrell
IIT Research Institute
10 West 35th Street
Chicago, Illinois

For

Goddard Space Flight Center
Greenbelt, Maryland

FACILITY FORM 602

N66 31893	
(ACCESSION NUMBER)	(THRU)
87	1
(PAGES)	(CODE)
CR-76525	15
(NASA CR OR TMX OR AD NUMBER)	(CATEGORY)

FINAL REPORT

For

INVESTIGATION OF THE EXPLOSION HAZARD OF CONTAMINATED DIFFUSION PUMP FLUIDS

(1 July 1965 - 1 June 1966)

IITRI Project No. K6090
Contract No. NAS5-9632

Prepared By

Jerry Farrell
IIT Research Institute
10 West 35th Street
Chicago, Illinois

For

Goddard Space Flight Center
Greenbelt, Maryland

PREFACE

This program was conducted for the NASA Goddard Space Flight Center with Mr. W. F. Hardgrove as NASA's Technical Director. At IIT Research Institute the program was directed by Frank Iwatsuki, Manager, Fluid Systems and Lubrication and Jerry Farrell, Project Engineer. Other IIT Research Institute personnel who have contributed to the technical efforts of the program are H. J. O'Neil, R. G. Scholz, J. Frerichs, and F. Grady.

ABSTRACT

This program was conducted to determine the effect of contamination on the explosion hazard potential of space simulation type diffusion pumps. One objective of the study was the determination of the type and quantity of contaminants present in the diffusion pump fluids supplied by NASA Goddard. Another objective was the determination and comparison of the explosion limits of the three (3) used DC-704 samples supplied by NASA Goddard with new samples of DC-704.

The program was conducted in four (4) phases as follows:

Phase I

The first phase consisted of two (2) parts. The first was a field survey to ascertain the number of combustion occurrences in diffusion pumps. The second part included a brief literature search and a review of specifications from vacuum equipment manufacturers, pump fluid suppliers, and research laboratories.

Phase II

The second phase was the determination of the explosion limits of the three (3) used fluids supplied by NASA Goddard, of deliberately contaminated DC-704 fluids, and of new DC-704 fluids.

Phase III

The third phase consisted of the chemical analysis of the new and used samples of DC-704.

Phase IV

The final phase was the stability studies conducted on DC-704. This included catalytic bath studies in air and stability studies conducted in a six inch diffusion pump vacuum system.

The results of the study show the explosion limit temperature of the used DC-704 samples to be slightly lower than the explosion limit temperature of the new DC-704 fluid. These used fluids contained small amounts of metallic contamination such as aluminum, magnesium, and calcium. Several volatile components were found in the used fluids, and new DC-704 was found to be susceptible to degradation in air at temperatures greater than 525°F. In addition, ozone was found to be very detrimental to the stability of DC-704 in an operating diffusion pump. However, DC-704 was found to be very stable under conditions normally encountered in an operating diffusion pump even when metallic dusts and cleaning agents were present in the system.

Future work should be conducted to determine the mechansim by which ozone can generate an explosion reaction in DC-704 in an operating diffusion pump system.

TABLE OF CONTENTS

LIST OF ILLUSTRATIONS

LIST OF ILLUSTRATIONS

(Continued)

LIST OF TABLES

INVESTIGATION OF THE EXPLOSION HAZARD OF CONTAMINATED DIFFUSION PUMP FLUIDS

1.0 INTRODUCTION

In 1963 IIT Research Institute under NASA Contract No. 9-7178 investigated the thermal stability of five commonly used diffusion pump fluids. This investigation was conducted with new, uncontaminated fluids. Therefore in early 1965, IIT Research Institute submitted an unsolicited proposal to NASA Goddard to investigate the effect of contamination on the stability of DC-704.

Subsequent to the time IIT Research Institute submitted its proposal, an explosion occurred in the Vertical Optical Bench at Goddard. Thus, this study was initiated to determine the influence of contamination on the explosion hazard potential of space simulation type diffusion pumps.

This program consisted of four (4) distinct phases. The first phase included a review of previous work at IIT Research Institute, a brief literature review, and an extensive field survey to determine accurately the frequency of explosions in diffusion pump systems. This was followed by two phases which were started simultaneously. These were explosion limit tests and chemical analyses on used DC-704 fluid samples supplied by NASA-Goddard. The chemical analyses were conducted to determine the type and quantity of contaminants contained in the used DC-704 samples.

The final phase of the program consisted of stability tests on DC-704, both in air at elevated temperatures and in a six-inch diffusion pump system.

2.0 CONCLUSION

2.1 Very few explosions have occurred in diffusion pumps under steady state high vacuum conditions.

2.2 A relatively large number of explosions have occurred in diffusion pump systems during pressurization with air or oxygen.

2.3 The temperature required to generate an explosion in the used fluids was slightly less than the temperature required for new DC-704 fluid.

2.4 The volume of the combustion apparatus has a significant influence on the explosion limit temperature at pressures less than 200 millimeters of mercury.

2.5 All the used fluids contained minute quantities of metallic contamination including magnesium, aluminum, and calcium.

2.6 Several differences were present in the gas chromatograms of the used fluids. These differences which were observed for both lighter and heavier components, with respect to the major component are due to alterations in the base fluid, but not necessarily contamination.

2.7 DC-704 fluid degrades badly in an air environment at 525°F. The products of degradation in the presence of air can be traced to the parent DC-704 fluid by both free radical and oxidation mechanisms.

2.8 DC-704 does not degrade significantly in air at 450°F.

2.9 Aluminum oxide acts as a retarder to degradation in DC-704 in an air environment.

2.10 Ozone has a detrimental influence on DC-704 in an operating diffusion pump system and under the proper conditions will result in an explosive reaction.

2.11 DC-704 is very stable under conditions normally encountered in an operating diffusion pump, even when metallic contaminants such as magnesium and aluminum are present in the system or when cleansing agents such as acetone have been used in the system.

3.0 EXPERIMENTAL EQUIPMENT AND PROCEDURES

The experimental program was conducted in four (4) phases. The first phase consisted of a field survey to ascertain more accurately the number of combustion occurrences in diffusion pumps. The next phase was the determination of the explosion limits of the diffusion pump fluids under test. The third phase was the analysis of the used pump fluids for contaminants. The last series of tests consisted of stability tests of DC-704 in catalytic baths exposed to air and stability studies in a six-inch vacuum system. The experimental procedures and equipment used in each phase of the tests are described in this section.

The term "explosion" is used repeatedly in the text of this report and, therefore, its meaning in the text will be defined here.

An explosion can be defined, in general, as "an uncontrolled spontaneous chemical reaction with a large release of energy." However, in a vacuum system the energy release as a result of an explosion is not always large because of the low system pressures. Therefore, we will redefine explosion as it refers to vacuum systems as "an uncontrolled spontaneous chemical reaction which results in a rapid pressure rise of many orders of magnitude.

The actual rate of pressure rise in a vacuum system such as the Vertical Optical Bench at NASA Goddard, or the six-inch Kinney system in this study is not known. However, the ratio of final pressure or explosion pressure to initial pressure exceeds 10^8. During the explosion limit tests, an explosion consisted of a rise in pressure normally accompanied by a flash of light and an audible crack. However, the pyrex glass flask was not broken by any of the explosions. All explosions resulted in excess carbon in the flask which was removed by boiling oxygen through the flask at elevated temperatures.

3.1 Field Survey

The method used to obtain more reliable information on the number of explosions which have occurred in the past and the condition of the systems at the time of these explosions was to send questionnaires to the two thousand

and six (2,006) members of the American Vacuum Society. These questionnaires asked the following questions:

a. Do you know of any explosions involving a diffusion pump?

b. If yes, do you have any information pertaining to the conditions under which the explosion occurred, and are you able to give us the details?

c. If you have no personal knowledge of the conditions that existed, can you direct us to someone who does?

Everyone who answered yes to the first two questions was contacted personally to obtain more specific information.

3.2 Explosion Limit Determination

Although a large number of investigators have developed methods for determining the explosion limits of volatile liquids and gases at atmospheric pressure and above, a reliable procedure had not been established for determining the explosion limits of liquids with low vapor pressures at reduced pressures. Therefore, a series of preliminary tests were conducted to develop an apparatus which could be used to study the explosion limits of fluids such as DC-704 at reduced pressures. During this preliminary testing, three (3) basic types of test apparatus were evaluated.

The first type of explosion limit test apparatus tested is shown in Figure 1. The major components of this system are the two 300 ml pyrex flasks, used as the oil reservoir and the combustion cell, and the pyrex tube connecting them. This system was operated by placing a small amount of the test fluid in the reservoir and evacuating the system. Then the combustion cell was raised to the test temperature and the reservoir to the proper temperature to provide the desired vapor pressure in the system. The tube connecting the combustion cell and the reservoir was maintained at a temperature 50°F greater than the oil reservoir. Next, oxygen was introduced to obtain the desired total pressure.

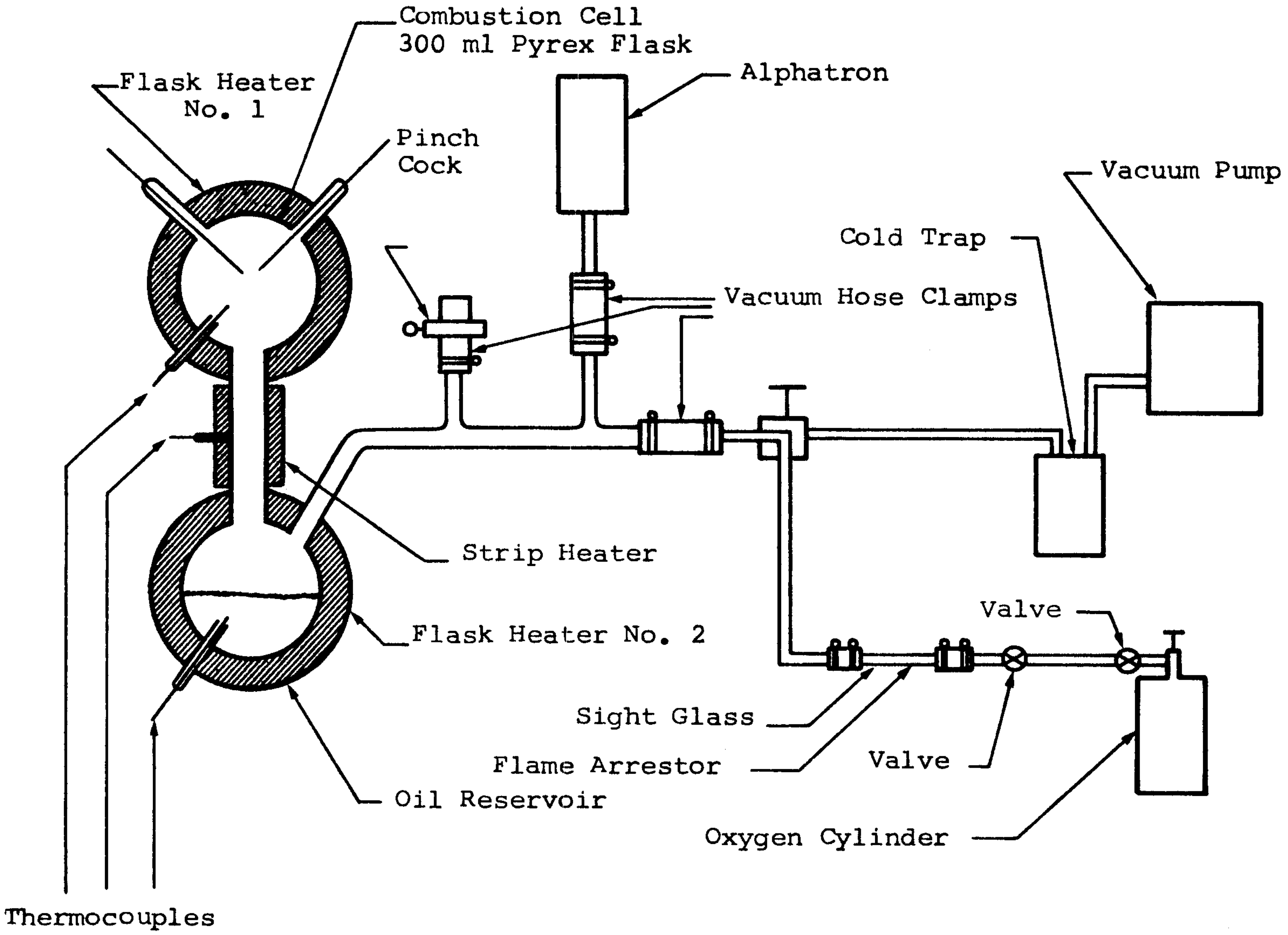


Figure 1 - Explosion Limit Test Apparatus No. 1

The second type of explosion limit test apparatus is represented by Figures 2 through 4. These systems are basically the same. The test fluid is introduced into the boiler flask and then the system is evacuated. Next, the boiler flask is heated to the proper temperature to give the desired vapor pressure and oxygen is introduced to obtain the proper mixtures.

The combustion cell is then heated to the test temperature and the glass break seal is punctured. Various types of break seals were tested to determine the influence the cold spot (break seal) had on the results.

The third type of explosion limit test apparatus is represented by Figures 5 and 6. In the original design shown in Figure 5, a glass stopcock was installed in each of the two capillary tubes. The system was evacuated while being heated to temperature with both glass stopcocks open. Then the pump was valved off and oxygen was introduced. Next, the glass stopcock in the capillary tube leading to the oxygen supply was closed and the test fluid was injected into the combustion cell through the silicone puncture seal. Thus, a known amount of fluid at a known oxygen pressure could be held at temperature indefinitely.

The apparatus shown in Figure 6 was similar to the apparatus shown in Figure 5; however, the size of the combustion cell was increased and the glass stopcocks were removed.

The fluid supplied by NASA Goddard from their Vertical Optical Bench was used as a baseline fluid for all explosion limit tests. Therefore, this sample of fluid was tested extensively from pressures of 50 mm of mercury to 250 mm of mercury with mole percentages of oxygen from 50 to 100.

The used samples of DC-704 fluid from pumps Number 5 and 7 of the Goddard large vacuum system as well as fresh and contaminated samples of DC-704 were tested only at sufficient points to determine the relative thermal stability of each fluid with respect to the Vertical Optical Bench fluid.

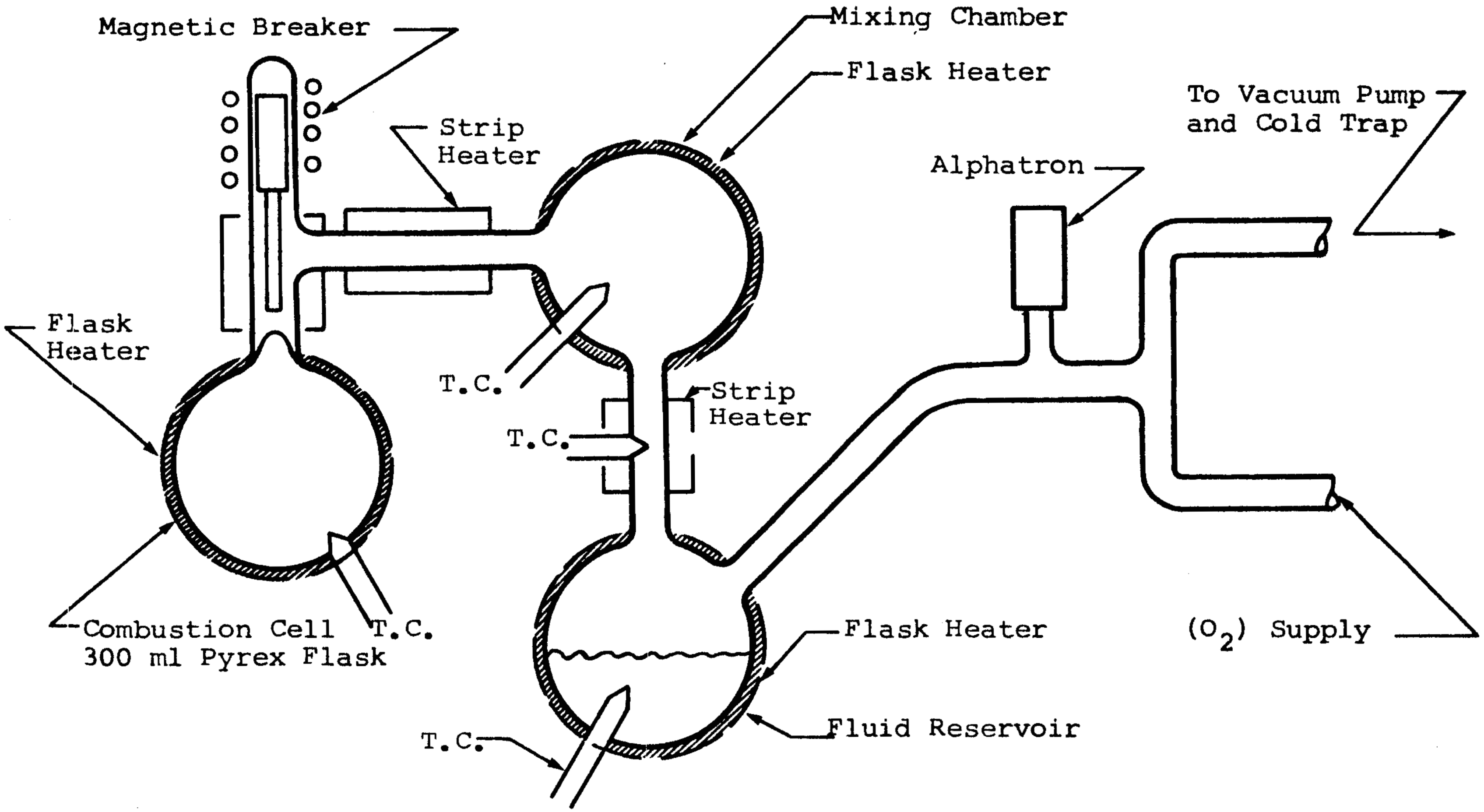


Figure 2 - Explosion Limit Test Apparatus No. 2

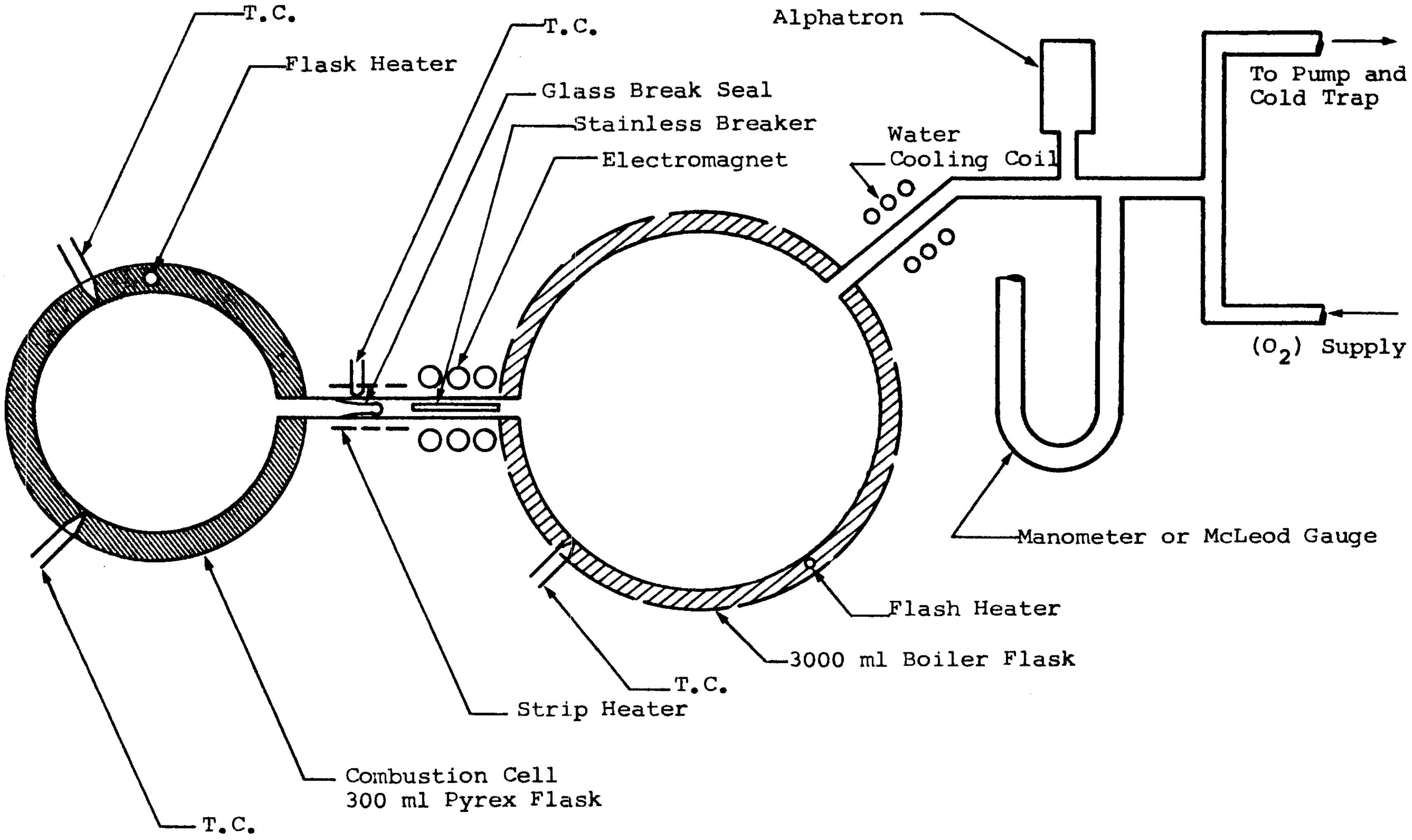


Figure 3 - Explosion Limit Test Apparatus No. 3

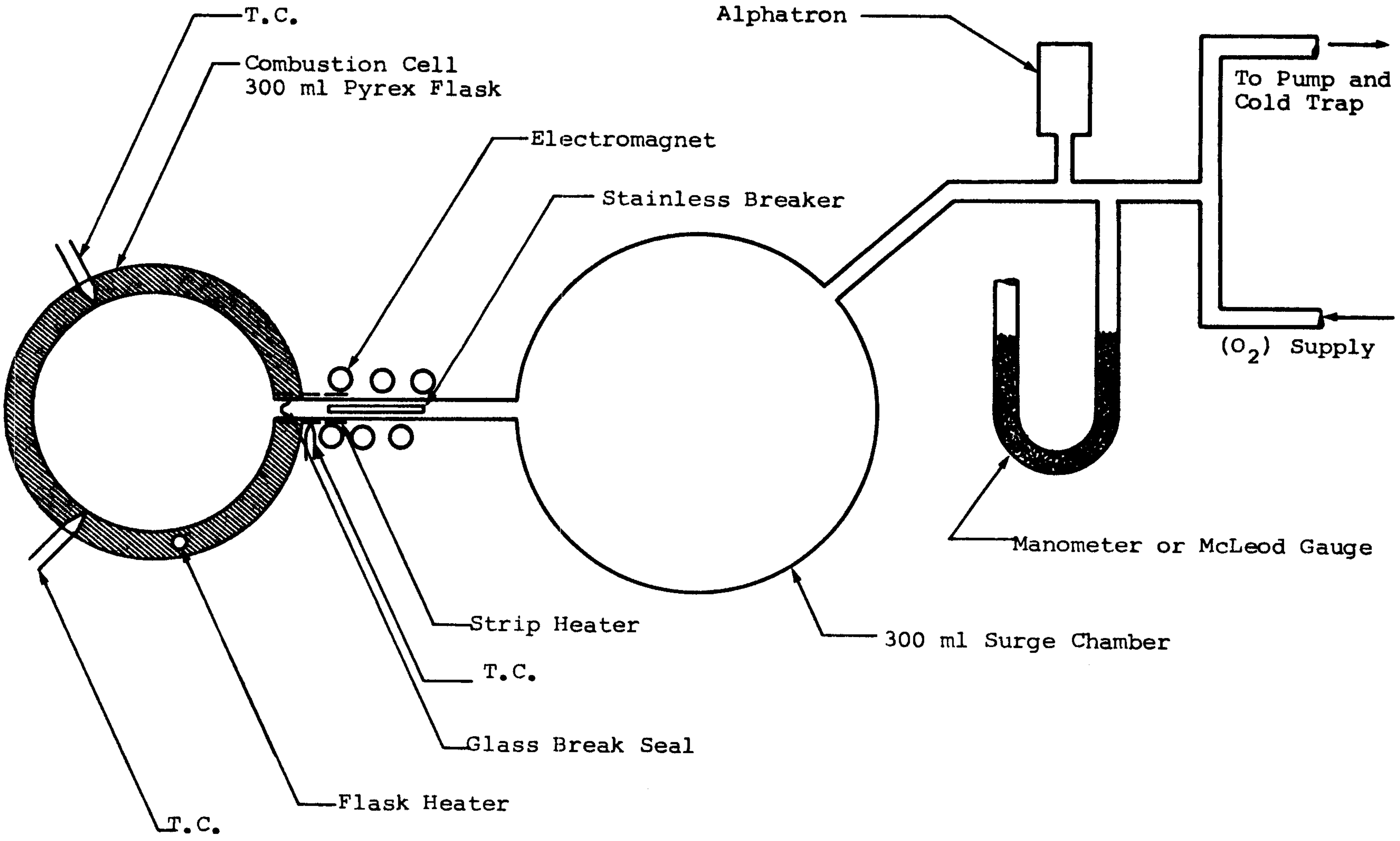


Figure 4 - Explosion Limit Test Apparatus No. 4

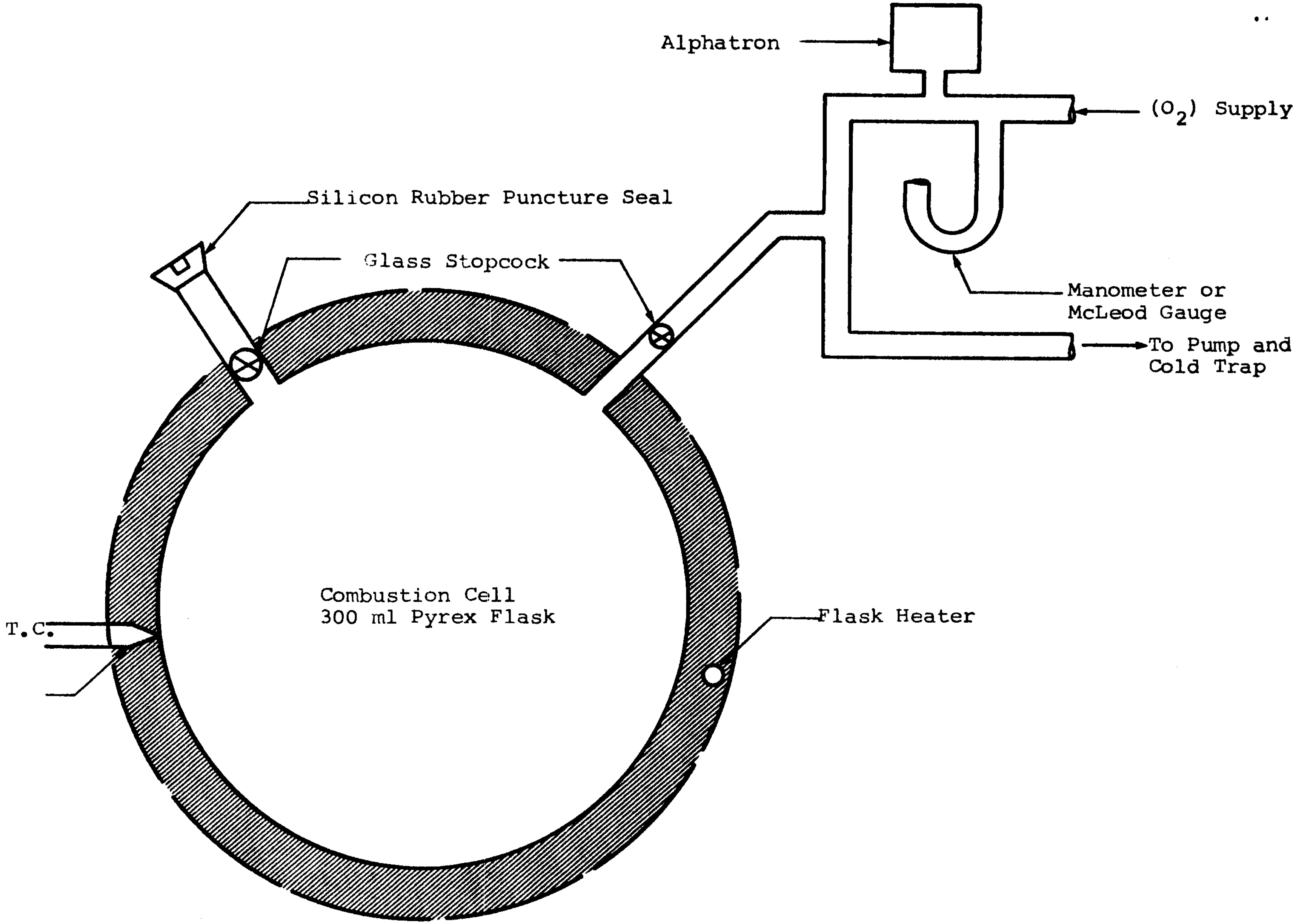


Figure 5 - Explosion Limit Test Apparatus No. 5

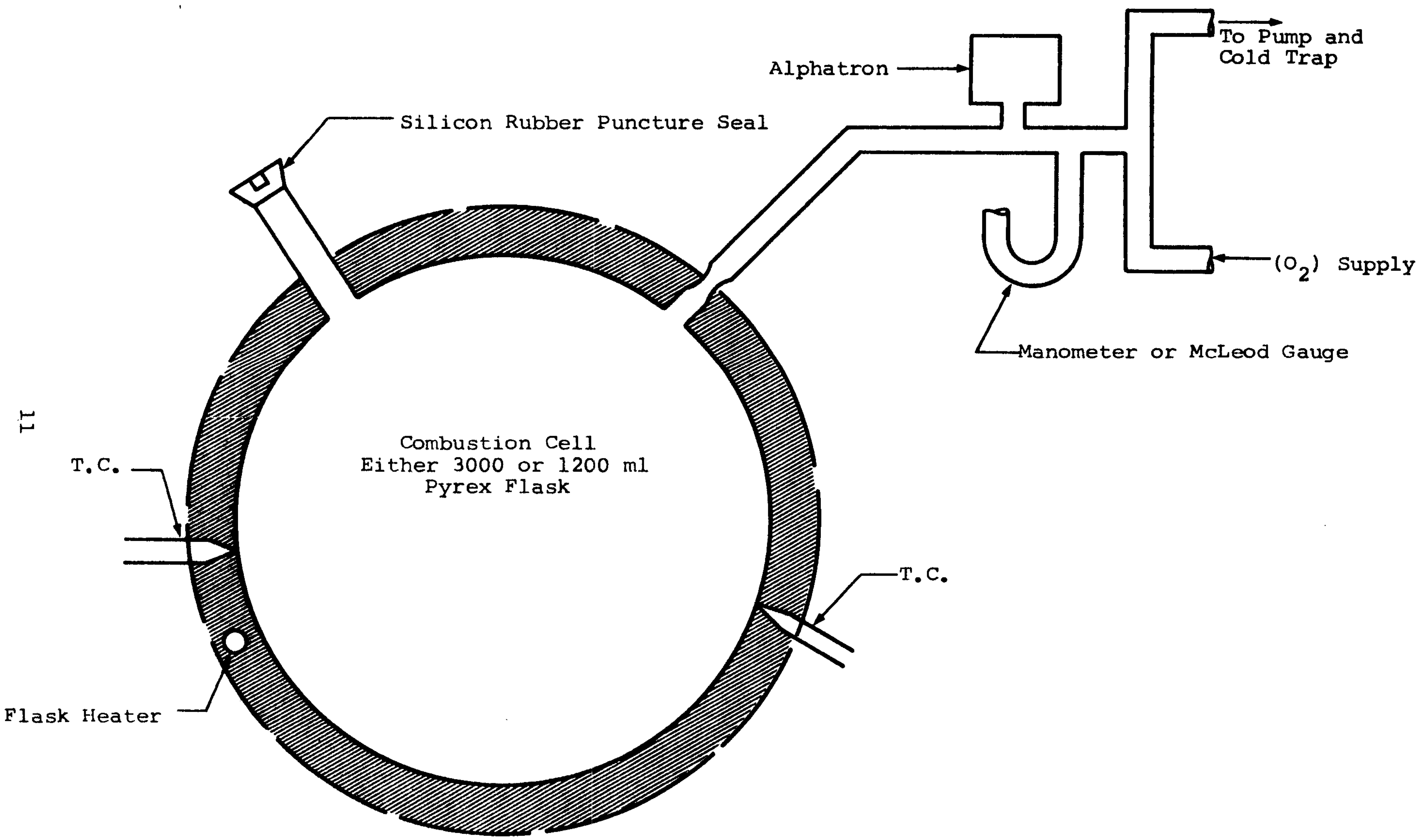


Figure 6 - Explosion Limit Test Apparatus No. 6

3.3 Analysis of Pump Fluids for Contaminants

Characterization studies were conducted on six (6) diffusion pump fluids. The fluids analyzed included two (2) fresh samples of DC-704 and four (4) used samples. The sample referred to as sample Number 1 was a used fluid supplied by NASA Goddard from the Number 5 pump on the Goddard large vacuum system. Sample Number 2 was from pump Number 7 on the same system. Sample Numbers 3 and 3A were both from the Goddard Vertical Optical Bench. This system was pumped by two (2) Kinney diffusion pumps. One of the pumps exploded in March of 1966. Samples 3 and 3A were removed from the pump which was not involved in the explosion. Since there appeared to be a physical difference between Samples 3 and 3A, each was treated as a separate sample. Sample Numbers 4 and 5 were fresh DC-704 samples.

The six (6) samples, as supplied, were dissolved in absolute methanol and scanned in the region of 220 to 440 mμ on a Cary, Model 14 ultra violet spectrophotometer. The scan speed was maintained at 10Å/sec with a full scale recorder range of 0-1 optical density units.

Each sample was also analyzed as a thin film on a NaCl window using a Perkin-Elmer Model 137 Infracord. This analysis was made to detect the presence of any contaminants having structural configurations different from fresh DC-704.

Initial gas chromographic studies were carried out on all six fluid samples isothermally at 300°C in a Loenco Model 70, dual-flow gas chromatograph. The coiled copper column used for analysis was 3/16-inch by 6-feet and contained a 60-80 mesh Chromosorb (ABS). Helium served as a carrier gas at an inlet pressure of 30 psig. The signal from the compensating electrometer was directed to a 0-1 multivolt recorder representing a signal current of 10^{-9} amperes full scale. For all preliminary analyses, a total sample volume of 1 microliter was used in order to maintain the major components of the DC-704 fluid on scale. In order to detect the remaining components, an increased sensitivity factor of 16X was used.

Each sample was further analyzed by gas chromatography on two (2) columns at low temperature to determine the number and amount of low boiling contaminants contained in each fluid. The operating system for the low temperature tests consisted of one 3/16-inch by 6-foot column with 3 percent SE at 75°C and another 3/16-inch by 6-foot column with 15 percent Carbowax 20M at 100°C.

After the initial screening of the samples was completed, an internal standard was added to Sample Number 1 to determine an order of magnitude of the impurity. Based on the assumption that the major low boiling constituent was "propanol" or a similar component, butanol was chosen as an internal standard. A weighed amount of butanol was added to 10 ml of the oil and appropriate dilutions made until the peaks (chromatographic) were approximately the same size. Calculating the area of each peak and assuming equal response factors, the level of "propanol" was determined to be 0.169 mg/ml in Sample Number 1. The remaining five samples were quantitated by employing this same technique. The level of impurity is given in the results.

For the purposes of isolating and identifying low levels of volatile contaminants in the Goddard samples, the samples were stripped under vacuum of their light end material. This was accomplished by placing approximately 30 ml of each fluid in a round bottom flask and evaporating into a specially designed vacuum line assembly. The fluid was cooled to liquid nitrogen temperatures at which time the head space air was evacuated by momentarily opening the sample to vacuum. The entire system was then closed off at 0.005 mm of Hg and the sample permitted to warm up to room temperature under vacuum. The nitrogen saturated porous granules placed at the bottom of the fluid degassed under vacuum and initiated ebullition for dispelling volatile material from the liquid phase. The volatile components were then collected in a sampling cold trap maintained at liquid nitrogen temperature. In several instances, on warming up to room temperature, the DC-704 fluid foamed considerably indicating rapid degassing of volatile components. This was especially true with Samples 1 and 2. After approximately four (4) hours or when degassing appeared to subside, the sampling container was closed off and removed from the line. This sample was then used for mass spectrometry analysis. In addition to the used fluids, two fresh DC-704 fluids (Samples 4 and 5) were carried through the same procedure in order to secure control specimens.

The six (6) samples of the diffusion pump fluids were prepared for analysis by mass spectrometry by adding approximately ten (10) microliters of the liquid to a pyrex sample holder, and cooling to liquid nitrogen temperature. The frozen liquid was sealed into the instrument sampling system and evacuated. The samples were then allowed to warm up to approximately 150°C whereupon the vapor thus far collected was analyzed from m/e = 12 to m/e = 100. By the time m/e = 100 was reached, the remaining sample had heated to 200°C whereupon the additional volatiles were analyzed from m/e = 12 to m/e = 500.

All six diffusion pump fluids were also screened on a Varian DP-60 Nuclear Magnetic Resonance spectrometer operating in the 56.4 mega cycle range. A high sensitivity coil was used, which would have detected fluroine concentrations of 1/2 to 1 percent.

3.4 Stability of DC-704

The stability of DC-704 under normal diffusion pump operating conditions was studied in a Kinney six-inch diffusion pump system. The system included a fifteen-inch bell jar, a liquid nitrogen baffle, a high vacuum valve, a water cooled cold cap, a mechanical roughing pump, and a liquid nitrogen cold trap. System pressures were monitored by a compensated thermocouple gauge in the chamber and foreline, and on an ionization gauge in the chamber. In addition, a sampling apparatus which was designed for removing liquid phase diffusion pump fluid samples from the operating system was mounted on the diffusion pump. This system is shown in Figures 15 and 16.

The sampling apparatus resembled a syringe. It consisted of a 3/16-inch outside diameter by 1/8-inch inside diameter stainless steel tube with a 1/8-inch diameter piston and special seals to maintain a vacuum as the syringe was inserted into the diffusion pump through a 3/4 ball type vacuum valve.

This system was charged with fresh DC-704 and operated continuously for sixty (60) days to study the stability under normal operating conditions of DC-704. Samples were removed daily from the liquid phase of the pump and analyzed by gas chromatography.

Twice during the sixty (60) day stability test of DC-704 in the six-inch system, the fifteen-inch bell jar was cleaned with acetone and then replaced in the system after it had air dried. During this series of tests the cold trap in the foreline was maintained at liquid nitrogen temperature. However, the liquid nitrogen baffle above the diffusion pump was not used. The six-inch Kinney diffusion pump vacuum system used for these tests was selected primarily because of its availability. Also, the superheater arrangement is very similar to others used in the vacuum industry.

The physical arrangement of the vacuum system used to study the influence of ozone on the stability of DC-704 is shown in Figure 17. The system consisted of the same six-inch Kinney vacuum system used in the previous stability studies, but modified by adding the adjustable Granville Phillips leak, the ozone generator, a stainless steel orifice plate, and an additional ionization gauge. These components were added to the system specifically for the ozone tests. Prior to this, the system had been in continuous operation for sixty (60) days. No significant change occurred in the fluid during this time. Therefore, fluid which had been used previously for sixty days was left in the pump.

The orifice plate consisted of a stainless steel plate with a 10 mm diameter sharp edged orifice at the center. This orifice plate was placed in the system to fix the pumping speed at a reduced value. Therefore, the rate of leakage into the system through the adjustable leak could be calculated as a function of the ultimate pressure above the orifice plate.

When the system reached steady state, the pressures in the system were 2.3×10^{-6} torr below the orifice plate and 7.0×10^{-6} torr above the orifice plate. At this time, liquid nitrogen was supplied to the cold trap in the foreline, but not to the liquid nitrogen baffle above the diffusion pump. At 9:00 am a sample of diffusion pump fluid was removed from the liquid phase of the pump.

At 10:00 am the lines between the dewar into which ozone was supplied by the ozone generator and the calibrated leak were evacuated and the ozone generator was started. Then the adjustable leak was opened until the pressure in the system above the orifice plate read 7.4×10^{-6} torr. This was equivalent to a calculated air leak of 3.2×10^{-6} torr-liters per second or 4.2×10^{-6} standard cc/sec. Since the ozone generator produces 20 ppm of ozone in air, this leak rate allows approximately 3.4×10^{-12} moles of ozone to enter the system per second. The ozone was generated by a corona arc type ozone generator which was previously calibrated as 20 parts per million in air.

Samples were removed from the liquid phase of the diffusion pump fluid through the sampling apparatus at 12:00, 2:00, 4:00, and 5:30. After the sample was removed at 5:30, the ozone generator was turned off and the adjustable leak was closed. Since no apparent problems had developed from bleeding ozone into the system, it was decided to allow the diffusion pump to remain in operation overnight. Thus, a sample could be removed in the morning to determine if the pump had purged itself of any ozone which had been incorporated into the fluid.

The effect of aluminum contamination on the thermal stability of DC-704 was investigated at 450°F and 525°F. Four (4) catalytic baths were operated for sixty-one (61) days at temperatures of 450°F and 525°F. All the catalytic baths were operated in a non-turbulent air environment at atmospheric pressure. Two of the baths were contaminated with aluminum and two were filled with fresh DC-704. One fresh and one aluminum contaminated DC-704 bath were maintained at 450°F and the other fresh and contaminated baths were held at 525°F.

4.0 RESULTS

4.1 Field Survey

Twelve hundred and fifteen (1,215) replies were received from the two thousand and six (2,006) members of the American Vacuum Society to whom we sent the diffusion pump questionnaires. Nine hundred and forty-five (945) of these were negative, since all three (3) questions on these questionnaires were answered no. Forty-eight (48) members requested clarification of the program, one hundred and forty-nine (149) gave information which was of no value to the program, and seventy-four (74) gave an affirmative answer.

Further analysis of the seventy-four (74) affirmative answers showed that the reported explosions occurred under a wide range of conditions. However, only one of the replies reported an explosion in a diffusion pump under steady state high vacuum conditions. The remaining affirmative replies reported explosions in diffusion pump systems, but not necessarily in or caused by the diffusion pump. These replies can be grouped into five (5) classifications as follows:

1. Pressurization of a hot diffusion pump with either air or oxygen. This can occur by improper valve sequencing, leaky seals, a break in the system, or by a normal pressurization procedure. Under these circumstances, an ignition source was normally present in the system such as an ionization gauge or a hot metal filament.
2. The forepump or roughing pump was turned off, while the diffusion pump remained in operation. Normally when this occurs, a hot metal filament or an ionization gauge acts as a glow plug.
3. Removal of liquid nitrogen from the cold trap which causes a rapid expansion of the trapped gases in the cold trap.
4. Pumping oxygen from vacuum systems with a mechanical pump.

5. Explosion which occurs during a change over such as opening or closing large vacuum valves, and therefore could be caused by any or all of the first four conditions.

4.2 Explosion Limit Determination

The results of all explosion limit tests on the DC-704 fluid samples identified in Section 3.3 conducted with test apparatus Numbers 1, 2, 3, 4, and 5 were negative. The test temperatures ranged as high as 1000°F. These five test apparatus are shown in Figures 1 through 5.

The results of explosion limit tests using test apparatus Number 6 are tabulated in Tables 1 and 2. Table 1 shows the results obtained when a 3000 ml pyrex flask was used, and Table 2 shows the results obtained when the vessel size of the test apparatus was increased to 12,000 ml.

The results shown in Table 1 indicate the explosion limit temperatures of the sample from Pump Number 7 and the sample from the Vertical Optical Bench are almost identical. These results also indicate that the explosion limit temperature of fresh DC-704 is approximately 50°F higher than that of either the Vertical Optical Bench fluid or the Number 7 pump fluid. In addition, these results indicate that samples of DC-704 which are contaminated with either copper or aluminum and aged in an air environment at 450°F for two (2) weeks will degrade slightly. This degradation will lower the explosion limit temperature by approximately 50°F as compared to the fresh DC-704 samples.

The results tabulated in Table 2 show the explosion limit temperatures of all used and contaminated DC-704 fluid samples tested using apparatus Number 6 with a 12,000 ml vessel were essentially the same.

Table 2 also contains the results of tests conducted on fresh samples of DC-704. These results show the explosion limit temperatures of fresh DC-704 are approximately 50°F higher than that of all used and contaminated fluids tested. The used and contaminated fluid results include tests with the three (3) used fluids of DC-704 supplied by NASA Goddard, samples contaminated with

TABLE - 1

RESULTS OF EXPLOSION LIMIT TESTS CONDUCTED WITH APPARATUS
NUMBER 6 USING 3000 ml FLASK

Combustion Cell Temp. (°F)	Pressure (O_2) (mm)	Volume of Fluid Injected (cc)	Pressure of DC-704 (mm)	Mole (O_2) (%)	Result	Induction Time If Explosion (Sec.)
			Vertical Optical Bench Samples			
1000	200	.110	4.1	98	Expl.	0 5
975	200	.114	4.2	98	Expl.	40
950	200	.108	3.9	98	No Expl.	---
950	200	.205	7.4	97	Expl	60
950	200	.400	14.4	93	Expl.	18
925	200	.400	14.1	93	Expl.	90
925	200	.600	21.1	91	Expl.	30
900	200	.800	27.7	87	Expl.	60
900	200	1.000	34.6	85	Expl.	35
900	200	1.200	41.6	83	Expl.	30 35
875	200	1.200	40.8	83	No Expl.	---
975	165	.990	36.2	82	Expl.	4
925	165	.990	34.9	82	Expl.	35
1020	150	.150	5.7	96	Expl.	12
975	150	.150	5.5	96	No Expl.	---
975	123	.770	28.1	82	Expl.	15
950	123	.770	27.6	82	Expl.	22
925	123	.770	27.1	82	Expl.	105
1000	100	.050	1.9	97	No Expl.	---
1020	100	.100	3.8	97	Expl.	50
1020	100	.200	7.5	93	Expl.	15
1000	100	.200	7.4	93	Expl.	20

TABLE - 1
(Continued)

Combustion Cell Temp. (°F)	Pressure (O_2) (mm)	Volume of Fluid Injected (cc)	Pressure of DC-704 (mm)	Mole (O_2) (%)	Result	Induction Time If Explosion (Sec.)
			Vertical Optical Bench Samples			
975	100	.200	7.3	93	No Expl.	---
1000	100	.600	22.3	82	Expl.	12
975	100	.600	21.9	82	No Expl.	---
			Sample From Pump #7			
1000	200	.108	4.0	98	Expl.	10
975	200	.114	4.2	98	Expl.	70
975	200	.228	8.3	96	Expl.	15
950	200	.205	7.4	97	Expl.	80
900	200	1.100	38.0	84	Expl.	105
			New DC-704			
1040	200	.110	4.2	98	Expl.	40
950	200	1.100	39.5	84	Expl.	30
			Deliberately Contaminated Samples Heated in Air			
			Two Weeks at 450°F			
			Aluminum Contaminated			
900	200	1.000	34.6	85	Expl.	50
			Copper Contaminated			
910	200	1.000	34.9	85	Expl.	150

TABLE - 2

RESULTS OF EXPLOSION LIMIT TESTS CONDUCTED WITH APPARATUS NUMBER 6 USING 12000 ml VESSEL

Combustion Cell Temp. (°F)	Pressure (O_2) (mm)	Volume of Fluid Injected (cc)	Pressure of DC-704 (mm)	Mole (O_2) (%)	Result	Induction Time If Explosion (Sec.)
		Vertical Optical Bench Samples				
900	200	4.8	41.5	83	Expl.	15
875	200	5.9	50.0	80	Expl.	180
950	186	1.6	14.0	93	Expl.	18
925	186	1.6	14.0	93	Expl.	40
900	165	4.0	35.0	83	Expl.	45
875	165	4.1	35.0	83	Expl.	153
900	160	4.8	41.5	80	Expl.	40
900	120	9.3	80.0	60	Expl.	70
975	100	2.4	21.9	82	Expl.	15
950	100	2.4	21.5	83	Expl.	25
925	100	2.4	21.1	83	Expl.	30
900	100	2.4	20.8	83	Expl.	90
875	100	2.4	20.4	83	No Expl.	---
975	90	1.1	10.0	90	Expl.	25
950	90	1.1	9.8	90	Expl.	210
950	70	3.3	30.0	70	Expl.	27
925	70	3.4	30.0	70	Expl.	45
975	50	1.2	10.9	82	Expl.	60
950	50	1.2	10.8	82	No Expl.	---
975	50	1.3	11.9	81	Expl.	40
975	50	1.0	9.1	85	No Expl.	---

TABLE - 2
(Continued)

Combustion Cell Temp. (°F)	Pressure (O_2) (mm)	Volume of Fluid Injected (cc)	Pressure of DC-704 (mm)	Mole (O_2) (%)	Result	Induction Time If Explosion (Sec.)
			Vertical Optical Bench Samples			
975	50	1.50	13.6	79	Expl.	28
975	50	2.0	18.3	73	Expl.	18
975	50	3.0	27.4	65	Expl.	18
950	50	3.0	26.9	65	Expl.	30
950	50	5.0	44.8	53	Expl.	30
950	50	5.6	50.0	50	Expl.	28
1000	39	1.2	11.1	78	No Expl.	---
975	36	1.5	13.7	72	No Expl.	---
1020	25	0.6	5.7	50	No Expl.	---
975	22	3.0	27.4	44	No Expl.	---
1000	22	3.0	27.8	44	No Expl.	---
			Sample From Pump #7			
950	186	1.55	14.0	93	Expl.	23
900	165	4.0	35.0	83	Expl.	50
875	165	4.12	35.0	83	Expl.	128
900	120	9.25	80.0	60	Expl.	63
			Samples From Catalytic Baths			
			DC-704 Control Bath at 450°F Three (3) Weeks			
925	186	1.6	14.0	93	Expl.	93
			Aluminum Contaminated at 450°F Three (3) Weeks			
925	186	1.6	14.0	93	Expl.	60

TABLE - 2
(Continued)

Combustion Cell Temp. (°F)	Pressure (O_2) (mm)	Volume of Fluid Injected (cc)	Pressure of DC-704 (mm)	Mole (O_2) (%)	Result	Induction Time If Explosion (Sec.)
Control Bath at 475°F Three (3) Weeks						
925	186	1.6	14.0	93	Expl.	75
Aluminum Contaminated at 475°F Three (3) Weeks						
925	186	1.6	14.0	93	Expl.	60
New DC-704						
925	200	5.8	50.0	80	Expl.	190
925	160	4.5	40.0	80	Expl.	53
900	160	4.5	40.0	80	Expl.	230
No. 5 Pump Fluid						
950	186	1.6	14.0	93	Expl.	30
900	165	4.0	35.0	83	Expl.	45
875	165	4.1	35.0	83	Expl.	150
900	120	9.3	80.0	60	Expl.	75
DC-704 Plus 50% By Volume Freon-113						
900	186	1.6	----	--	No Expl.	
DC-704 Plus .007 Inch Particles Magnesium						
900	186	1.6	----	--	No Expl.	
DC-704 Plus 50% By Volume Freon-113 Plus .007 Inch Particles Magnesium						
900	186	1.6	----	--	No Expl.	
900	165	4.0	----	--	Expl.	45

magnesium, samples contaminated with aluminum and aged in an air environment at 450°F and 525°F for up to sixty (60) days, as well as uncontaminated samples of DC-704 aged at 450°F and 525°F in an air environment.

Figure 7 shows the effect of vessel size on the spontaneous ignition temperature of the fluid from the Vertical Optical Bench (Sample 3A) at various total system pressures and 83 mole percent oxygen. These curves show two (2) distinct characteristics. First, these curves indicate that a higher temperature is required to generate an explosion with a 3000 ml vessel than with a 12,000 ml vessel. Secondly, these curves demonstrate that a low pressure limit exists for each vessel size below which it is very difficult to generate an explosion. This limit appears to be approximately 120 mm of mercury with the 3000 ml vessel and 50 mm of mercury with the 12,000 ml vessel.

The curves in Figure 7 represent the approximate explosion limits for the DC-704 from NASA Goddard's Vertical Optical Bench. These were obtained as shown in Figures 8 and 9. These curves only approximate the boundary of the explosion region for each vessel size, since the exact limit would require much more extensive testing. The limits were approximated by the length of induction period preceding an explosion and by the points at which no explosion resulted.

Figure 10 demonstrates how the spontaneous ignition temperature of DC-704 from the Vertical Optical Bench varies as a function of the mole percent of oxygen present at total system pressures of 100 and 200 mm of mercury. These curves show a marked decrease in the explosion limit temperature as the percentage of DC-704 is increased. In addition, the curves show that 875°F is the minimum temperature at which an explosion could be generated.

4.3 Analysis of Pump Fluids for Contaminants

The results of the ultra violet analysis of the four (4) samples of the three (3) used fluids and two (2) new fluid samples supplied by NASA Goddard are tabulated in Table 3. As would be expected, the overall absorption spectrum for each sample was, for the most part, very similar. However, by scanning at high concentrations,

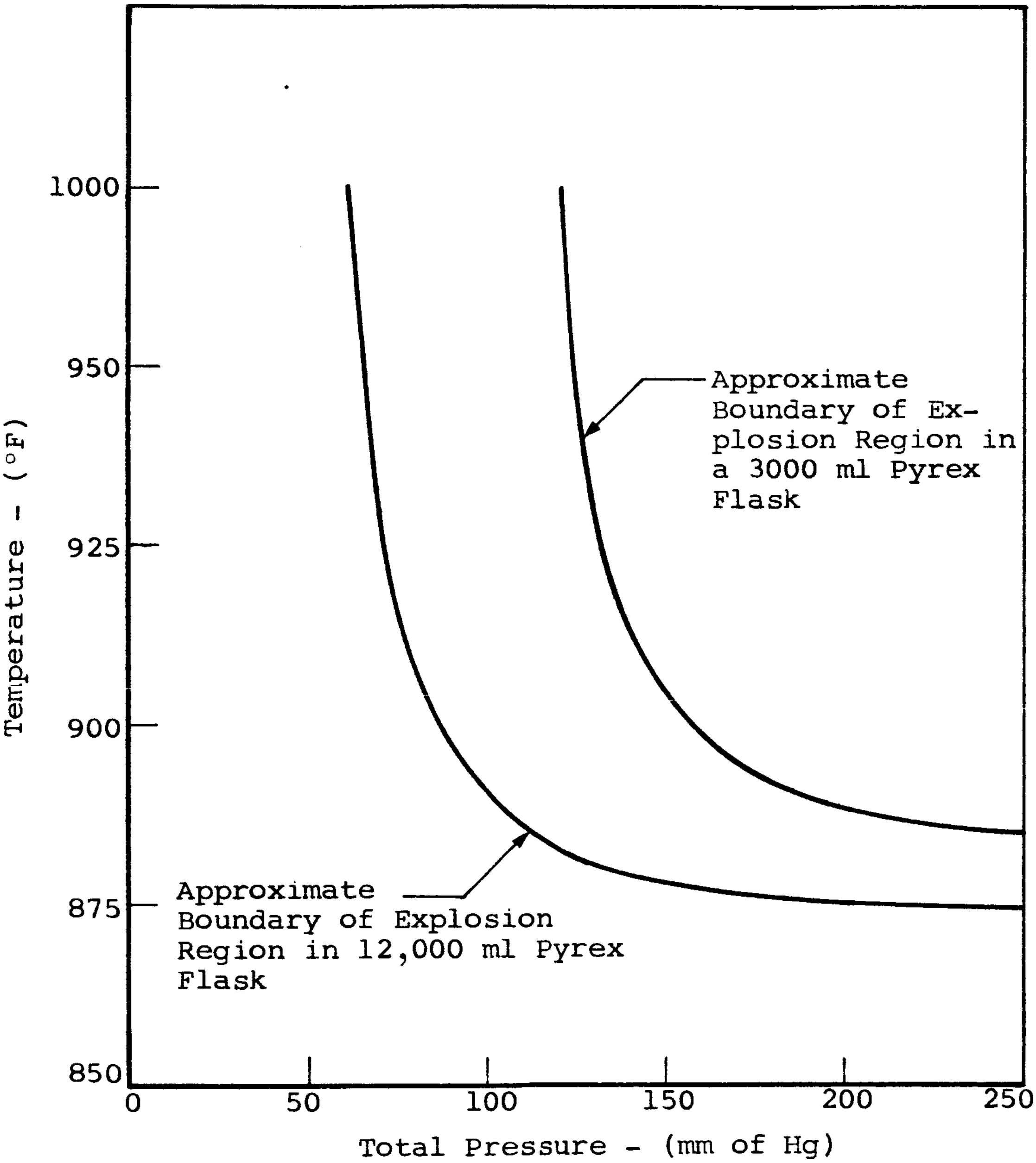


Figure 7 - Spontaneous Ignition Temperature, of DC-704 from Goddard Vertical Optical Bench, as a Function of Pressure at 83 Mole Percent Oxygen Using a 12,000 ml and a 3000 ml Pyrex Flask

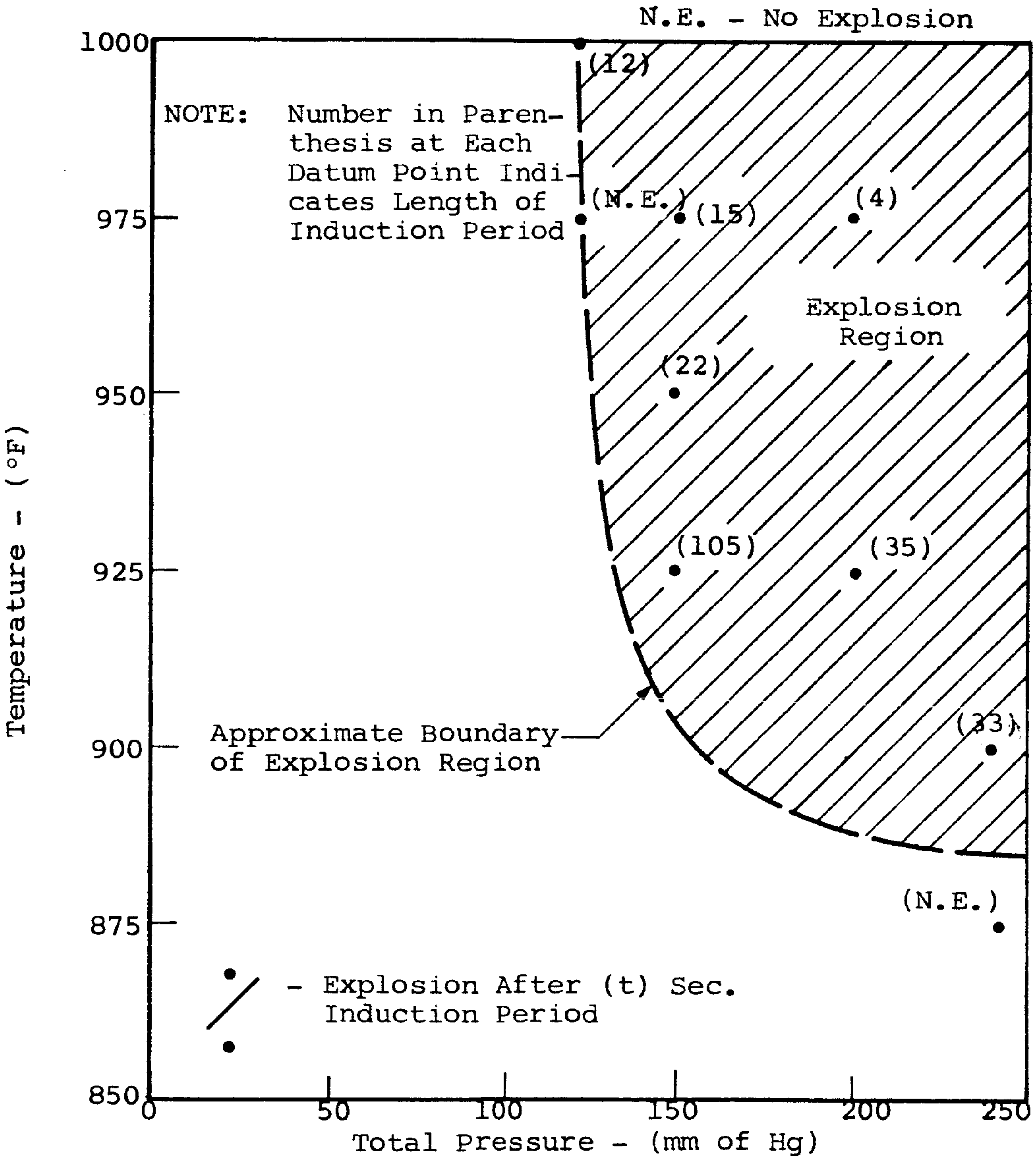


Figure 8 - Spontaneous Ignition Temperature, as a Function of Pressure at 83 Mole Percent Oxygen Using Explosion Limit Apparatus No. 6 with a 3000 ml Flask, of DC-704 from Vertical Optical Bench

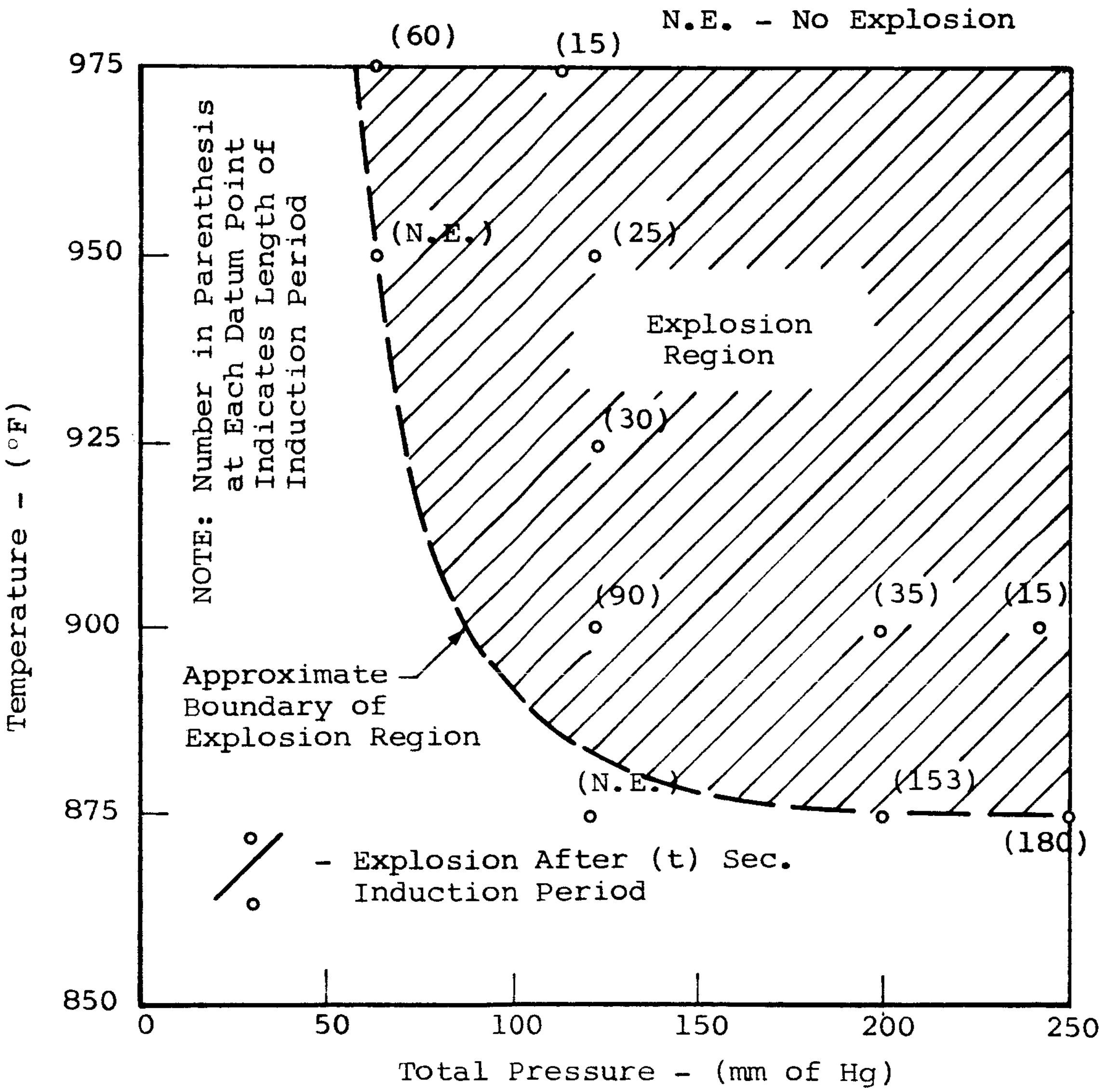


Figure 9 - Spontaneous Ignition Temperature as a Function of Pressure at 83 Mole Percent Oxygen Using Explosion Limit Apparatus No. 6 with a 12,000 ml Flask, of DC-704 from Goddard Vertical Optical Bench

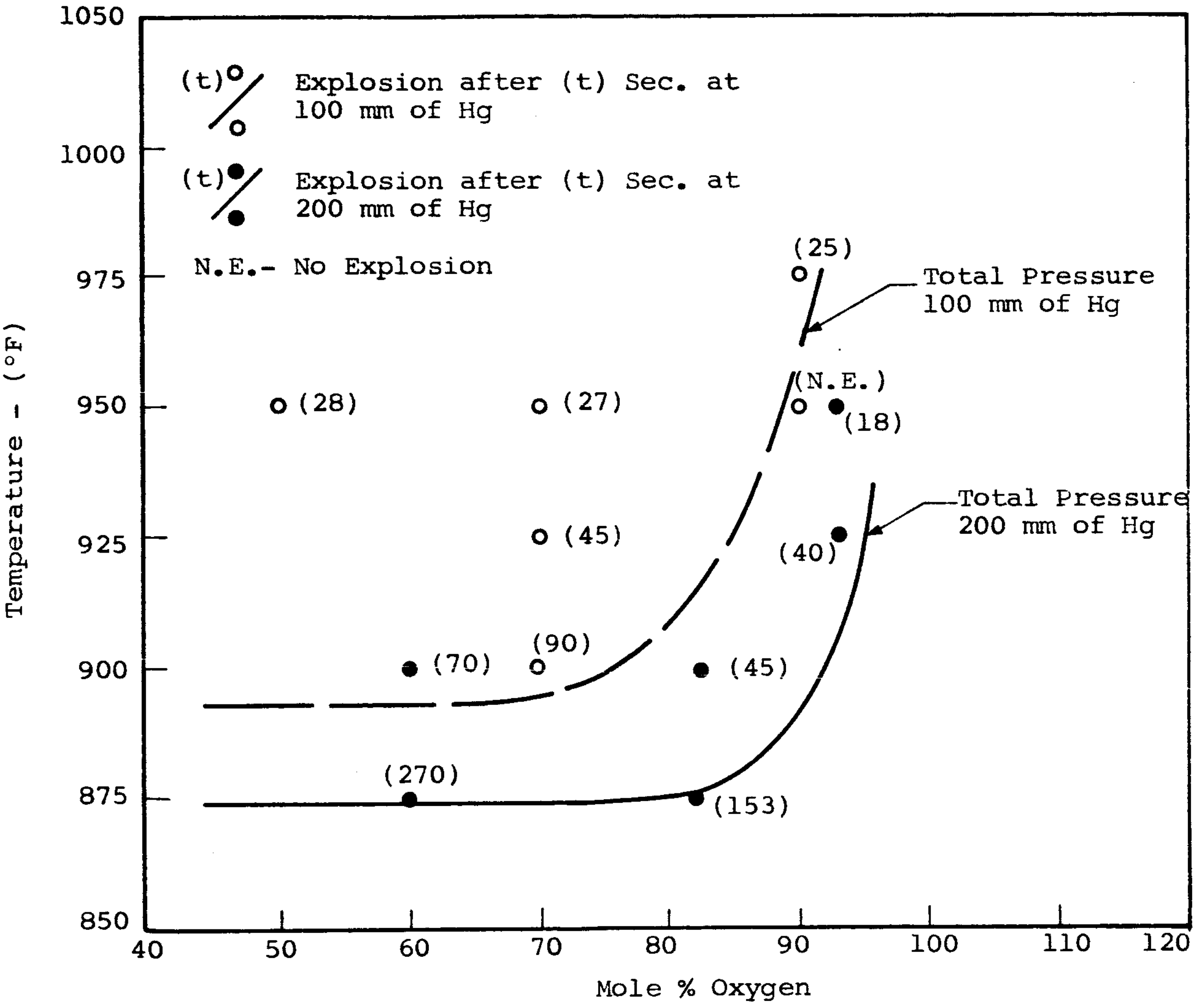


Figure 10 - Spontaneous Ignition Temperature, as a Function of Mole Percent Oxygen in a 12,000 ml Pyrex Flask of DC-704 from Goddard Vertical Optical Bench

TABLE - 3

DIFFERENCES OBSERVED IN THE ULTRA VIOLET REGION FOR NEW AND USED DC-704 FLUIDS

Sample	Identification	Concentration mg/ml	Optical Density 285 mμ	322 mμ
1	Pump #5 at NASA-Goddard's large space chamber	3.49	Trace	0.066
2	Pump #7 at NASA-Goddard's large space chamber	3.51	Trace	0.058
3	NASA-Goddard's Vertical Optical Bench	3.50	0.014	0.292
3A	Second sample of (3)	3.49	0.004	0.142
4	New DC-704	3.51	0.005	0.120
5	New DC-704	3.51	0.005	0.120

small differences did become apparent. The main differences observed were associated with absorption bands at 285 and 322 mμ. Infrared analysis on these same samples showed no basic compositional differences.

The low temperature gas chromatography screening of each sample showed the presence of one or more low boiling components. The results are tabulated in Table 4. The major contaminant was not identified, but appears to be proponal or a closely related material. This identification is based only on the relative retention time obtained from the gas chromatographic tracing and the mass spectrographic analysis which indicated a peak with a m/e = 31 which could be due to a CH_2OH moiety. This is characteristic of alcohols and some ethers.

Gas chromatographic studies of the six (6) DC-704 samples were carried out at both low and high column temperatures in order to study the overall composition of each fluid. The high temperature analyses showed the presence of as many as fifteen (15) different components in each sample. The tracings obtained from Sample Nos. 1, 2, 3A, and 5 are shown in Figures 11, 12, 13, and 14 respectively. The relative percent composition of the three (3) major peaks Numbers 5, 7, and 10 were calculated and are tabulated in Table 4A. The remaining components which were observed only at the higher sensitivity settings represented components at concentration levels in the region of .005 percent by weight or less. The overall results indicate that peak Number 10 shows a marked decrease in the used fluids. However, peak Number 7, which would represent a higher vapor pressure component, appears for the most part to have remained constant or to have increased slightly.

Considerable differences were noted for these samples by low temperature fractionation where the volatile components were concentrated. These volatile components were trapped as they eluted and were analyzed by mass spectrometric analysis. These results are tabulated in Table 5.

The mass spectrometric analysis of the six (6) DC-704 samples identified in Table 3 results in a very complex spectra for all the samples. Outstanding in each spectra were the several metastable peaks which appear to be

TABLE - 4

PERCENT VOLATILE COMPONENTS BY LOW TEMPERATURE GAS CHROMATOGRAPHY

Sample	Weight % Volatile Component*
1	0.017
2	0.012
3	0.004
3A	1.2
4	0.003
5	0.001

*Calculated as m = Butanol

TABLE - 4A

RELATIVE DISTRIBUTION OF THREE MAJOR COMPONENTS OBSERVED FOR NEW AND USED DC-704 FLUIDS BY GAS-LIQUID CHROMATOGRAPHY

	Peak No. (wt.%)		
Sample	5	7	10
1	0.63	99.19	0.18
2	0.58	99.35	0.07
3	0.15	99.66	0.19
3A	0.21	99.10	0.69
4	0.24	98.48	1.28
5	0.27	98.40	1.33

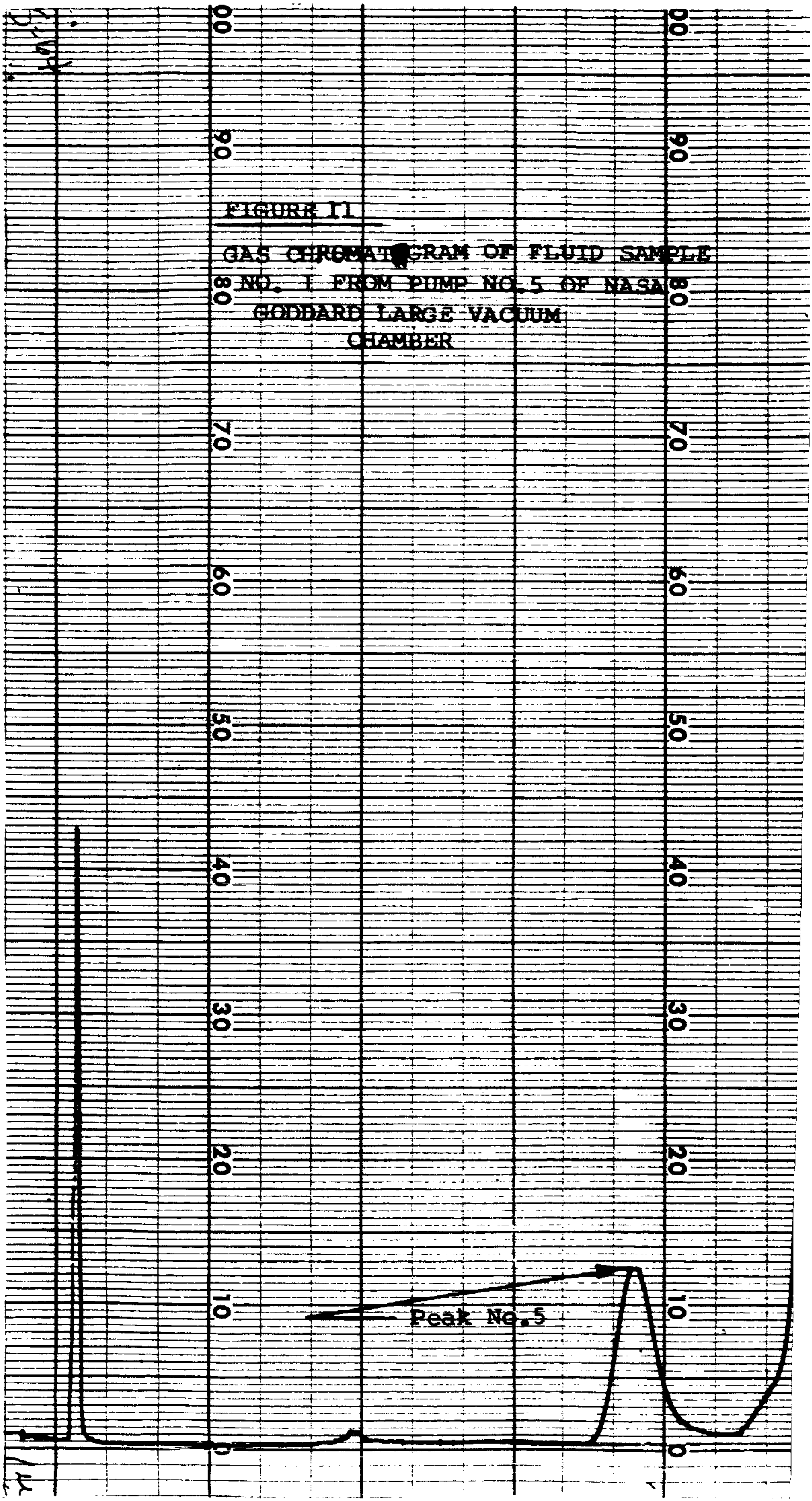
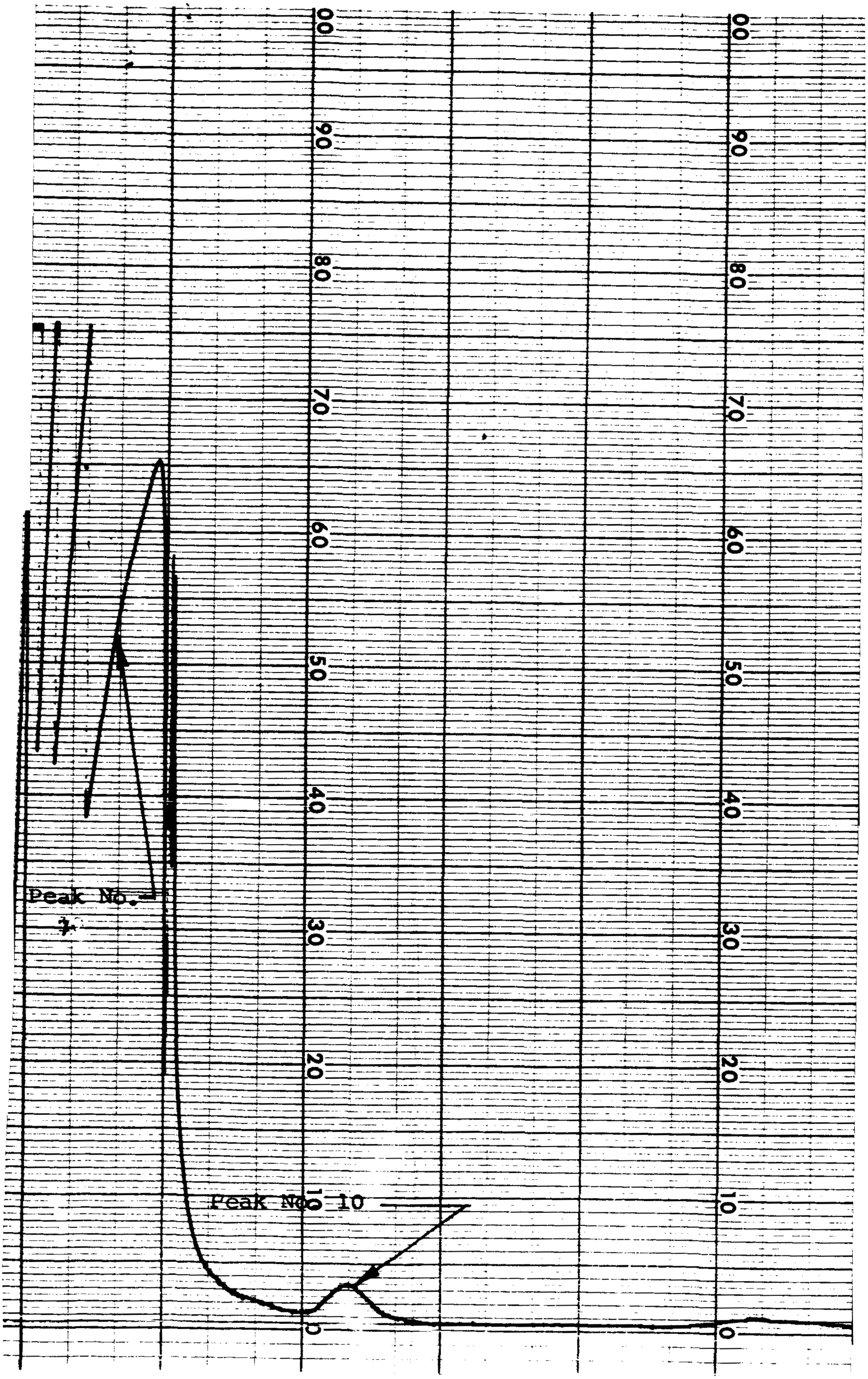
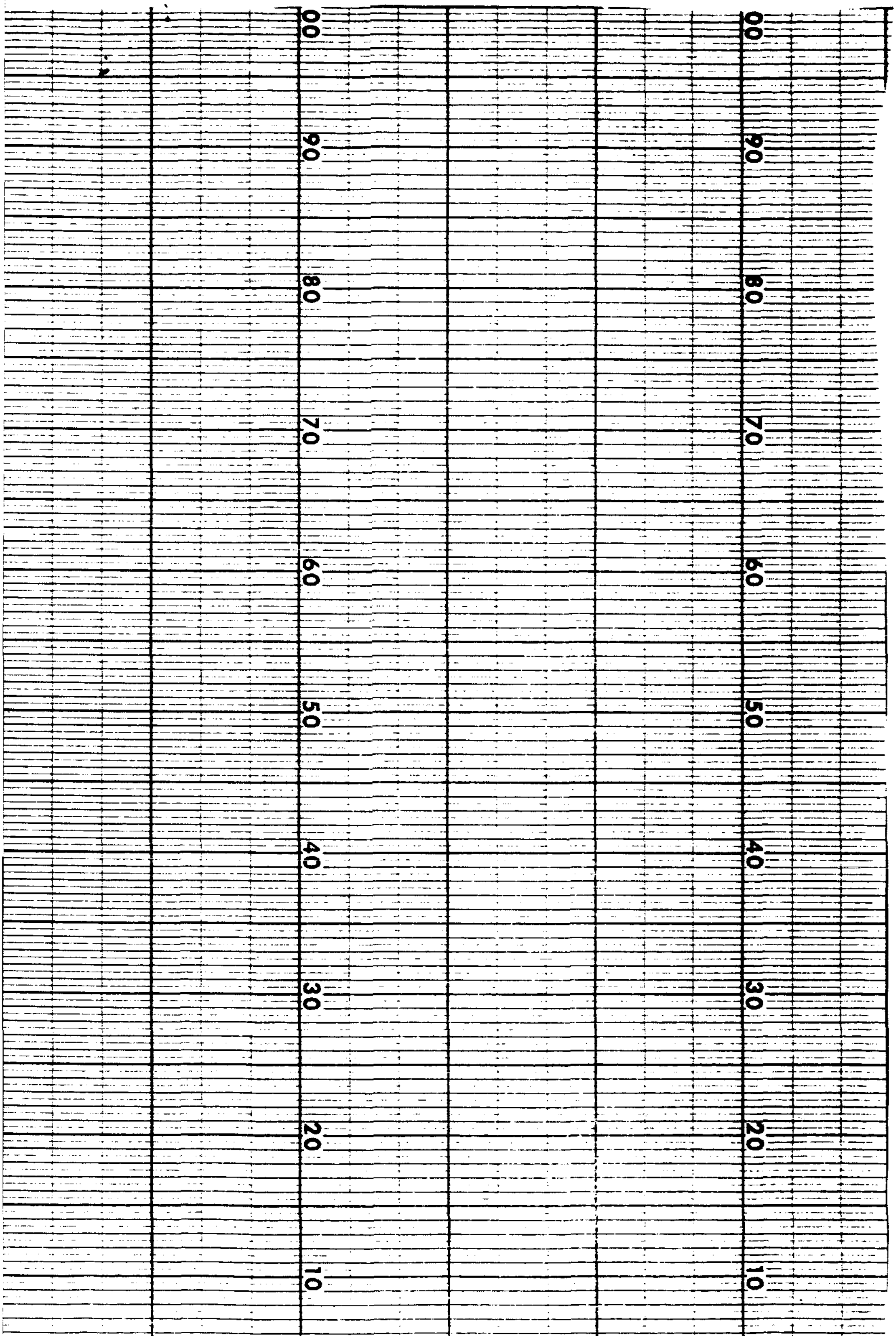


FIGURE 11

GAS CHROMATOGRAM OF FLUID SAMPLE NO. 1 FROM PUMP NO.5 OF NASA GODDARD LARGE VACUUM CHAMBER


00
90
80
70
60
50
40
30
20
10
0
Peak No.
7
Peak No. 10


100
90
80
70
60
50
40
30
20
10
0
100
90
80
70
60
50
40
30
20
10
0

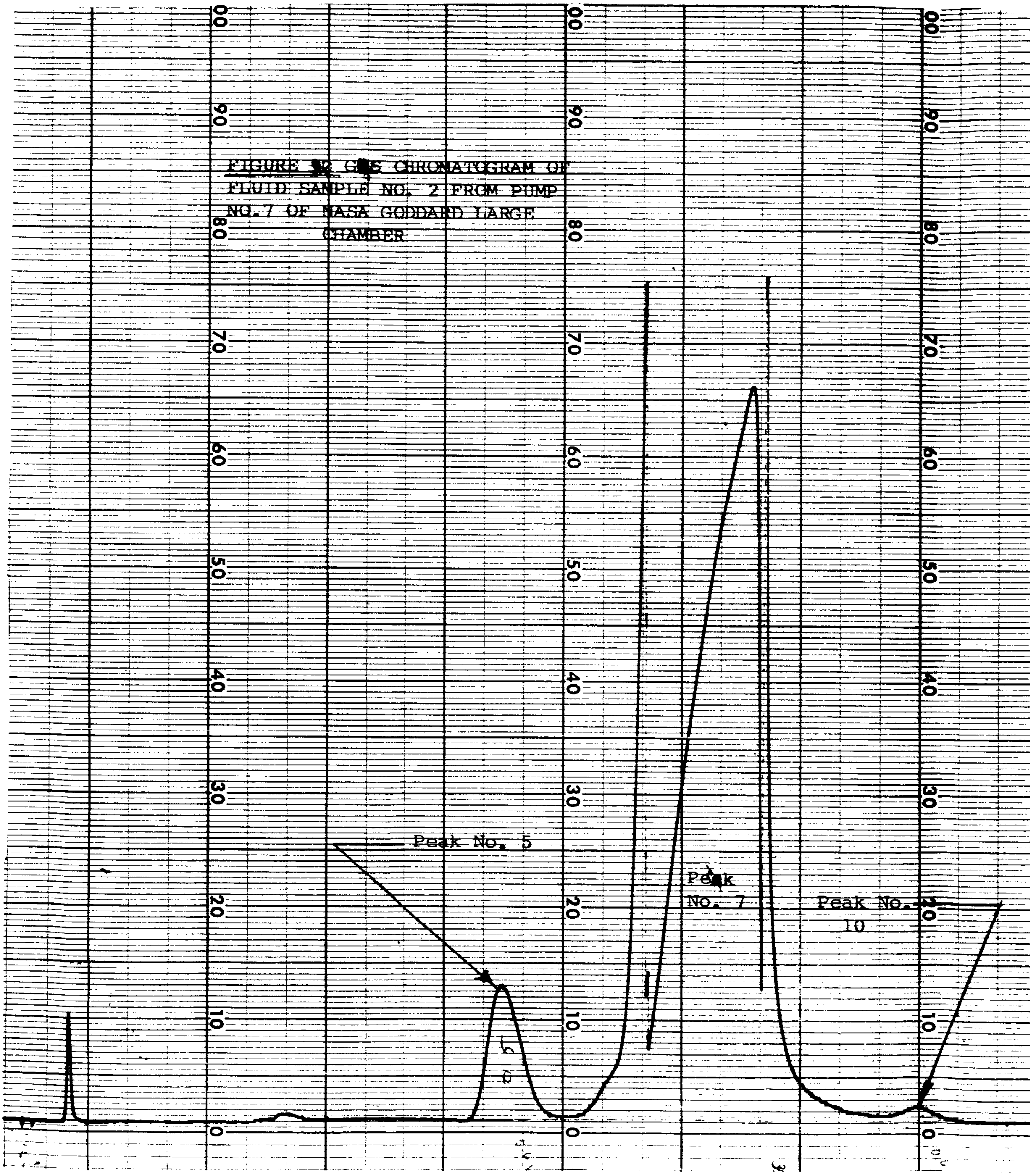
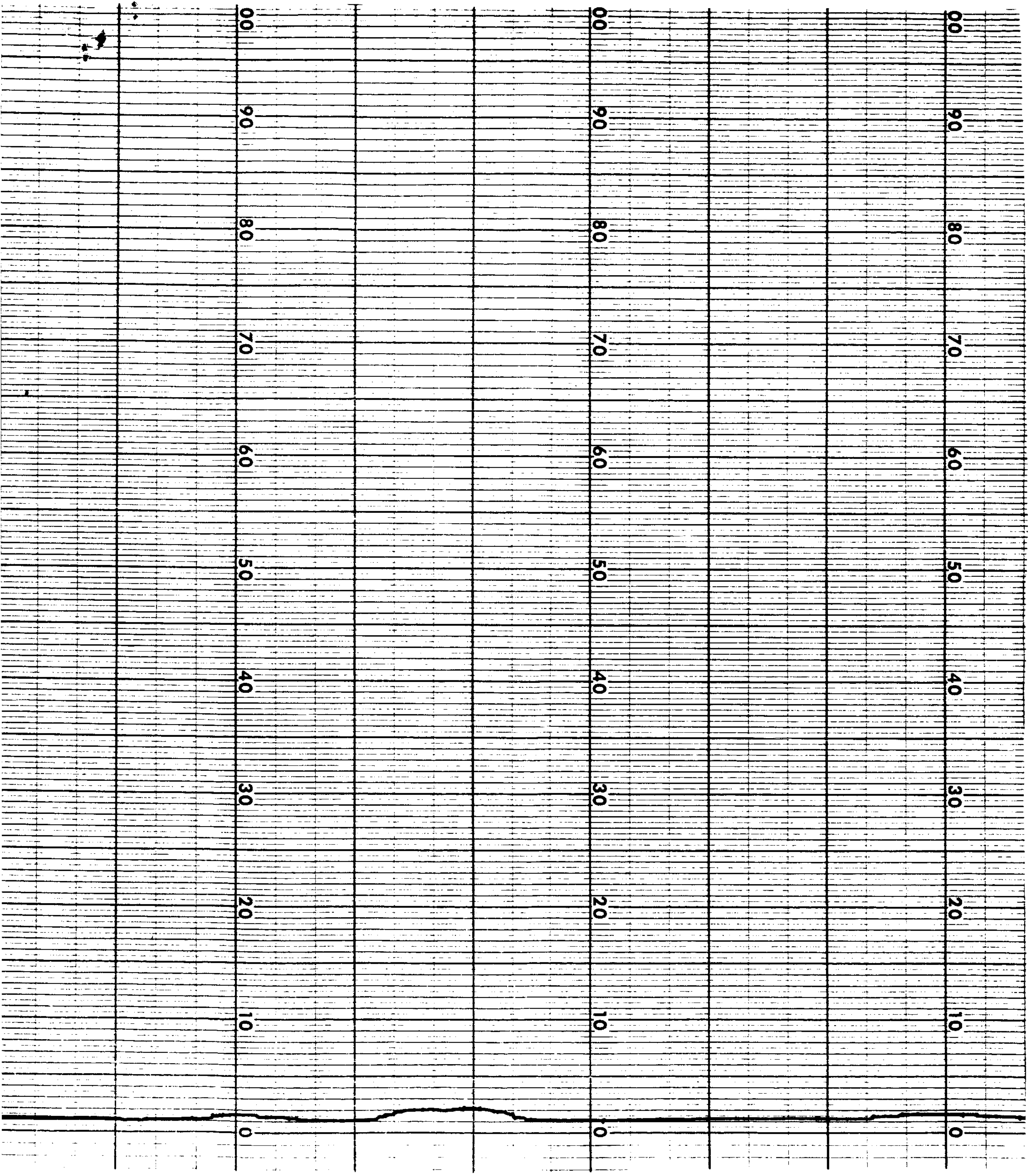


FIGURE 12 GAS CHROMATOGRAM OF FLUID SAMPLE NO. 2 FROM PUMP NO. 7 OF NASA GODDARD LARGE CHAMBER


00
90
80
70
60
50
40
30
20
10
0
00
90
80
70
60
50
40
30
20
10
0
00
90
80
70
60
50
40
30
20
10
0

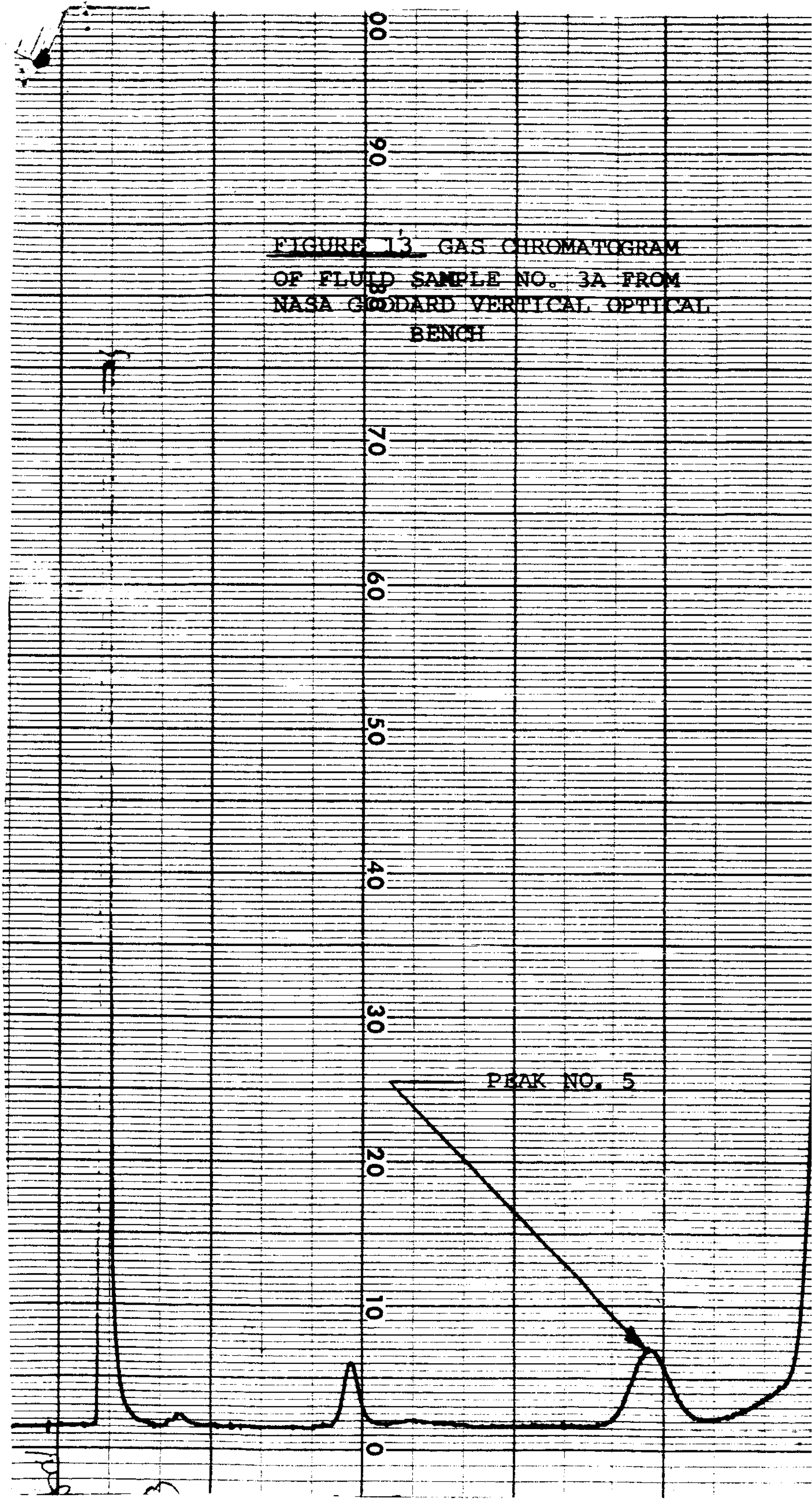
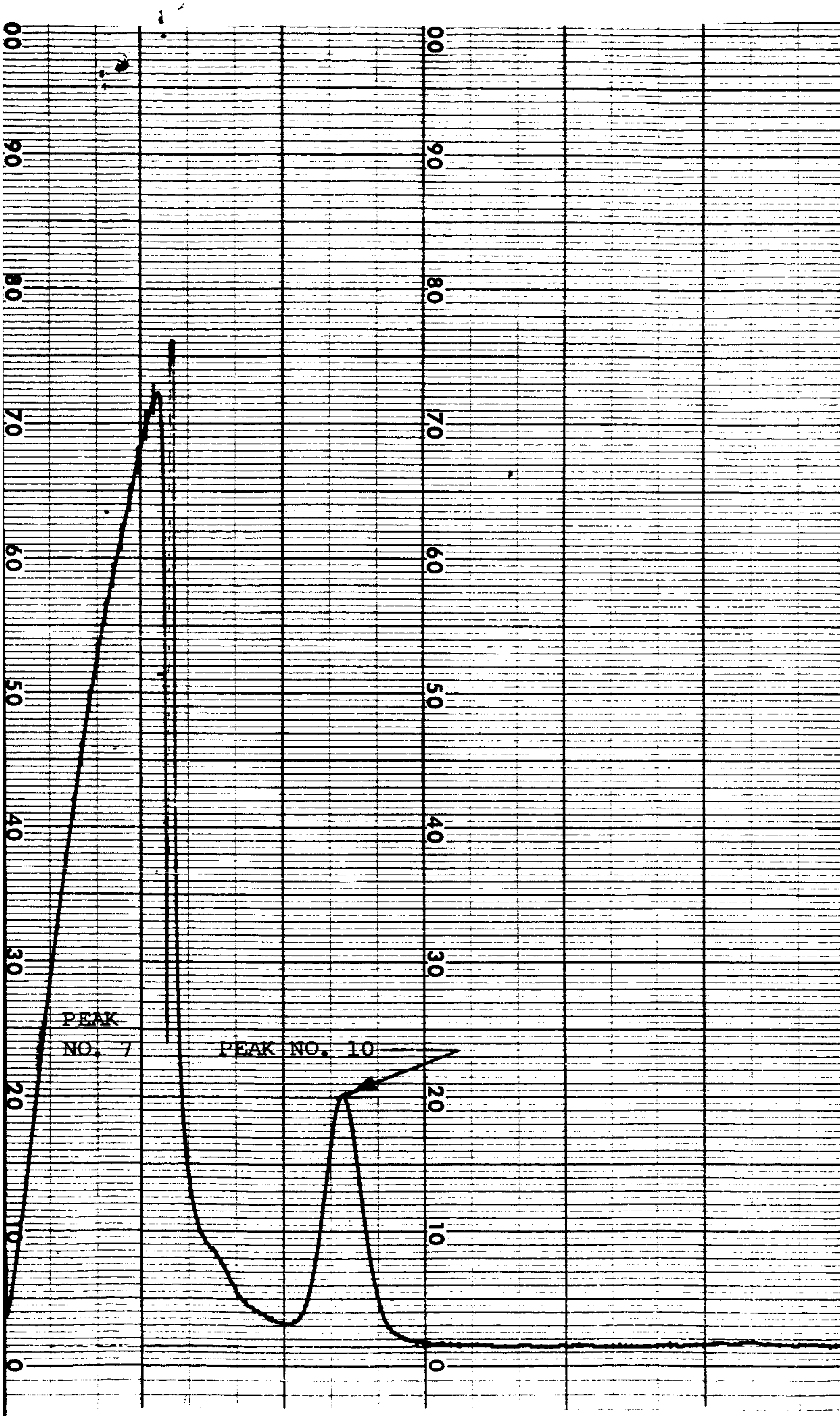
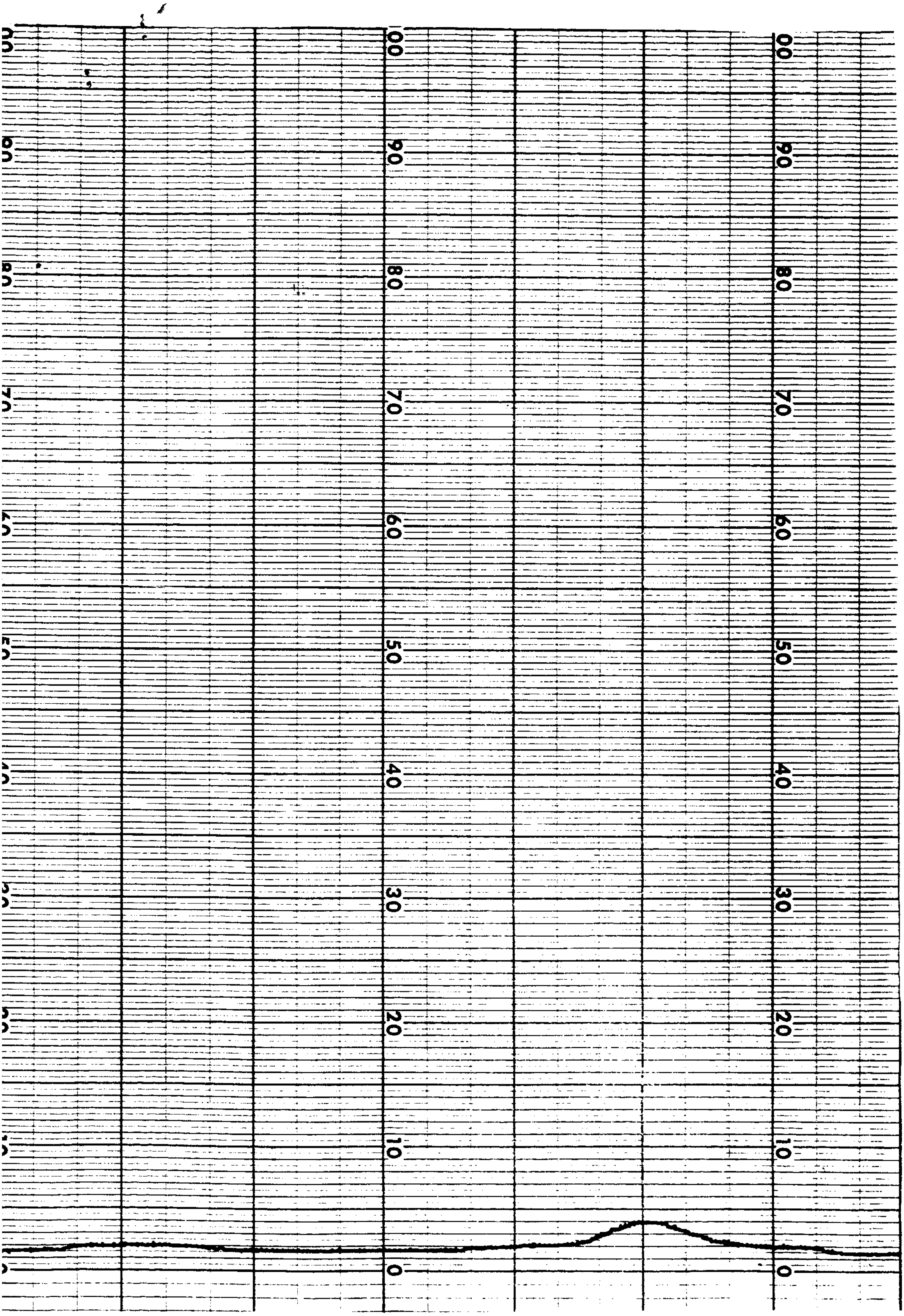


FIGURE 13 GAS CHROMATOGRAM OF FLUID SAMPLE NO. 3A FROM NASA GODDARD VERTICAL OPTICAL BENCH



84-2



3

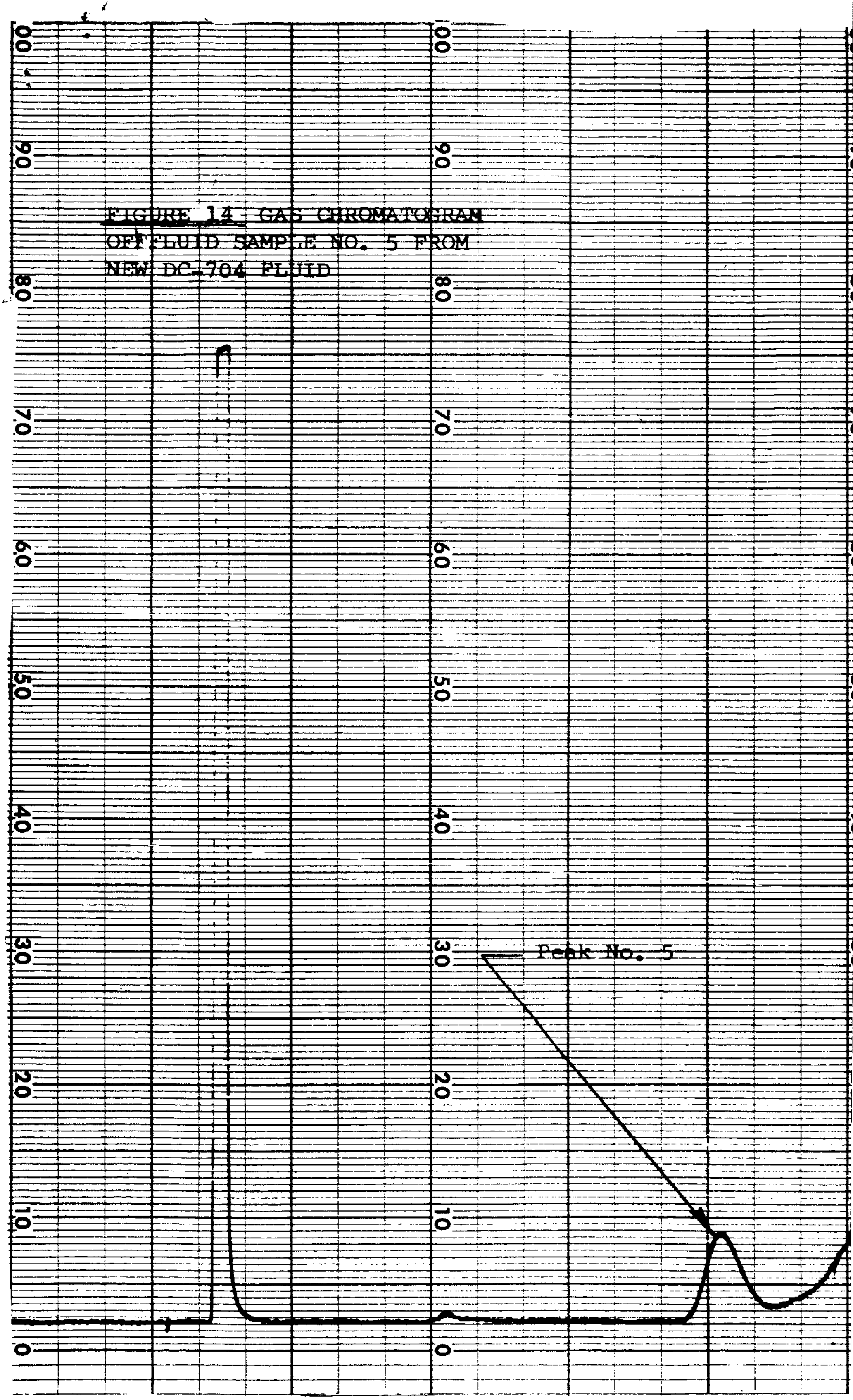
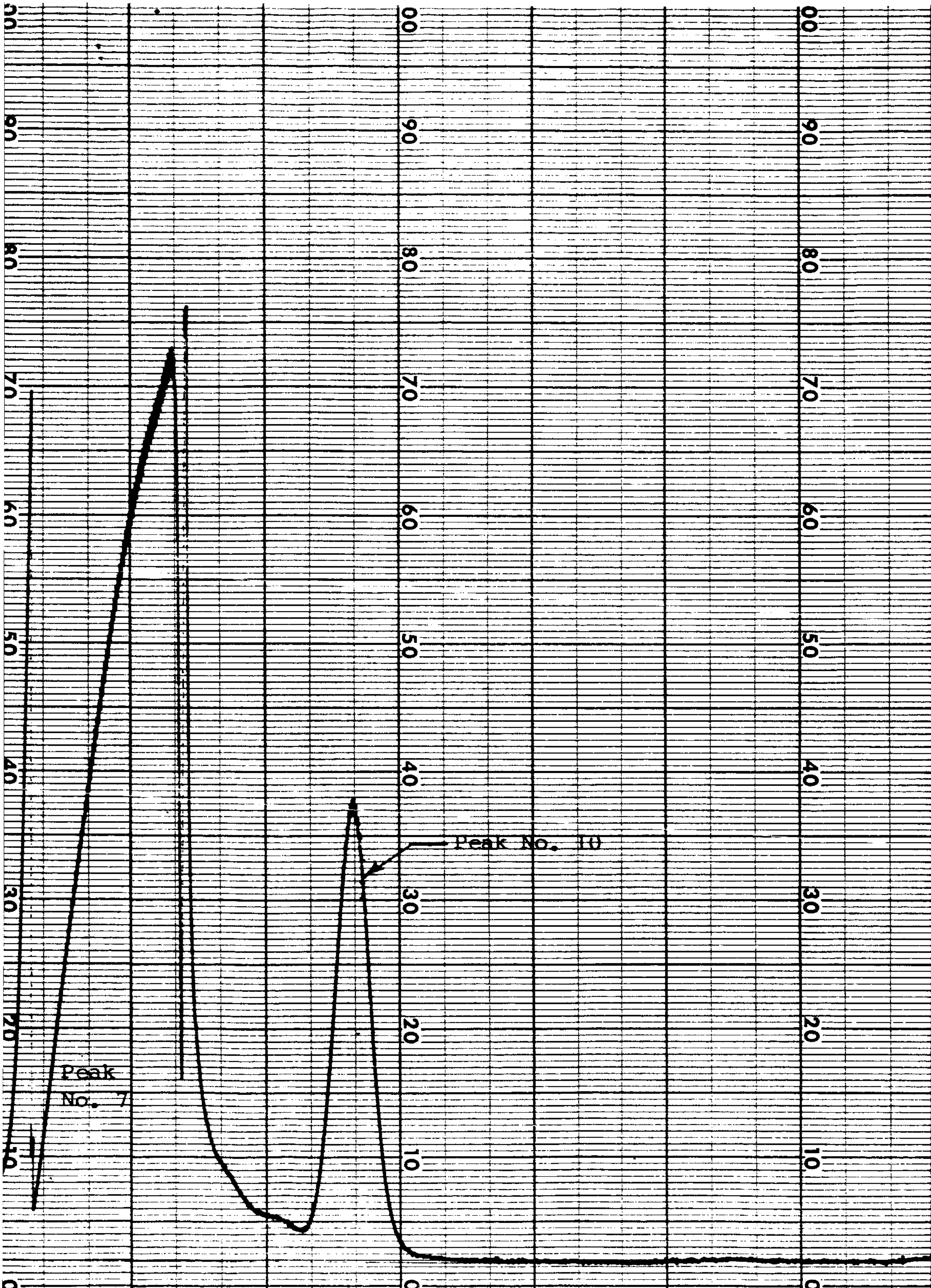
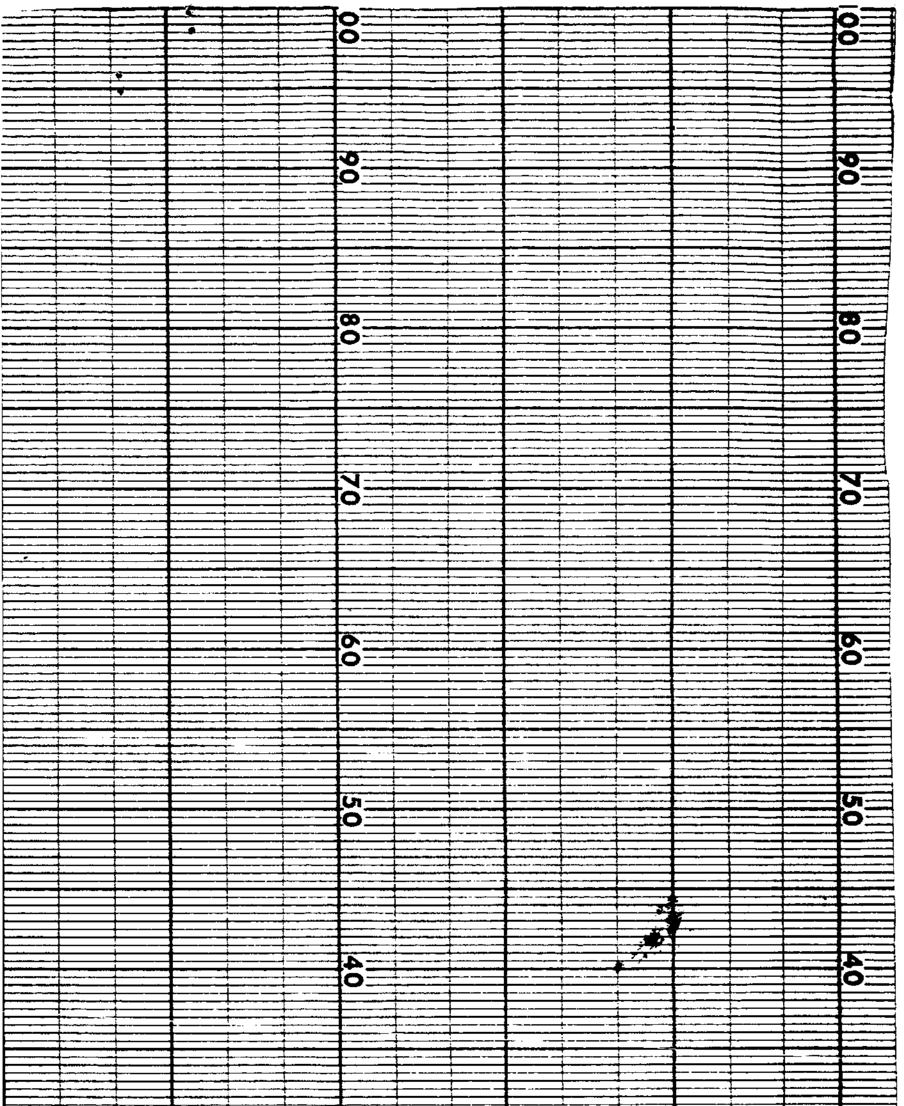


FIGURE 14. GAS CHROMATOGRAM OF FLUID SAMPLE NO. 5 FROM NEW DC-704 FLUID



35-2



6

TABLE - 5

MASS SPECTROMETRIC ANALYSIS OF VOLATILE COMPONENTS FROM FRESH AND USED DC-704 FLUIDS

Sample	Approximate Bulb Pressure (mm Hg)	Sample Pressure (mm)	mm Hg Analysis Pressure Initial	Final	Results
1. Large Vacuum Chamber Pump No. 5	59	57.5	2×10^{-6}	1.4×10^{-6}	m/e values of 31,59, 74 and m/e values of 31, 45, and 46 perhaps only indicates ethers and alcohols in the dimethyl or ethyl range. m/e - 52 and 78 suggests benzene.
2. Large Vacuum Chamber Pump No. 7	>100	>100	9×10^{-6}	$\sim 8 \times 10^{-6}$	m/e - 31,45, 46 indicates an alcohol in the methanol or ethanol range or dimethyl ether if we disregard m/e 31 peak. m/e - 78 benzene; 43 and 58 acetone;(1) 30 SiH_4.
3. First Sample of VOB	>100	94	3.3×10^{-6}	2.7×10^{-6}	No indication of impurities over fresh fluid.
3A. Second Sample of VOB	>100	94	3.3×10^{-6}	2.7×10^{-6}	An increase in mass peaks 101, 103 and 151 would suggest Freon 113 (data inconclusive due to small increase in intensity over the blank).
4. Fresh DC-704	69	67	2×10^{-6}	1.5×10^{-6}	No indication of impurities
5. Fresh DC-704	>100	89	3.2×10^{-6}	2.4×10^{-6}	No indication of impurities

(1) Could be due to solvent used for cleaning sampling traps. However, traps were rinsed and oven dried.

characteristic of the silicone oils. The only significant difference noted in the mass spectra was the absence of small peak at m/e = 31 in Samples 3, 3A, 4, and 5, and the larger abundance of this peak in Samples 1 and 2. Sample 2 has the greater abundance of the two samples. Peak m/e = 31 is often found with diethyl ether and normal alcohols through butanol. However, for diethyl ether there should be a significant peak at m/e = 59 which is absent. On the other hand, an increase in abundance was noted for m/e = 27 and 29 which strongly suggests along with the m/e = 31, the presence of propanol.

In addition, the analysis showed an increase in the abundance of m/e = 43, 45, and 46 in Sample No. 1 compared to the other samples. The significance of these peaks cannot be ascertained in the complex spectra obtained. The peak at m/e = 43 is indicative of a propyl group originating from either propanol, a hydrocarbon, or a corresponding ketone. The mass at 45 suggests alcohols or ethers with 2- propanol and 2- butanol as possibilities because of their contribution to masses 27, 29, 31, and 43.

The Nuclear Magnetic Resonance analysis of the used fluids indicated no fluorine containing compounds were present at the detection limits (or 1%) employed.

Emission spectrographic analysis of the used fluids identified the presence of magnesium and aluminum along with ether metallic impurities such as Si, Ag, Zn, Na, Cr, Ti, and Fe. Their quantitative level was determined by wet-chemical procedures involving acid degradation of the DC-704 fluid. The Number 5 pump fluid contained 8 ppm of aluminum, but no detectable amounts of calcium or magneisum. However, the Number 7 pump fluid from the same vacuum system showed 15 ppm calcium, 7 ppm magnesium, and 8 ppm aluminum. The Vertical Optical Bench samples (3 and 3A) yielded 28 ppm calcium, 7 ppm magnesium, and 8 ppm aluminum.

4.4 Stability of DC-704

The results of the stability test conducted on DC-704 under normal diffusion pump operation are tabulated in Table 6. These results indicate that no significant change occurred in the fluid during the forty-nine (49) day test period. The relative percent distribution of

TABLE - 6

RELATIVE % DISTRIBUTION OF DECOMPOSITION PRODUCTS OF DC-704 FROM STABILITY STUDIES IN A NORMAL DIFFUSION PUMP SYSTEM

Peak No.	1	3	7	21	39	49
6-7	0.05	0.36	0.11	0.43	0.27	0.18
10						0.28
11	0.37	0.34	0.27	0.26	0.27	0.33
12	98.07	97.85	97.94	97.74	98.03	97.54
13	x	x	x	x	x	x
14	1.39	1.36	1.57	1.47	1.43	1.67
16	0.12	0.09	0.11	0.10		x
19	x	x	x	x	x	x
	100.00	100.00	100.00	100.00	100.00	100.00

decomposition products is essentially constant. The effect of washing down the bell jar twice during the test period with acetone does not appear to have influenced the stability of the DC-704 fluid.

The results of the tests conducted to determine the influence of a 4 x 10^{-6} standard cc/second air leak containing 20 parts per million of ozone are explained in this section. The mixture of ozone and air was allowed to leak into the operating diffusion pumped vacuum system, shown in Figure 17, for a period of seven and one-half (7-1/2) hours. At the end of this period of time, a sample of diffusion pump fluid was removed from the liquid phase and the calibrated leak was closed. Since no problems were evident, it was decided to leave the vacuum system in operation overnight. Thus, a sample could be removed in the morning to determine if the pump had purged itself of any ozone which had been incorporated into the fluid. The procedure called for the ozone leak to be initiated again the following day.

Approximately six (6) hours after the ozone leak had been closed off, an explosion occurred in the vacuum pump. Following the discovery of the explosion, the entire vacuum system was examined in detail. Figures 18, 19, and 20 are photographs of the system taken immediately after the explosion.

The fifteen inch bell jar was broken into several relatively large pieces. All of these pieces from the bell jar were found in the area under the bell jar and the rubber seal under the lower edge of the bell jar was blown out. This indicates the bell jar was blown upward against its restraining straps, which had been placed over the bell jar for safety, and cracked when it fell back on the support plate. The jar was coated on the inside surface with a very thin wet carbon film.

The stainless steel orifice plate which had been held down by a stainless steel flange was turned completely over. The upper surface of the orifice plate was coated with a thick wet carbon film, except for a small annular area on which the flange had rested prior to the explosion. The lower side of the orifice plate outside the O-ring was also coated with a wet black film. However, the inside of the O-ring was covered with a dry bluish-white deposit. This dry powder would indicate the occurrence of very high temperatures.

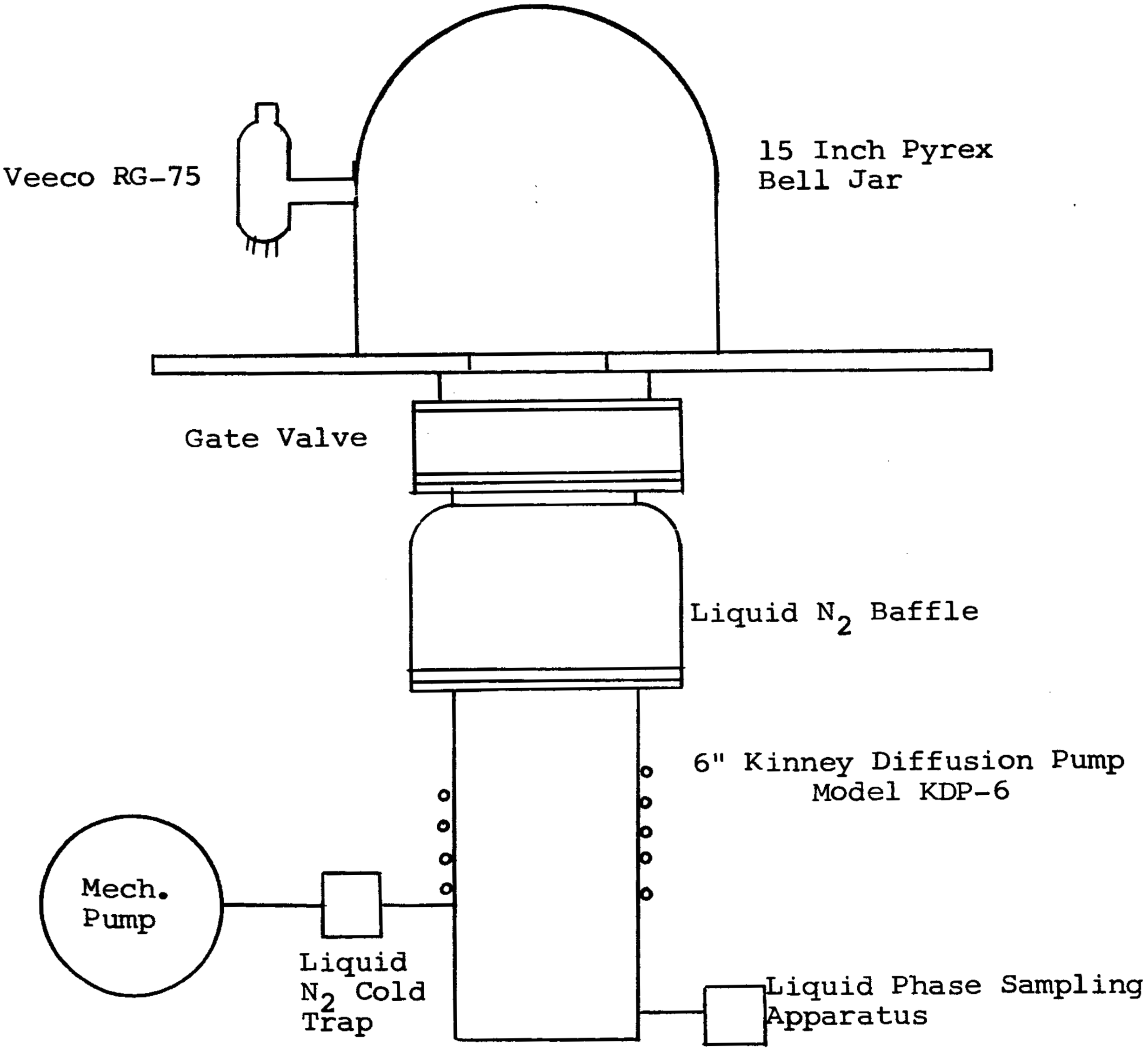


Figure - Six Inch Kinney Vacuum System

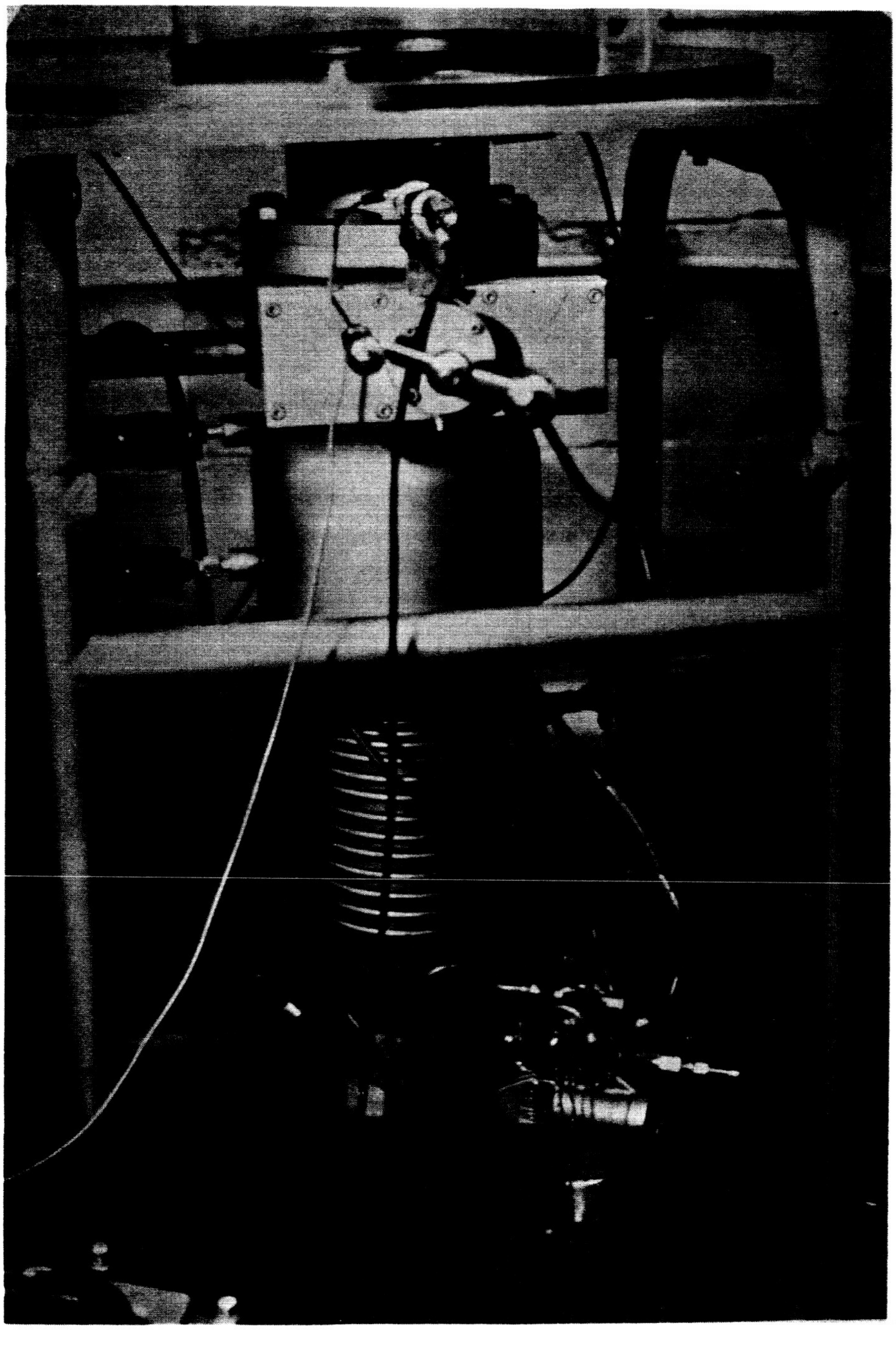


Figure 16 - Sampling Apparatus for Removing Liquid Phase Samples for Six-Inch Kinney Diffusion Pump

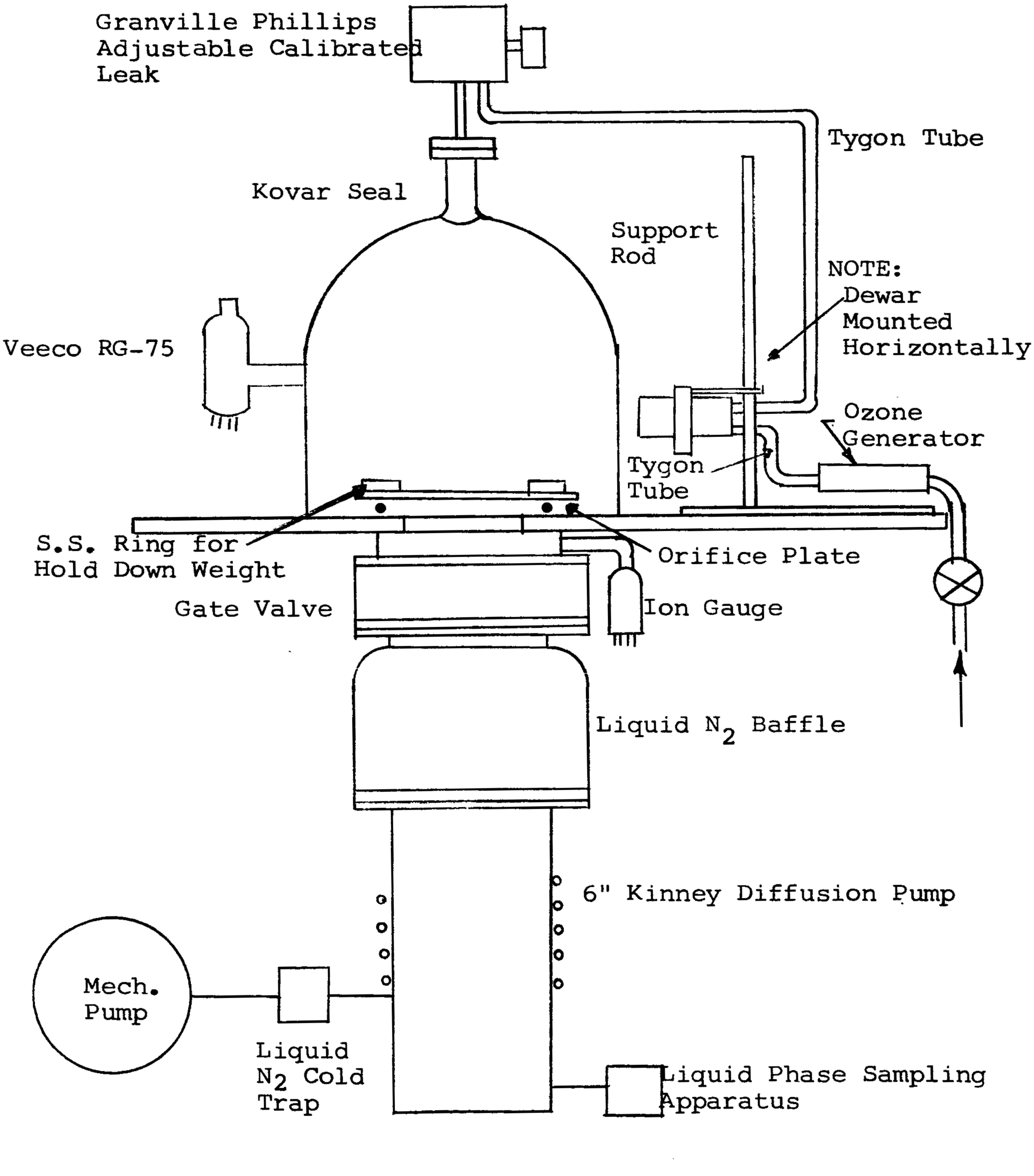


Figure 17 - Six Inch Kinney Vacuum System Used for Ozone Stability Studies

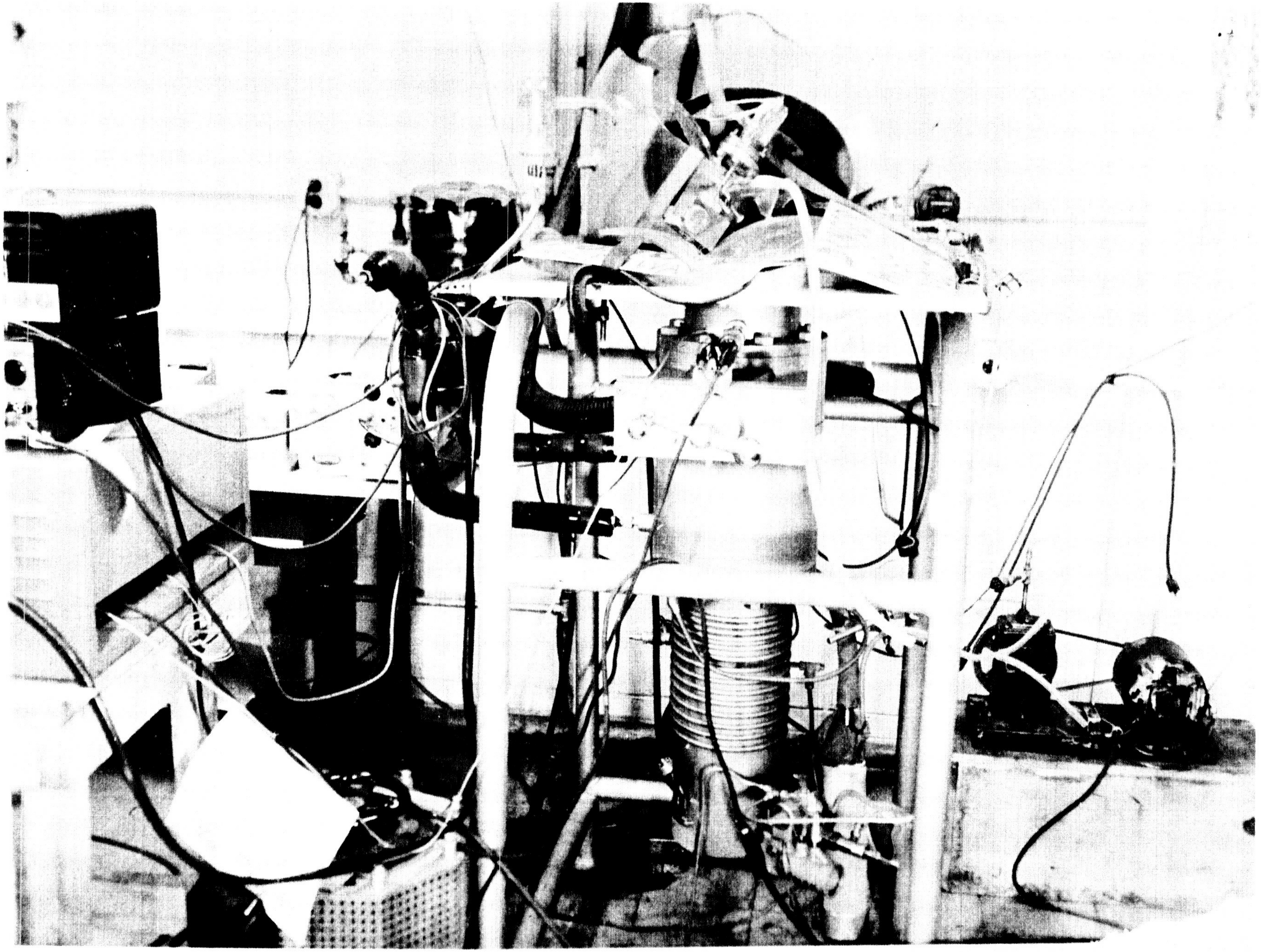


Figure 18 - 6" Kinney Diffusion Pump System After Explosion Initiated by Ozone Leak

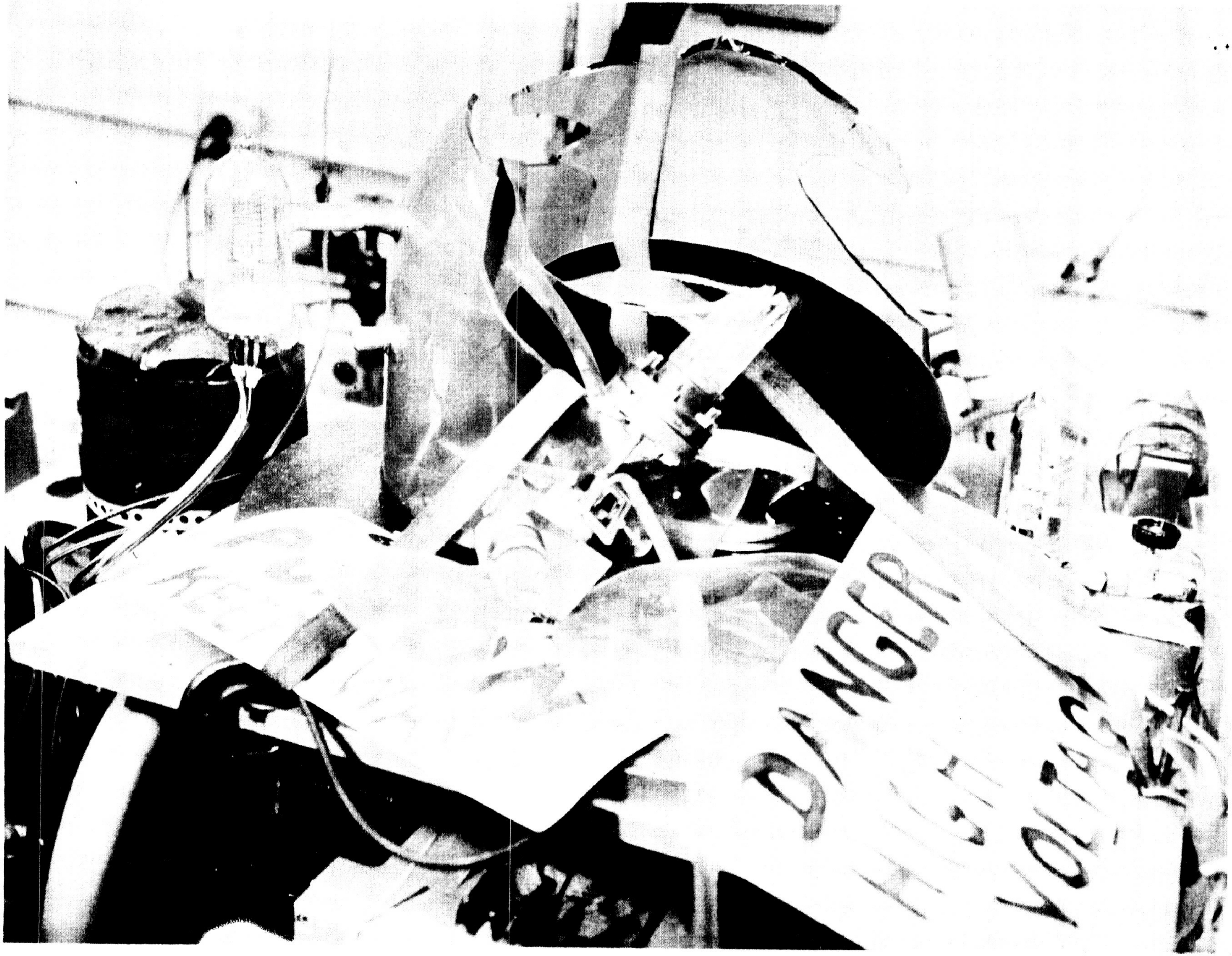


Figure 19 - Broken Bell Jar in 6" Kinney Diffusion Pump System
After Explosion Initiated by Ozone Leak

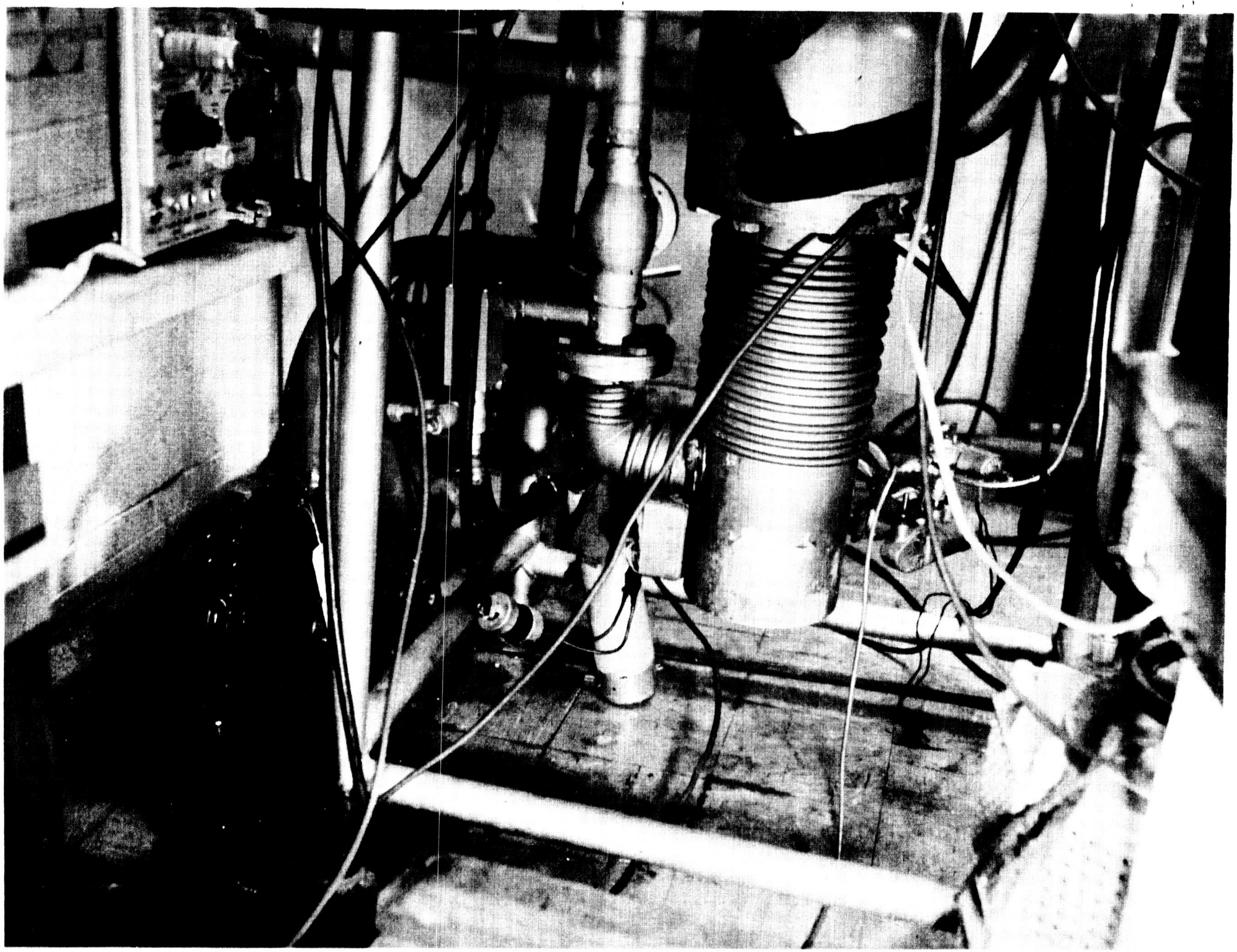


Figure 20 - Diffusion Pump and Foreline Containing Unbroken Pyrex Cold Trap Following Explosion Initiated by Ozone Leak

The diffusion pump jet assembly was relatively clean on the outside. The upper two-thirds of the chimney and the inside surface of the jets were coated with a dry brownish-black powder, while the lower third was a dry blue-white powder.

The foreline to the diffusion pump was coated with a thin carbon film back to the cold trap which was also coated with carbon. However, the foreline including the pyrex cold trap was undamaged. The cold trap still contained liquid nitrogen at the time the explosion was discovered.

The sample removed from the liquid phase of the diffusion pump before ozone was leaked into the system and the samples removed at the end of each two (2) hour period during the test were analyzed by gas chromatography and mass spectrometry. Figures 21 and 22 show the results of the analyses on the control sample removed before the initiation of the ozone leak and the last sample which was removed seven and one-half (7-1/2) hours after the initiation of the leak. Comparison of the results obtained by mass spectrometry analysis indicate no significant change in the diffusion pump fluid during the 7-1/2 hour ozone test. However, the gas chromatography comparison showed a marked decrease in one of the higher peaks as can be seen in Figure 22.

Preliminary infrared analysis of the residue material recovered from the orifice plate following the explosion indicated it was from the DC-704 and not the mechanical pump fluid. Similar analysis was conducted on the fluid which was drawn into the cold finger in the foreline of the roughing pump after the bell jar was broken by the explosion. This analysis indicated this fluid was DC-704 and that a very strong (OH) band was present in the fluid. Gas chromatographic analysis of the fluids recovered from the orifice plate and from the cold trap in the foreline following the explosion showed the existence of a peak in the fluid from the cold trap similar to that found in the sample (see peak with arrow in Figure 22) removed from the diffusion pump before ozone was leaked into the system. However, this peak was not present in the sample removed from the orifice plate. These results indicate the presence of a transient component which could only be positively identified by transferring the material directly from the gas chromatograph to the mass spectrometer for analysis of this peak.

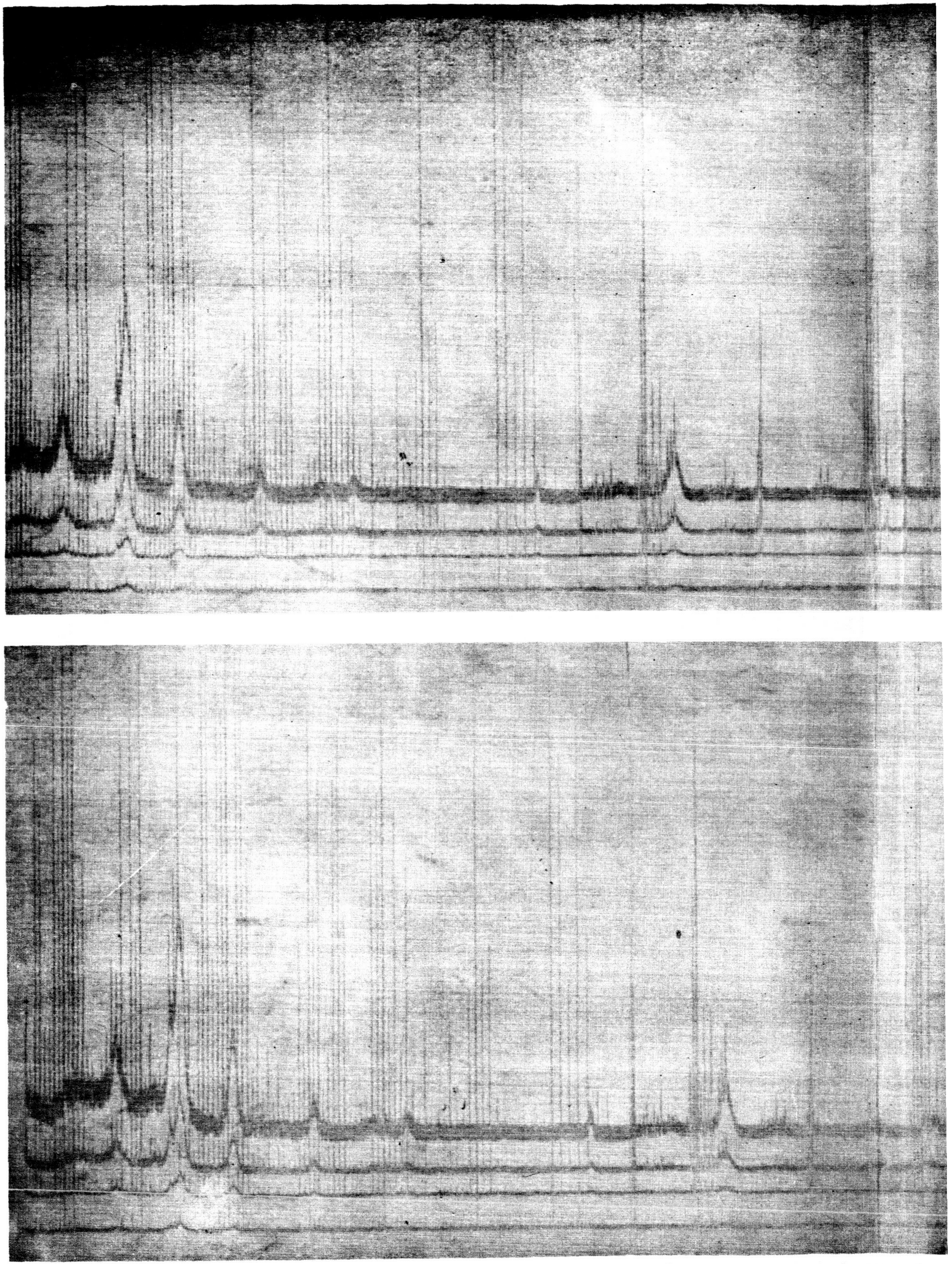
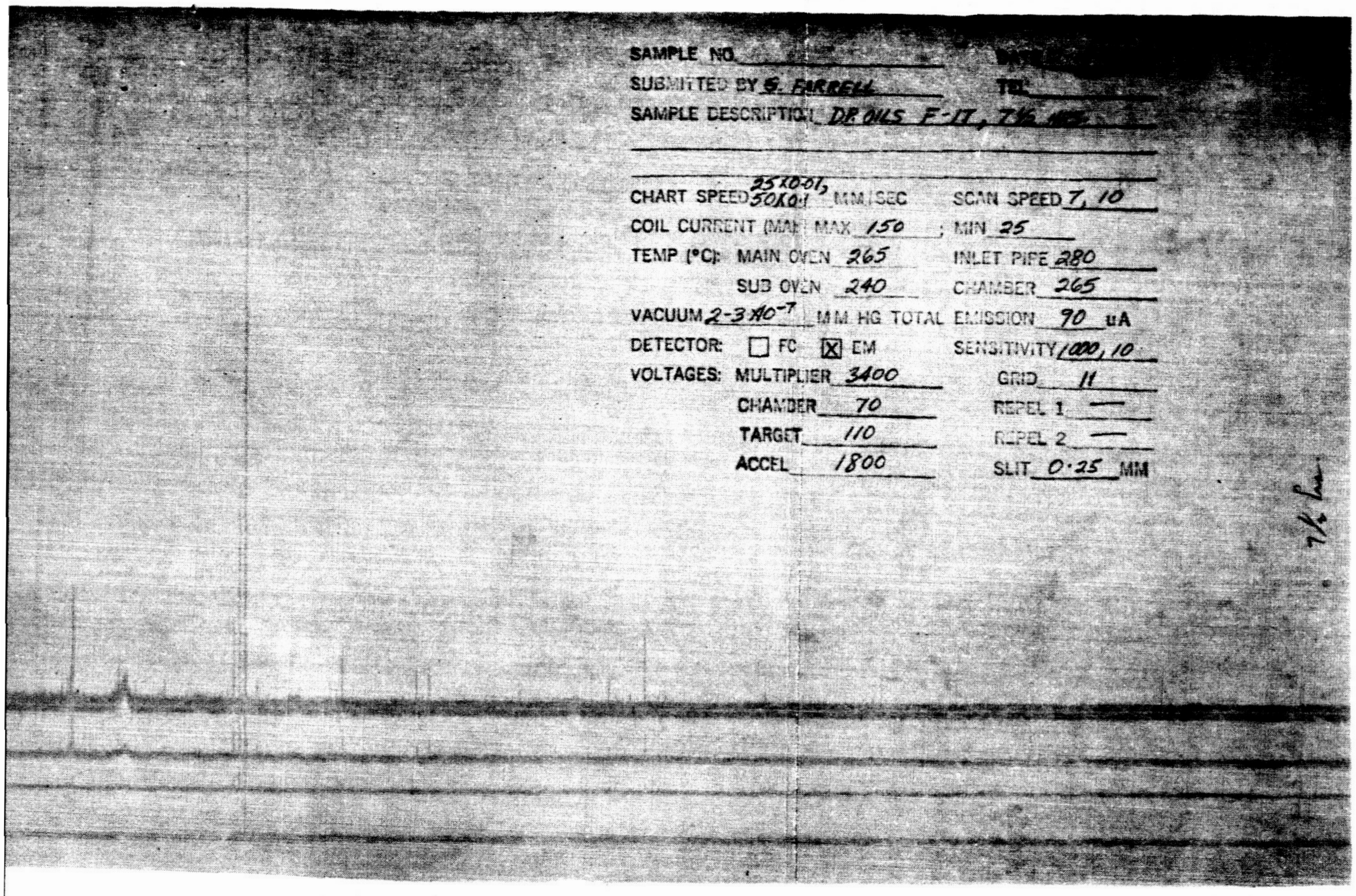


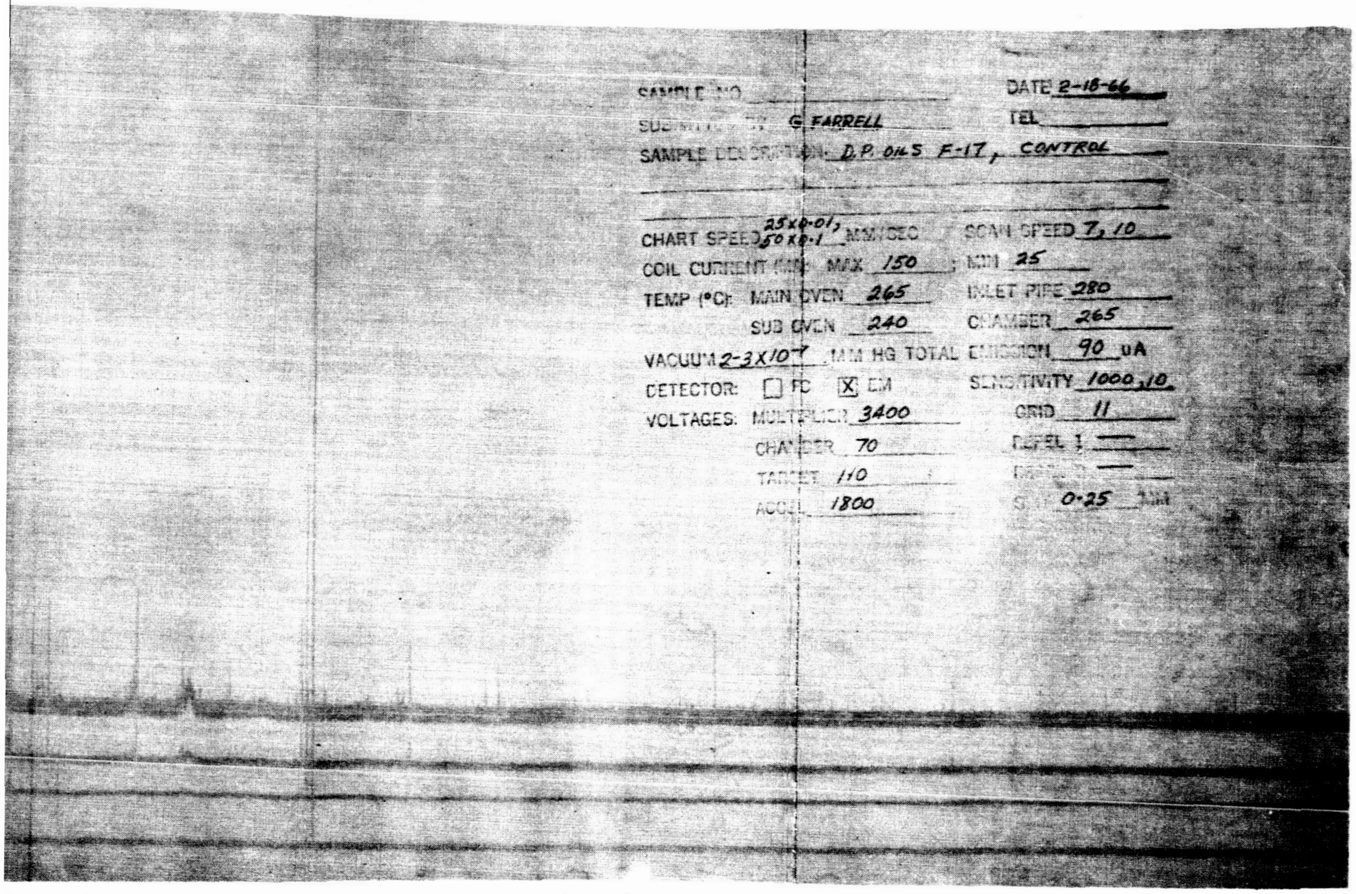
Figure 21 - Mass Spectrometry Comparison of Control Sample
Initiation of Ozone Leak and Sample Removed Jus
Ozone Leak



SAMPLE NO.
SUBMITTED BY G. FARRELL
TEL
SAMPLE DESCRIPTION DP OILS F-17, 7½ HRS

CHART SPEED 25X0·01, 50X0·1 MM/SEC
SCAN SPEED 7, 10
COIL CURRENT (MA): MAX 150 ; MIN 25
TEMP (°C): MAIN OVEN 265
INLET PIPE 280
SUB OVEN 240
CHAMBER 265
VACUUM 2-3X10⁻⁷ MM HG
TOTAL EMISSION 90 uA
DETECTOR: ☐ FC ☒ EM
SENSITIVITY 1000, 10
VOLTAGES: MULTIPLIER 3400
GRID 11
CHAMBER 70
REPEL 1 —
TARGET 110
REPEL 2 —
ACCEL 1800
SLIT 0·25 MM

7½ hr



SAMPLE NO.
DATE 2-18-66
SUBMITTED BY G FARRELL
TEL
SAMPLE DESCRIPTION D.P. OILS F-17, CONTROL

CHART SPEED 25X0·01, 50X0·1 MM/SEC
SCAN SPEED 7, 10
COIL CURRENT (MA): MAX 150 ; MIN 25
TEMP (°C): MAIN OVEN 265
INLET PIPE 280
SUB OVEN 240
CHAMBER 265
VACUUM 2-3X10⁻⁷ MM HG
TOTAL EMISSION 90 uA
DETECTOR: ☐ FC ☒ EM
SENSITIVITY 1000,10
VOLTAGES: MULTIPLIER 3400
GRID 11
CHAMBER 70
REPEL 1 —
TARGET 110
REPEL 2 —
ACCEL 1800
SLIT 0·25 MM

Removed from Diffusion Pump Prior to
t Prior to the Elimination of the

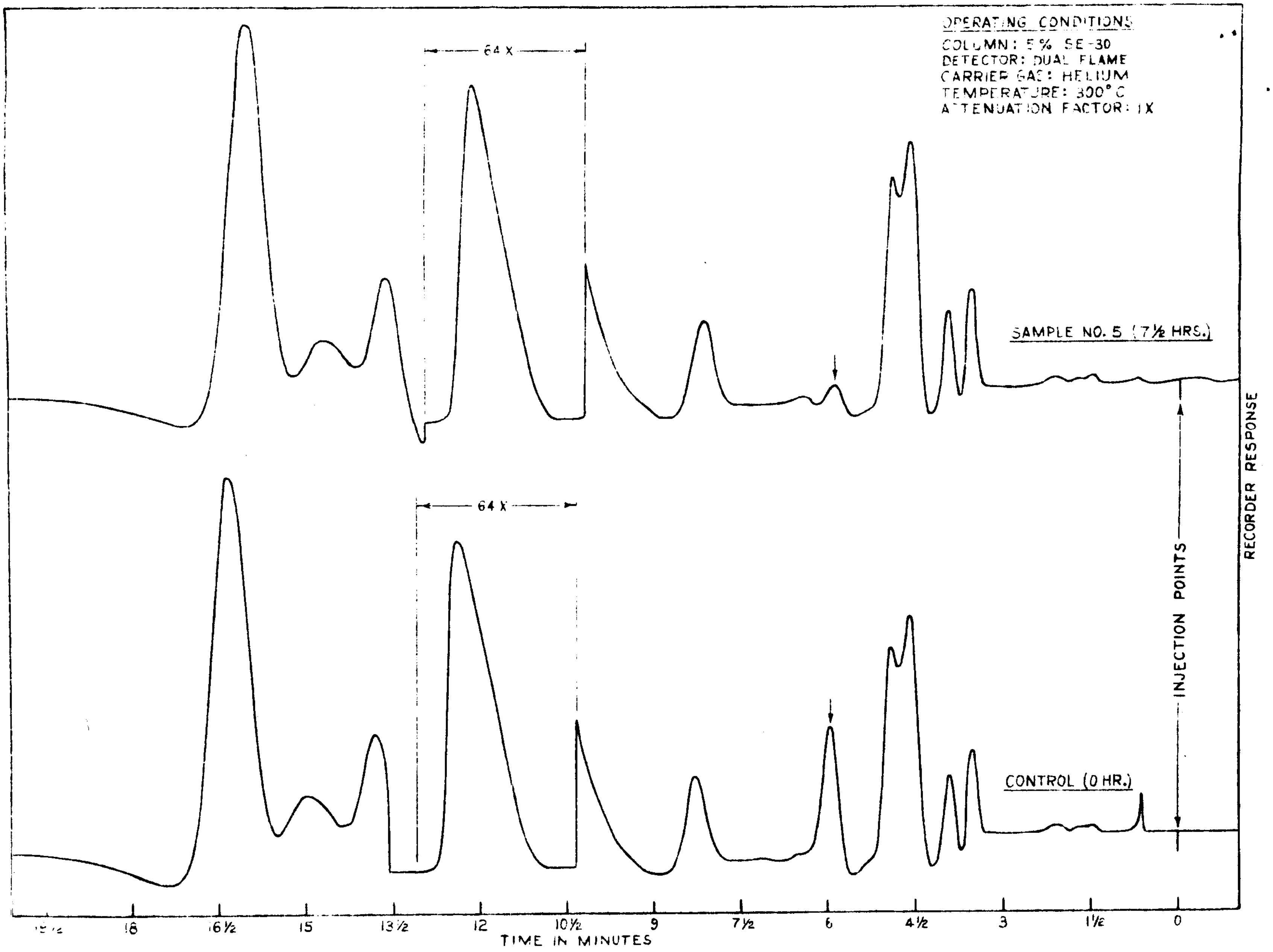


Figure 22 - Gas Chromatography Comparison of Control Sample Removed from Diffusion Pump Prior to Initiation of Ozone Leak and Sample Removed Just Prior to the Elimination of the Ozone Leak

The results tabulated in Tables 7 through 10 and shown in Figures 23 and 24 demonstrate the influence of aging uncontaminated (control samples) of DC-704 and aluminum contaminated DC-704 in an air environment at temperatures of 450°F and 525°F.

The gas chromatography results in Table 7 show that very little degradation occurs in uncontaminated DC-704 when aged at 450°F for sixty-one (61) days. Peak Number 12 which is the major peak in DC-704 changes by less than 1-1/2% during this period. This change in peak Number 12 is shown in Figure 23 as a function of time.

The results in Table 8 show that the percentage change in Peaks 1 through 21 for DC-704 when contaminated with aluminum and aged at 450°F in air for sixty-one (61) days is very small. This change as a function of time is also plotted in Figure 23. Table 9 is a similar tabulation of the results of analyses conducted on an identical catalytic bath contaminated with aluminum, but with the temperature increased to 525°F. These results show that only a very slight change occurred in this fluid even at 525°F. This change is only slightly greater than the changes which occurred with either the contaminated or the uncontaminated low temperature (450°F) baths.

The results tabulated in Table 10 show that gross degradation occurred in the uncontaminated bath which was aged in air at 525°F. The curves in Figure 23 show the rate at which peak Number 12 decreased as a function of time with respect to the other samples studied. The curves in Figure 24 show how all of the peaks in sample Number 4 varied as a function of time. These results show the major peak decreases from greater than 98 percent to less than 22 percent. At the end of the test period the sample had changed to a heavy black viscous jell.

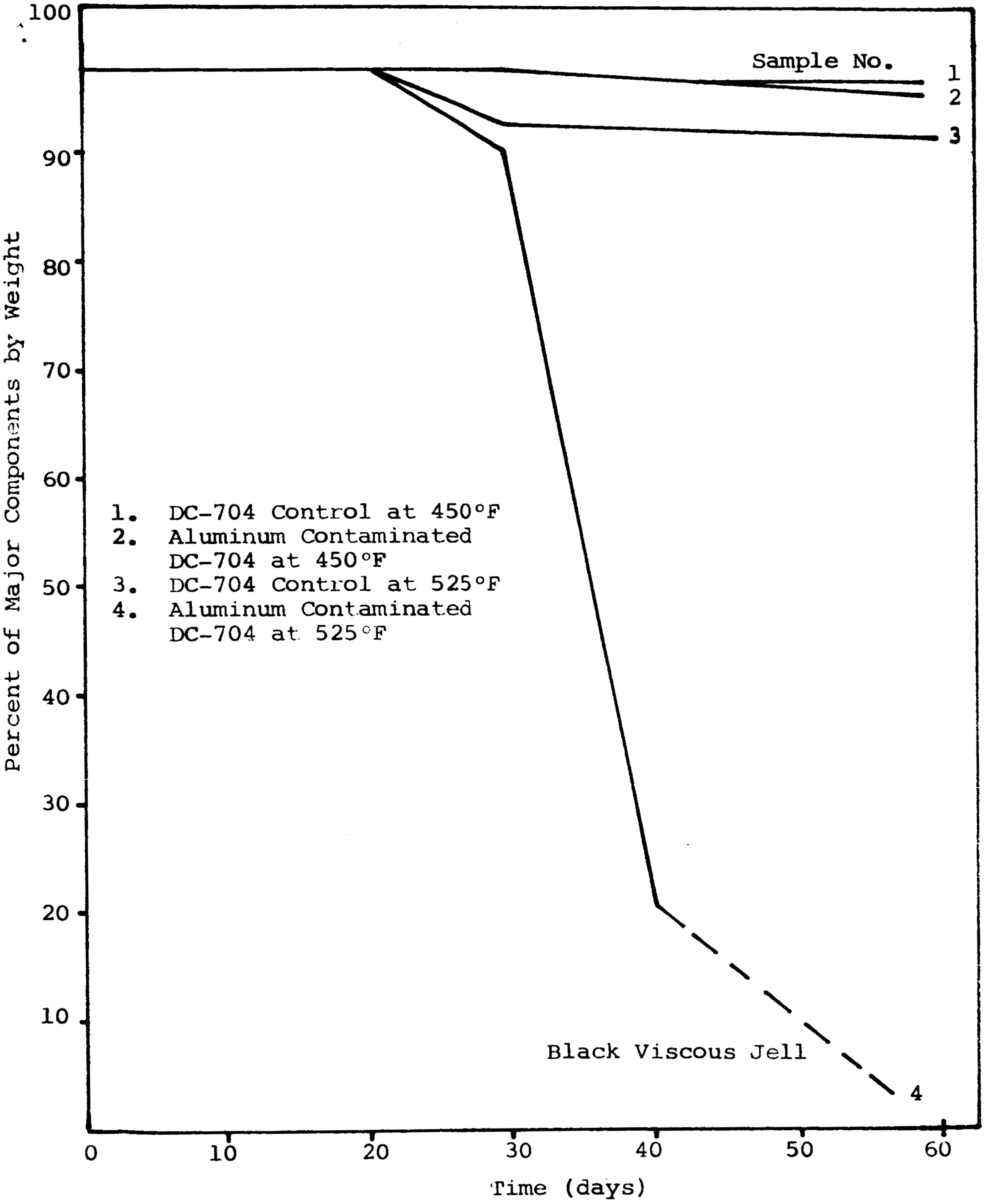


Figure 23 - The Percent Change of Peak No. 12 in Four Catalytic Baths as a Function of Time

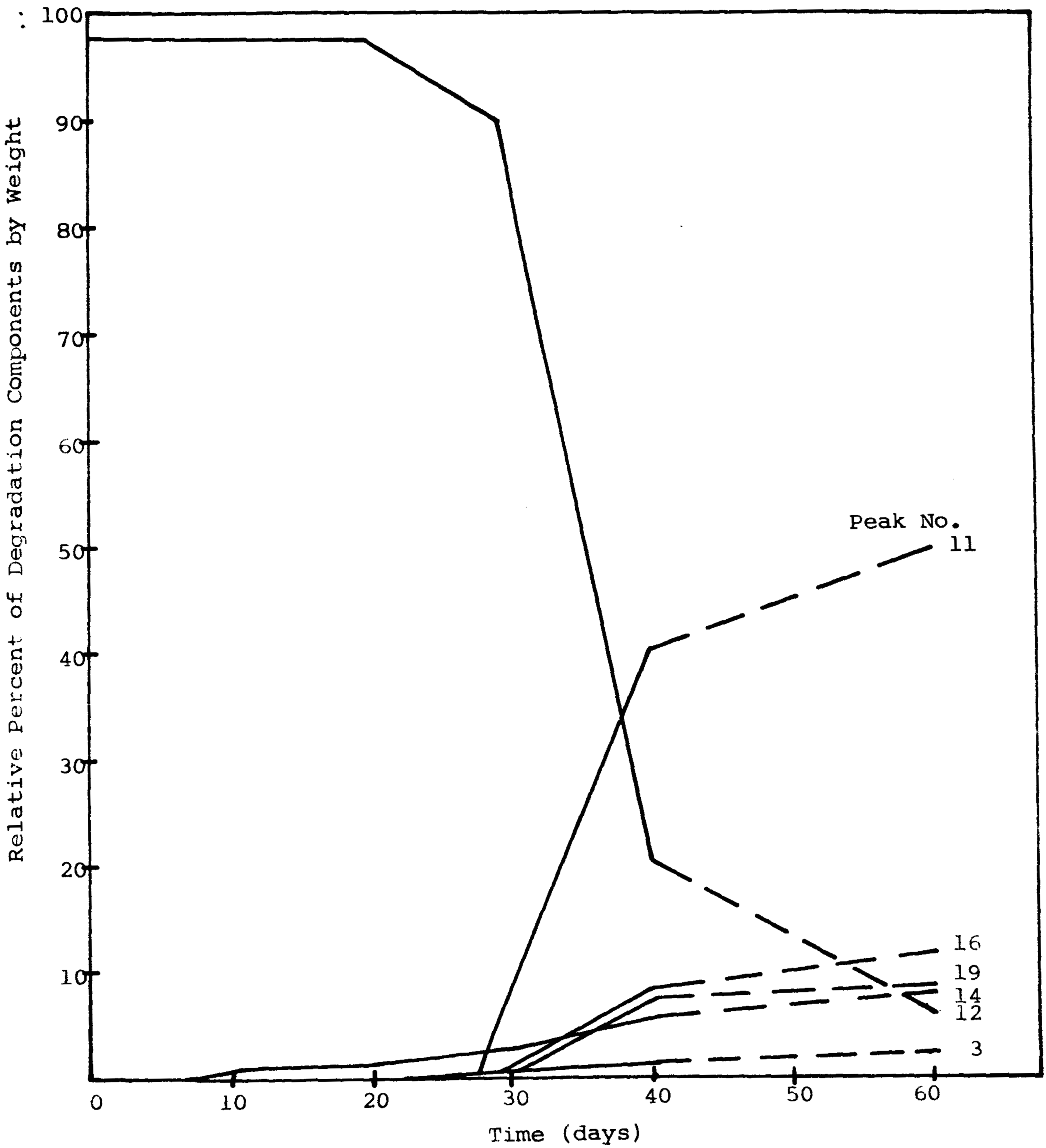


Figure 24 - Degradation of DC-704 in Air at 525°F
as a Function of Time

TABLE - 7

RELATIVE % DISTRIBUTION OF DECOMPOSITION PRODUCTS OF UNCONTAMINATED DC-704 DURING CATALYTIC AGING STUDIES IN AIR AT 450°F

Peak No.	Time (Days)						
	6	10	15	21	27	38	61
1							
2							
3					x	0.10	
4					x	0.06	
5							
6						x	
7						x	
8							
9							
10							
11	0.40	0.38	0.38	0.52	0.71	0.73	0.78
12	98.43	98.30	98.28	97.99	97.29	96.67	96.97
13	x	x	x	x	x	x	
14	1.17	1.32	1.34	1.23	1.37	1.47	1.02
15				x	x	0.10	0.13
16	x	x	x	0.16	0.19	0.24	0.28
17	x	x	x	x	x	x	
18					x	x	
19	x	x	x	0.10	0.25	0.37	0.43
20						x	
21				x	0.19	0.26	0.39
22							
	100.00	100.00	100.00	100.00	100.00	100.00	100.00

TABLE - 8

RELATIVE % DISTRIBUTION OF DECOMPOSITION PRODUCTS OF ALUMINUM OXIDE CONTAMINATED DC-704 DURING CATALYTIC AGING STUDIES IN AIR AT 450°F

Peak No.	Time (Days) 6	10	15	21	27	38	61
1							
2						x	
3	x	x	x	x	x	x	
4	x	x	x	x	x	x	
5							
6						x	
7						x	
8							
9							
10							
11	0.46	0.47	0.42	0.36	0.47	0.56	1.04
12	98.08	98.31	98.00	98.05	97.87	96.75	95.08
13	x	x	x	x	x	x	
14	1.46	1.22	1.29	1.33	1.35	1.69	1.35
15	x	x	x	x	x	0.16	0.21
16	x	x	0.12	0.08	0.15	0.19	0.46
17	x	x	x	x	x	x	
18			x	x	x	x	0.13
19	x	x	0.17	0.18	0.16	0.41	1.10
20				x		x	
21				x	x	0.25	0.63
22							
	100.00	100.00	100.00	100.00	100.00	100.00	100.00

TABLE - 9

RELATIVE % DISTRIBUTION OF DECOMPOSITION PRODUCTS OF DC-704 DURING CATALYTIC AGING STUDIES IN AIR

Sample No. 4 - Aluminum Contaminated at 525°F

Peak No.	Time (Days) 6	10	15	21	27	36	61
1						x	
2							
3				x	0.31	0.82	
4				x	0.22	0.53	
5					x	x	
6					0.09	0.36	
7							
8						x	
9						x	
10						x	
11	0.32	0.36	0.42	0.41	1.10	1.96	1.70
12	98.29	97.88	97.67	97.75	93.65	89.93	93.61
13	x	x	x	x	x	x	
14	1.32	1.65	1.53	1.52	2.47	2.37	1.58
15				x	0.21	0.32	0.18
16	0.08	0.11	0.12	0.08	0.28	0.51	0.54
17		x	x	x	0.15	0.19	0.54
18		x			0.15	0.21	0.15
19	x	x	0.26	0.24	0.78	1.51	1.33
20					0.10	0.30	0.28
21					0.49	0.99	0.68
22							
	100.00	100.00	100.00	100.00	100.00	100.00	100.00

TABLE - 10

RELATIVE % DISTRIBUTION OF DECOMPOSITION PRODUCTS OF UNCONTAMINATED DC-704 DURING CATALYTIC AGING STUDIES IN AIR

Sample No. 3 - Control at 525°F

Peak No.	Time (Days) 6	10	15	21	27	38	61
1						x	
2						x	
3					0.27	1.79	
4	x	x	x	x	0.29	1.26	
5			x	x	x	x	
6					x	0.54	Bath turned off when temperature rose to 700°F without additional heat. Fluid turned to a black viscous jell.
7					x	0.48	
8					x	x	
9					x	x	
10					x	0.27	
11	0.26	0.37	0.43	0.53	2.87	39.16	
12	98.82	98.64	98.22	97.83	90.94	21.61	
13	x	x	x	x	x	0.21	
14	0.92	0.99	1.18	1.26	2.31	4.97	
15		x		0.05	0.33	3.0	
16	x	x	0.12	0.13	0.40	8.40	
17				x	x	2.70	
18				x	0.25	0.27	
19		x	0.05	0.20	1.31	7.38	
20					0.29	0.64	
21					0.74	4.49	
22						2.83	

5.0 DISCUSSION

5.1 Field Survey

The results of the field survey which are listed in Section 4.1 indicate that explosions seldom occur under steady state conditions at high vacuum levels. However, many explosions were reported which occurred while oxygen or air was bled into a system. These results seem to contradict the results obtained during IITRI's previous study, "Hazard Potential of Diffusion Pump Fluids" under NASA Contract NAS9-1178. During this study, a six-inch diffusion pump and a thirty-five-inch diffusion pump were pressurized when in operation with oxygen without causing any explosions. However, these results were generated by completely different systems.

Several factors must be considered when comparing such results from entirely different sources. The most important variables to be considered are the type of fluid used, the temperature of the diffusion pump system and fluid, the past history of the fluid, and rate of pressurization. The type of fluid used has a marked influence on the safe operating limits of the system. Review of available literature indicated the silicone fluids to be much more stable at elevated temperatures than the normally used hydrocarbon fluids. The results of the explosion limit tests conducted during this study would certainly substantiate this. In addition, the results obtained during our stability studies of DC-704 indicate that the past history or usage of the diffusion pump fluid could drastically influence the condition of the fluid and, therefore, the number and quantity of transient or volatile components present.

The results of the present ozone studies with DC-704 indicate that very minute quantities of oxygenated species may significantly change the thermal stability of the fluid. These degradation products could no doubt change the reaction rate of the fluid and in all probability, these components lower the activation energy. Therefore, fluids which have been repeatedly exposed to oxygen or air while hot, such as fluids in industrial metal platers, may be more susceptible to an explosion during pressurization procedures, whereas fluids which are relatively new, such as the fluids used in the previous pressurization tests at IITRI would be less susceptible to an explosion.

The effect of the system and fluid temperatures on the probability of an explosion being generated during pressurization is quite obvious. During a pressurization process, the pressure and temperature of the air and vapor increase as a function of the rate of pressurization and the original temperature and pressure.

Therefore, the results from the field survey tie in very nicely with the results from the stability phase of this study. The explosions which occur under steady state at high vacuum probably require a fluid with a relatively low activation energy, while the explosions which occur during pressurization do not require such a reduced activation energy level because of the increased temperature resulting from the compression process.

5.2 Explosion Limit Determination

The results obtained during the explosion limit tests which are tabulated in Tables 1 and 2 are quite straight forward. In general, they indicate that all used and deliberately contaminated samples of DC-704 tested had explosion limit temperatures from 25°F to 50°F below that of new DC-704. However, several trends became apparent during the tests which should be discussed.

First, the pronounced influence of the vessel size on the explosion limit temperature was noted. Figure 7 demonstrates the difference that results when the vessel size is increased from 3000 ml to 12,000 ml. In addition, no explosions were generated with a 300 ml vessel even with temperatures in excess of 1000°F. Thus, the surface area to volume ratio is very critical when testing DC-704 at reduced pressure. This phenomenon may not occur at pressures greater than 200 millimeters of mercury.

Another interesting phenomenon which is demonstrated in Figure 10 is that the explosion limit temperature decreases with increasing percentages of fluid. All explosions occurred with mixtures in which the fuel was in excess of a stoichiometric mixture.

These tests definitely show that the explosion limit temperatures of all the used fluid are slightly less than the new DC-704. However, the change is so slight as to be almost insignificant. Since the minimum temperature at which an explosion could be consistently generated was 875°F, all the used fluids tested should have been very stable in a vacuum system. It should be remembered, however, that the fluid samples tested were not immediately tested as they were removed from their respective vacuum systems. Therefore, certain transient components may not have been present when the explosion limit tests and chemical analyses were conducted on the used samples.

5.3 Analysis of Pump Fluids for Contaminants

The ultra violet data presented in Table 3 exhibits minor differences in absorption properties toward the longer wavelengths in the UV region and the position of such bands would indicate such structures as hydroquinones or quinones. However, the concentrations of these components seem to vary since two of the used fluids (Samples 1 and 2) contain lower levels than present in the fresh oil, while Samples 3 and 3A contain larger quantities. A possible explanation may be advanced from the point of view that these components, present in the original fluid, are further oxidized at low levels in use and distilled out of the diffusion pump fluid. The samples containing the larger quantities may represent fluids which are undergoing degradation processes (oxidative degradation) at a rate greater than they can be removed. Since the DC-704 represents an aromatic structure (phenyl substitution), degradation and splitting off of phenyl rings could easily be oxidized to these same types of structures if trace levels of oxygen are present. This fluid would represent a potentially troublesome fluid since free radical cleavage and/or oxidative processes are presumably occurring. Such combined effects were observed in the catalytic studies. However, in this case an oxygen supply was readily available.

Infrared studies carried out in the six (6) samples identified in Table 3 yielded similar spectra for all samples. However, the sensitivity of this method is such that any differences or contaminants present at levels less than a few percent would not be expected to be observed. Even the carbonyl region (5.6 to 5.9 mμ) did not show any differences which would indicate the formation of oxidation products. However, here again, sensitivity is the determining factor as to the detection of such functional groups.

The gas chromatographic studies carried out on the six (6) samples submitted to our laboratory exhibited fifteen (15) components, one of which (Peak No. 7) represented over 98% of the total samples. The other two minor peaks (5 and 10) were considerably lower and, in all probability, represent structures varying in molecular weight due to the CH_3/C_6H_5 ratio in the molecules.

As indicated by this preliminary data, Component No. 10 decreases over 10 fold from the used fluid. Since its elution position indicates a lower vapor pressure component than No. 7, it would not seem reasonable that it would be preferentially lost by volatilization during operation. It would seem more reasonable to consider it as a labile structure and the possibility existing that Peak No. 5 might represent one of its decomposition products, since the concentration of Peak No. 5 is greatest in Samples 1 and 2 where Peak No. 10 is lowest. However, since both components (5 and 7) are present in the original fluids, they may also very well represent components or contaminants resulting from the synthesis procedure which resisted the clean-up procedures.

The highly complex spectra of DC-704 and the relatively small changes in relative peak intensity precludes the possibility of positive contaminant identification by mass spectrometry. However, the results tabulated in Table 5 represent changes in intensity at m/e = 31 of as great as ten (10) fold between supposedly identical DC-704 samples. These increases were particularly prominent in the samples from the large vacuum chamber at NASA Goddard.

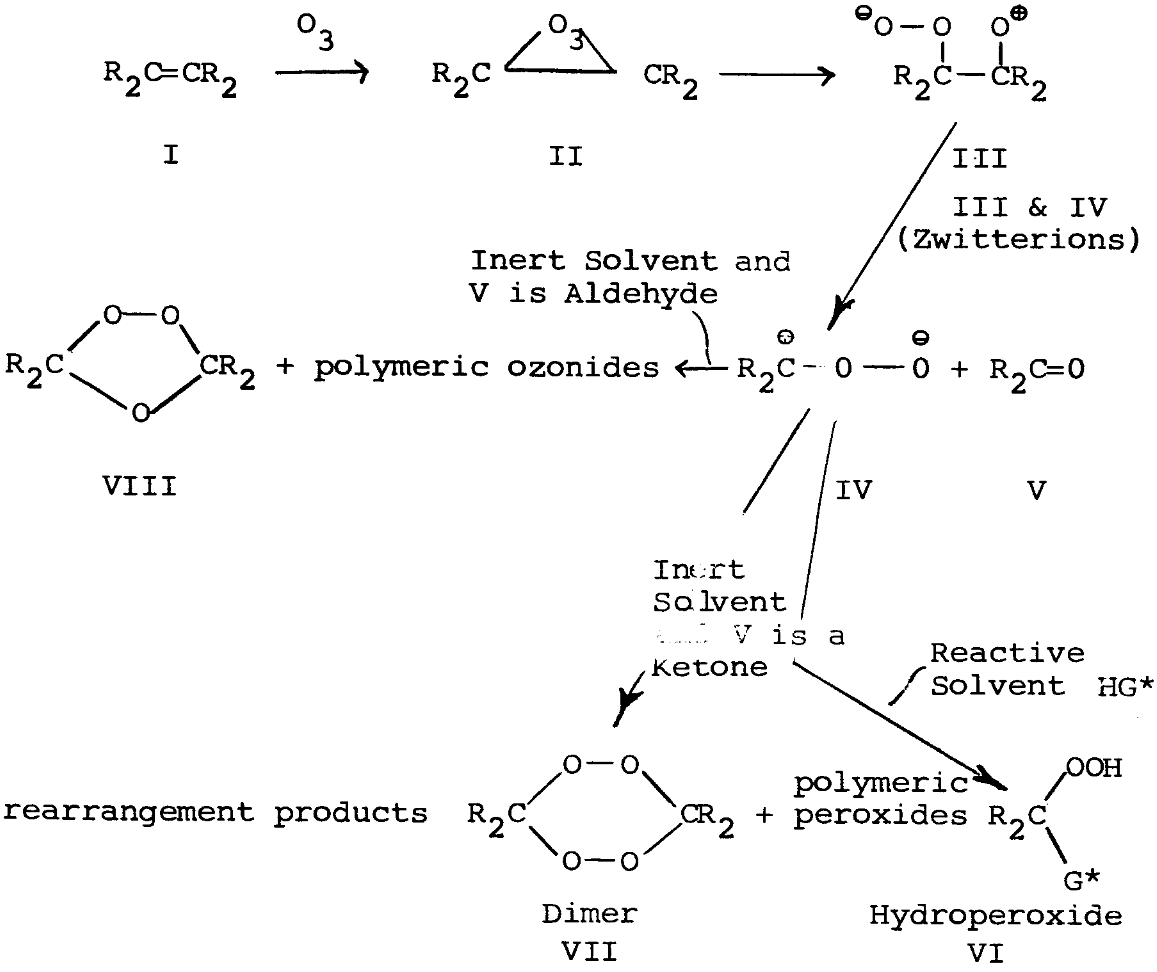
Close examination of the mass spectrometry results of Samples 1 and 2 show marked changes in m/e = 31 peak only. If this change resulted from a contaminant such as freon TF, then associated changes should also have occurred at m/e = 101, 151, and 103. However, no such changes occurred and, therefore, freon TF should be ruled out in these samples. Similar reasoning indicates such changes could only be caused by a contaminant whose base peak is m/e = 31. Further examination of lesser peaks for associated compounds were obviated by background interference. Therefore, it can only be stated that the mass spectrometry results possibly suggest m/e = 31 peak is CH_2OH.

5.4 Stability of DC-704

The results obtained when air containing twenty (20) parts per million of ozone were allowed to leak into an operating diffusion pump system are very significant. This was the first time that an explosion had been generated under controlled conditions. The total amount of ozone leaked into the system during the seven and one-half hour (7-1/2) period was approximately 9 x 10^{-11} moles. Therefore, only one (1) mole of ozone was present for every 10^{10} moles of DC-704 provided all of the ozone remained in the system.

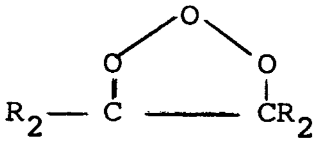
The exact mechanism by which the ozone initiated an explosive reaction in the DC-704 can only be postulated. The results obtained from analyses of the samples removed while ozone was being leaked into the system are inconclusive. In addition, no samples are available from the diffusion pump just prior to the explosion.

The most feasible explanation of the influence of ozone on the stability of DC-704 is that the ozone attacks the phenyl ring of the DC-704 molecule. The exact mechanism by which this attack occurs is highly speculative to say the least, since ozonolysis itself is very poorly understood even under closely controlled and known conditions. The elevated temperature of the fluid in an operating diffusion pump complicates the problem even more since at elevated temperatures alternate pathways (free radical) are possible. For instance, ozonolysis under ideal (temperature, solvent) conditions is believed to proceed via an ionic mechanism since ozone alone has not been found to initiate the polymerization of olefins, such as styrene which are known to proceed via free radical mechanisms. Also, ozonolysis, under normal operating conditions, is carried out at reduced temperatures in order to stabilize the highly reactive but structurally unknown intermediates shown below as II, IX, or X. This general reaction is regarded as the first step in the addition of ozone to olefinic bonds by the Criegee mechanism.



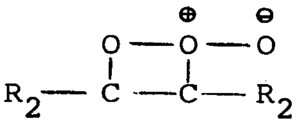
*G = OH, OR, or OCOR

The structure of the transient intermediate II is postulated to be in the form of either IX or X,



IX

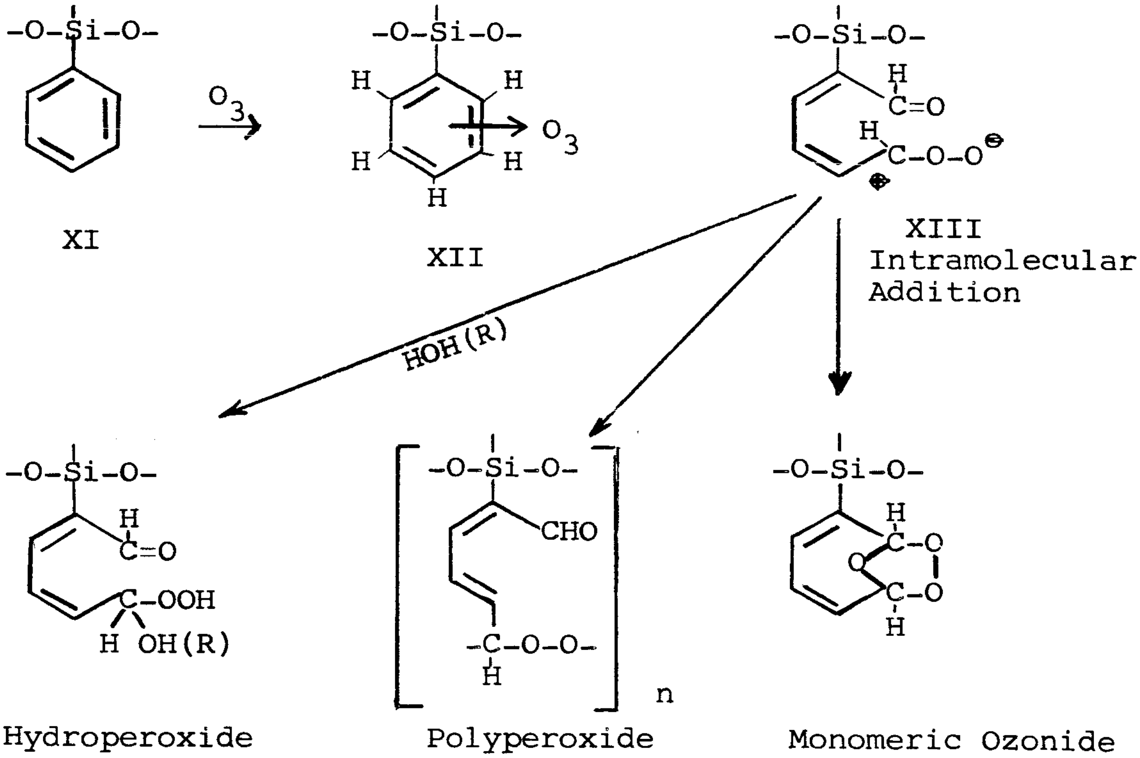
or



X

both of these forms are extremely unstable. These forms cannot be isolated, and their explosive properties are entirely unpredictable. The zwitterion IV is also very unstable. These zwitterions can be stabilized in several ways; however, in most instances, no single mechanism can be considered the sole route. When a reactive solvent of the type ROH is present, the zwitterion IV yields mainly the hydroperoxide VI. This cannot occur in our system unless water or alcoholic components are present. Due to the relatively low level, or absence, of such constituents this seems unlikely. In the presence of an "inert" medium the zwitterion can either react with itself to form a peroxide dimer VII or react with V to form an addition product. If V is an aldehyde, a monomeric ozonide of structure VIII is favored. If V represents a ketone, the carbonyl group being less susceptible to nucleophilic attack than most aldehydes, it usually will not react and one again obtains a dimer type product of structure VII and other polymerization products.

In the case of the DC-704 fluid, the initial attack of ozone would probably occur at the phenyl ring in the molecule according to the following sequences.



XI

XII

XIII

Hydroperoxide
XIV

Polyperoxide

Monomeric Ozonide
XV

Structures XII, XIV, and XV would also represent extremely labile components and, at the temperatures of reaction, could very well decompose by several types of self sustaining, free radical mechanisms.

The actual energy releasing mechanism for any of these reactions would result from the attempt of the unstable intermediates to form more stable configurations, especially of the types represented II, III, or XII and XIII. In many instances, ozonides of structure XV are also extremely unstable. The almost non-existent work done in this area with respect to reactants such as silicone fluids, leaves much to be desired in attempting to advance a specific reaction mechanism. The best approach to this problem would be to conduct ozonolysis experiments directly on these fluids and to study their reactions, mechanisms, products formed and stability of products. Even with controlled systems such studies would be difficult, but would, in all probability, be the only method by which useful information concerning this problem could be obtained.

Closely related to this discussion is the fact that many attempts to prepare the mono-ozonide derivative of butadiene ($CH_2 = CH - CH = CH_2$) have been unsuccessful due to the explosive nature of the product. These explosions occurred when stoichrometric levels of ozone were added to form the mono-ozonide. Other attempts to form ozonides of multiple olefins of small chain compounds have caused similar results.

The structural similarity of butadiene to the phenyl rings of the DC-704 fluid suggest that similar results would be obtained with DC-704. Apparently even when stoichiometric levels of ozone are employed, small quantities of the diozonide or one of its precursors was formed which was extremely unstable.

It is of interest that the data resulting from catalytic bath studies indicate a stabilization effect due the presence of aluminum. Previous studies,(1) conducted to study the effect of metal ions on gel times of silicone fluids, indicated that the addition of metallic Cu, Ag, Al or Ti had no significant effect on the gel time with or without specific gelatin inhibitors of the condensed aromatic series. The actual mechanism of the aluminum reaction in our catalytic studies could not have functioned as an oxygen scavenger in reducing oxidation since the aluminum was added as the oxide form, a form which should exhibit degradative activity towards organic materials. However, if methyl cleavage is taking place as the initiating step in the silicone fluid breakdown, the presence of aluminum must retard both chain cross-linking reactions which results in the formation of a viscous polymer and also fragment oxidation which was so obvious in the samples where aluminum was omitted. It should be pointed out that although the curves for the two high temperature (525°F) catalytic studies are grossly different, it does appear that the degradative processes are initiated at the same time interval with or without aluminum. However, the slope of the curves show the function of aluminum as a moderator or retarder, rather than an inhibitor. If the aluminum showed the latter function, the time interval for degradation of the two samples should have differed. It would appear that the aluminum functions as a complexation agent for reactive species which tend to accelerate the degradative reactions by alternate pathways.

---

(1) Silverstein, R. M., Mayo, F. R., "Gelatin Inhibitors for Silicone Oils," U.S. 3, 146, 202 (Aug. 25, 1964).

6.0 RECOMMENDATIONS FOR FUTURE WORK

6.1 Further studies should be conducted to determine the mechanism by which ozone generates an explosive reaction in DC-704 in an operating diffusion pump.

6.2 Studies should be initiated to determine if air or oxygen under the proper conditions could result in the same type of reaction as ozone.

6.3 When the mechanism by which ozone generates an explosive reaction is determined, monitoring techniques should be developed to indicate the initiation of such a mechanism.

7.0 BIBLIOGRAPHY

7.1 Reid, R. C. and Sherwood, T. K., "The Properties of Gases and Liquids," New York, McGraw Hill, 1958.

7.2 Frank-Kammetsku, "Some Problems in Chemical Kinetics and Reactivity," Vol 2, Princeton Univ., 1959.

7.3 Lewis, B., and von Elbe G., "Combustion Flames and Explosion of Gases," Academic Press, 1961.

7.4 Dushman, S., "Scientific Foundations of Vacuum Techniques," 2nd Ed., John Wiley & Sons, Inc.

7.5 Lewis, B., Peace, R. N., and Taylor, H. S., "Combustion Processes," Princeton, 1956.

7.6 NRC Equipment Corporation Advertising Literature for HS6-1500 Oil Diffusion Pump.

7.7 Silverstein, R. M., and Mayo, F. R., "Gelatin Inhibitors for Silicone Oils," U. S. Patent 3,146,202, Aug. 25, 1964.

7.8 Sokolib, H. S., "Self-Ignition Flame and Detonation in Gases," Published for U. S. National Aeronautics and Space Administration and the National Science Foundation, Washington, D. C., (N64-25875).