

ENGINEERING REPORT

35276-02

NAS8-32200

EVALUATION OF ANALYTICAL METHODOLOGY
FOR HYDROCARBONS IN HIGH PRESSURE
AIR AND NITROGEN SYSTEMS

Prepared For:

NATIONAL AERONAUTICS & SPACE ADMINISTRATION
MARSHALL SPACE FLIGHT CENTER, ALABAMA

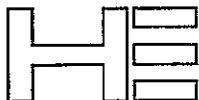
JULY 29, 1977

(NASA-CR-150409) EVALUATION OF ANALYTICAL
METHODOLOGY FOR HYDROCARBONS IN HIGH
PRESSURE AIR AND NITROGEN SYSTEMS (Harmon
Engineering, Huntsville, Ala.) 62 p
HC A04/MF A01

N77-33379

Unclas
49995

CSSL 20L G3/31



HARMON ENGINEERING

SCIENTISTS • ENGINEERS • SURVEYORS

AUBURN INDUSTRIAL PARK / BOX 2249 / AUBURN, ALA. 36830 / (205) 821-9250
A DIVISION OF G.R. HARMON & ASSOCIATES, INC.

35276-02

NAS8-32200

EVALUATION OF ANALYTICAL METHODOLOGY
FOR HYDROCARBONS IN HIGH PRESSURE
AIR AND NITROGEN SYSTEMS

Prepared For:

NATIONAL AERONAUTICS & SPACE ADMINISTRATION
MARSHALL SPACE FLIGHT CENTER, ALABAMA

Prepared By:

HARMON ENGINEERING
3706 KENWOOD DRIVE, N.W.
HUNTSVILLE, ALABAMA 35810

APPROVED BY:



BRUCE B. FERGUSON

DATE: JULY 29, 1977

ABSTRACT

The following methods can be used to determine the hydrocarbon concentrations in LOX, GN₂ and missile grade air in a range below the capabilities of previous methods. Concentration of the sample is achieved by adsorption on Tenax-GC, Molecular Sieve 5A and activated charcoal. A very large volume of gas can be passed through these adsorbents to collect the hydrocarbons. The trapped hydrocarbons are then desorbed and transferred to an analytical column in a gas chromatograph. Thus all of the contaminants of a gaseous sample ranging from 100 ml to 100 liters is reduced to microliter volumes necessary for gas chromatography analysis. The hydrocarbons can be identified and quantified by comparing their retention times and peak areas to those of known standards.

Studies in recoverability and reproducibility were done to verify the value of this method. The procedures were then tested on actual samples of liquid oxygen, high pressure nitrogen, low pressure nitrogen and missile grade air.

The sensitivity of this method depends on the volume of gas passed through the adsorbent tubes. A sample volume of 3 liters gives a sensitivity of approximately one part per billion (ppb), a sample volume of 30 liters - one-tenth ppb, etc.

The versatility of this method makes its applications unlimited. Proper selection of adsorbents, analytical columns and sample volumes

enable this to be applied to infinite applications in gaseous and liquified gas contaminant determination and quality control. By using comparison of contamination this can be used in lock-up testing simply by testing the blank level of impurities of the virgin lock-up gas and comparing it to the existing gas. Using this method of collection and concentration in conjunction with a Gas Chromatography-Mass Spectroscopy system, exact determinations of identity and quantity of the contaminants can be determined and, the source of contamination can be more easily isolated.

Because of the explosive nature of LOX when contacting hydrocarbons, we feel that periodic monitoring of LOX and anything contacting LOX, including pressurization GN₂, for hydrocarbons is necessary. The use of the reported method will enable these two systems to be routinely monitored to determine low-level increases in specific hydrocarbon concentration that could lead to potentially hazardous conditions.

TABLE OF CONTENTS

LIST OF TABLES -----	i
LIST OF FIGURES -----	ii
1.0 INTRODUCTION -----	1
2.0 APPARATUS -----	3
2.1 Sampling Hardware -----	3
2.2 Analysis Hardware -----	6
2.3 Chemicals -----	6
3.0 PROCEDURES -----	10
3.1 Sampling -----	10
3.2 Separation and Concentration -----	11
3.3 Analysis -----	14
4.0 RESULTS AND DISCUSSION -----	17
4.1 Reproducibility and Recoverability Studies -----	17
4.2 LOX Analysis -----	27
4.3 High Pressure Nitrogen -----	28
4.4 Low Pressure Nitrogen -----	35
4.5 Missile Grade Air -----	37
5.0 CONCLUSIONS -----	42
5.1 Current Hydrocarbon Monitoring -----	42
5.2 Method of Analysis -----	42
5.3 Hydrocarbons in High Pressure Nitrogen -----	42
5.4 Condensable Hydrocarbons -----	43
5.5 LOX Filters -----	43
5.6 Compatability Studies -----	44
5.7 Hydrocarbon Contaminants Limits -----	44
5.8 Applications -----	44
6.0 RECOMMENDATIONS -----	46
6.1 Comparison of Methods for Determining Condensable Hydrocarbons -----	46
6.2 Sample LOX Routinely -----	48
6.3 LOX Compatability Studies -----	49
6.4 Routinely Sample High & Low Pressure Nitrogen Systems -----	49
6.5 Routine Analysis of Missile Grade Air -----	52
6.6 Adsorbent Study -----	52
APPENDIX 1 -----	53

LIST OF TABLES

<u>TABLE</u>		<u>PAGE</u>
1	REPRODUCIBILITY OF METHANE ANALYSES ON DIFFERENT COLUMNS -----	19
2	HYDROCARBON CALIBRATION DATA -----	20
3	RETENTION TIMES OF HIGHER MOLECULAR WEIGHT -----	21
4	RECOVERABILITY OF SELECTED COMPOUNDS -----	25
5	METHANE IN LOX -----	27
6	HIGH PRESSURE N ₂ SAMPLE 8 TENAX PEAKS -----	34

LIST OF FIGURES

<u>FIGURE</u>		<u>PAGE</u>
1	LOX SAMPLING APPARATUS -----	4
2	PHOTOGRAPHS OF SAMPLING SYSTEM -----	5
3	THE ANALYSIS SYSTEM -----	7
4	CLOSE-UP OF GC OVEN WITH LN ₂ TRAP ON CHARCOAL COLUMN -----	8
5	SAMPLING AT THE HIGH PRESSURE NITROGEN TANK -----	12
6	SAMPLING FROM THE LOX STORAGE TANK -----	12
7	SAMPLE CALIBRATION CURVE FOR METHANE -----	18
8	NORMAL ALKANES ANALYZED ON A SILICA GEL COLUMN -----	22
9	HYDROCARBON ANALYSIS ON EMULPHOR ON 870 COLUMN -----	23
10	SCHEMATIC DRAWING OF APPARATUS USED FOR RECOVERABILITY STUDIES -----	24
11	MIDWEIGHT HYDROCARBONS IN LOX -----	29
12	HIGHER MOLECULAR WEIGHT HYDROCARBONS IN LOX -----	30
13	ANALYSIS OF HYDROCARBONS IN HIGH PRESSURE NITROGEN TRAPPED ON MOLECULAR SIEVE 5A -----	32
14	HIGHER MOLECULAR WEIGHT HYDROCARBONS IN HIGH PRESSURE NITROGEN -----	33
15	MIDWEIGHT HYDROCARBONS IN LOW PRESSURE NITROGEN -----	36
16	HIGHER MOLECULAR WEIGHT HYDROCARBONS IN LOW PRESSURE NITROGEN -----	38
17	MIDWEIGHT HYDROCARBONS IN MISSILE GRADE AIR -----	39
18	HIGHER MOLECULAR WEIGHT HYDROCARBONS IN MISSILE GRADE AIR -----	40

LIST OF FIGURES (Cont'd)

<u>FIGURE</u>		<u>PAGE</u>
19	CHROMATOGRAM OF CONDENSABLE HYDROCARBONS -----	47
20	SCHEMATIC DRAWING OF SAMPLING SYSTEM -----	48
21	CHROMATOGRAM OF FREON TF USED TO WASH LOX FILTER -----	50
22	CHROMATOGRAM OF HIGH MOLECULAR WEIGHT HYDROCARBONS -----	51

1.0 INTRODUCTION

Compressed gases (air and nitrogen) are routinely monitored to determine the total hydrocarbon content of the gases. This is accomplished using a 1 cm³ sample of the gas at room temperature and pressure (RTP) injected through an empty capillary column and detected by a flame ionization detector (FID). The limit of sensitivity using this method is approximately 0.1 part per million by volume (ppm). This sensitivity is sufficient for most cases but the gases that are used to compress liquid oxygen (LOX) to 5,000 psi must be extremely clean to prevent explosion. This problem is explained in detail in the Phase 1 report of this contract.

At the present time, the purity of the LOX is being monitored only by removing in-line filters and removing hydrocarbons by washing them with an appropriate solvent. Concentration measurements are made with an infrared spectrometer. This procedure is extremely time consuming and does not truly reflect the state of the LOX. Several thousand gallons of LOX must flow through the filters before the hydrocarbons become concentrated enough for measurement. This method of measurement more closely reflects the cleanliness of the system and the most likely place for an explosion is at the filters.

The overall objective of this study was to develop procedures to qualitatively and quantitatively analyze the gases for hydrocarbon content. Major emphasis has been given to analysis of the LOX and the 8,000 psi nitrogen system. This was done due to the safety requirements of these

two systems. The same basic procedures were also used to determine the hydrocarbons in low pressure nitrogen (GN_2) systems and in missile grade air.

The instrumentation available for hydrocarbon analysis was evaluated. Gas chromatography offered the best method to obtain separation of the basic hydrocarbons and to quantify the amounts present. To obtain measurable quantities of individual constituents, concentration techniques were required. Large quantities of gas were passed through adsorbents to trap and concentrate the contaminants. The contaminants were then desorbed by heat and trapped on a loop of the analytical column immersed in liquid nitrogen. The concentrated contaminants were then injected as a "plug" onto the analytical GC column and were analyzed with a flame ionization detector.

All background information and literature references of previous work is given in the Phase 1 report which was published earlier. This report will detail the experimental work that was proposed earlier. The results are also discussed in the light of developing routine procedures for the analysis of the gases.

2.0 APPARATUS

2.1 Sampling Hardware

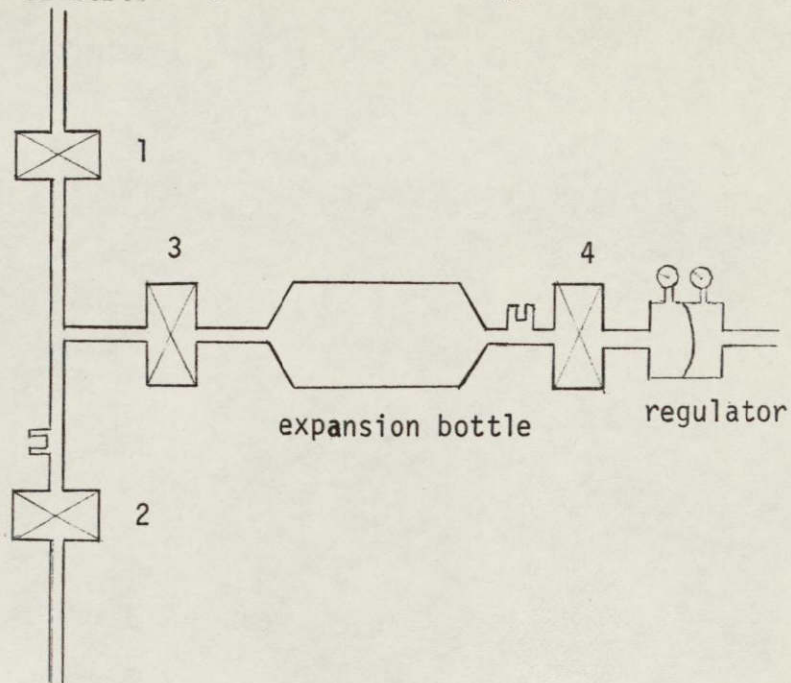
The sampling equipment was designed and constructed by Harmon Engineering to meet the requirements of this project. Figure 1 shows a schematic drawing of the LOX sampling system and a photograph of the LOX sampler. Figure 2 is an actual photograph of the apparatus. All components of the sampling train were cleaned to LOX specifications per MSFC-SPEC-164.

All parts of the sampling system were constructed from stainless steel material. The valves in contact with LOX were Nupro bellows valves. The chamber between the valves to trap the LOX was made from 5' of $\frac{1}{4}$ " stainless steel tubing. A Nupro safety release valve was installed in the line to prevent overpressurization of the line. The liquid trap was foam insulated to aid in cooling.

The expansion chamber was a 300 ml spun stainless steel bottle fitted with a rupture disc at one end. A Union Carbide regulator was attached directly to the valve. A Nupro fine needle valve was used to regulate the flow through the absorbent tubes.

The adsorbent tubes were made from stainless steel tubing packed with one of three different adsorbing materials. The $C_2 - C_6$ hydrocarbons were adsorbed on Molecular Sieve 5A and the molecular weight compounds C_4 and up were adsorbed on Tenax GC. Tubes for both these adsorbents were $\frac{1}{4}$ " stainless steel tubing, 4" long with Swagelok compression fittings on each end. The methane was trapped on a one foot long $1/8$ "

(a) Schematic Drawing of LOX Sampling System



(b) Photograph of the LOX Sampler

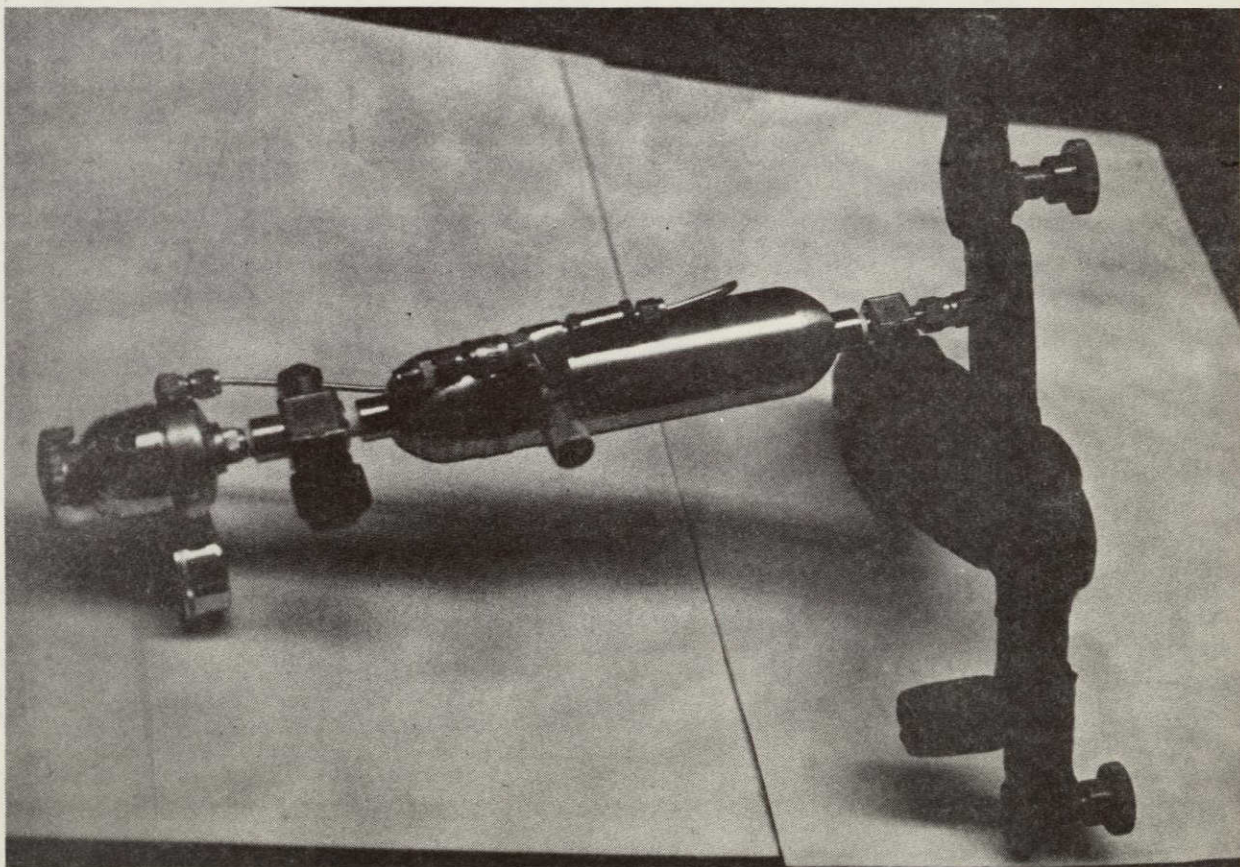
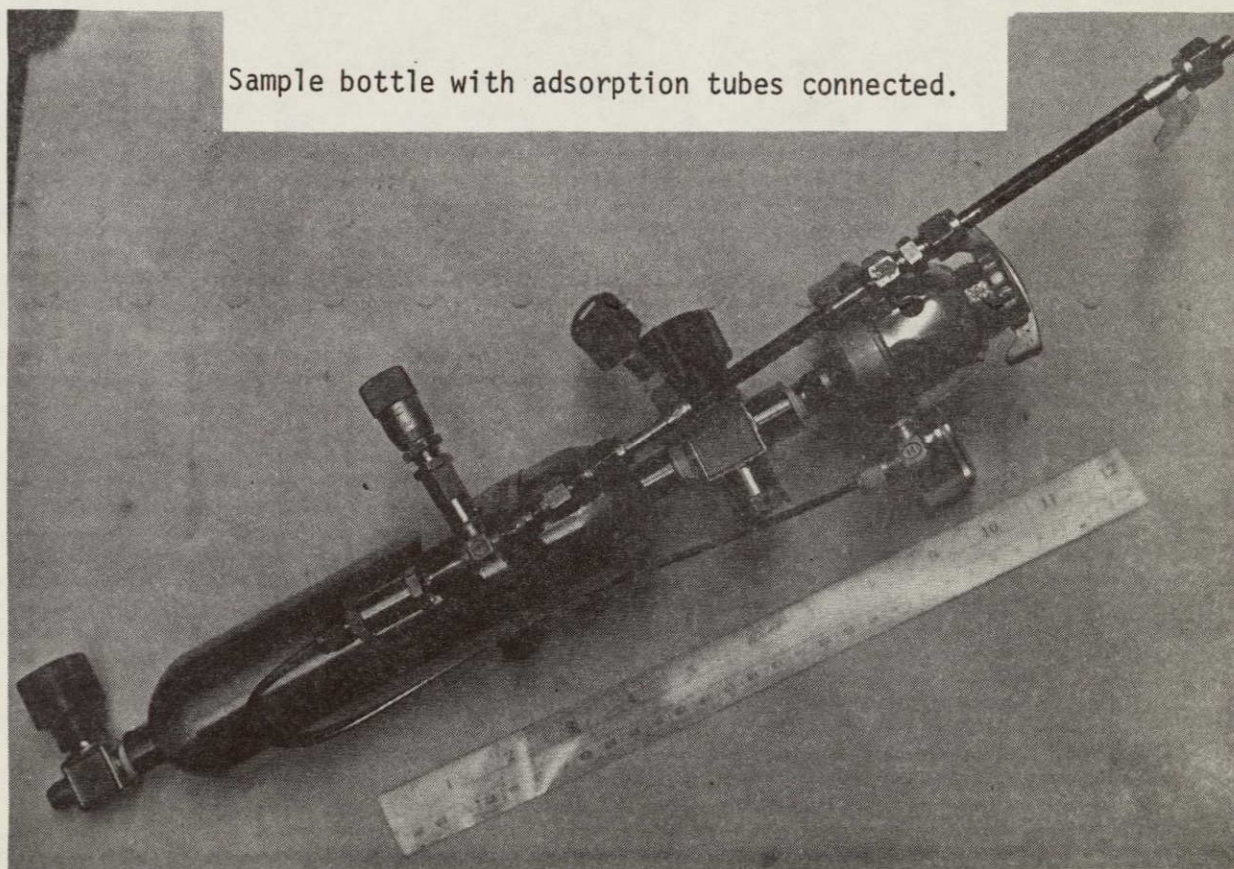
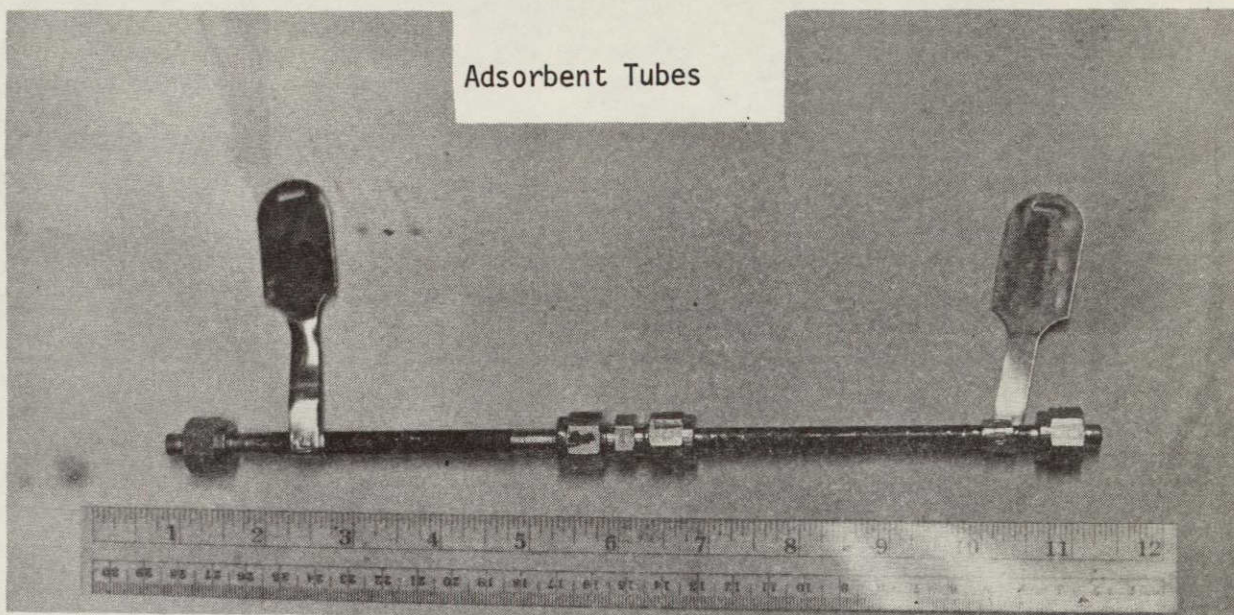


FIGURE 1. LOX Sampling Apparatus

REPRODUCIBILITY OF THE
ORIGINAL PAGE IS POOR



REPRODUCIBILITY OF THE ORIGINAL PAGE IS POOR

FIGURE 2. Photographs of Sampling System

stainless steel column packed with charcoal. This column was immersed in an LN_2 bath to cool it enough to trap the methane and any ethane which went through the molecular sieve column.

2.2 Analysis Hardware

The analysis of all hydrocarbons was performed using a Bendix Model 2200 Gas Chromatograph. This instrument is equipped with a flame ionization detector (FID) and a large, temperature-programmable oven. A Hewlett Packard Model 7128A recorder was used to record the chromatograms. A schematic drawing and a photograph of the system is given in Figure 3. Figure 4 shows a close up of the GC oven with LN_2 trap on the charcoal column. A Hewlett Packard Model 3370A integrator was used to determine retention times and areas.

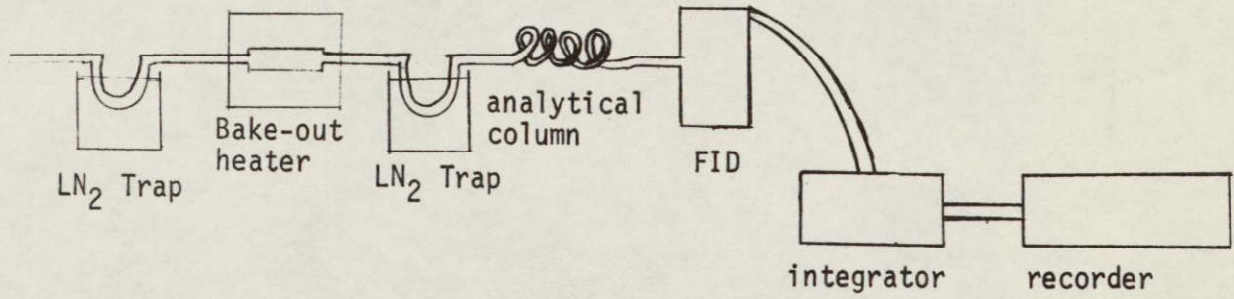
The bake-off oven was designed by Harmon Engineering to fit the adsorption tubes. The oven consisted of a slotted aluminum block with a 100 watt cartridge heater to supply heat. The box contained 1" of fiberglass insulation around the block for temperature stability. A thermocouple well was drilled in the block to allow the temperature to be monitored.

Glass sample bottles with Teflon stopcocks were used throughout the study when dilutions were required. These bottles, supplied by Altech Associates, had a rubber septum for sample withdrawal.

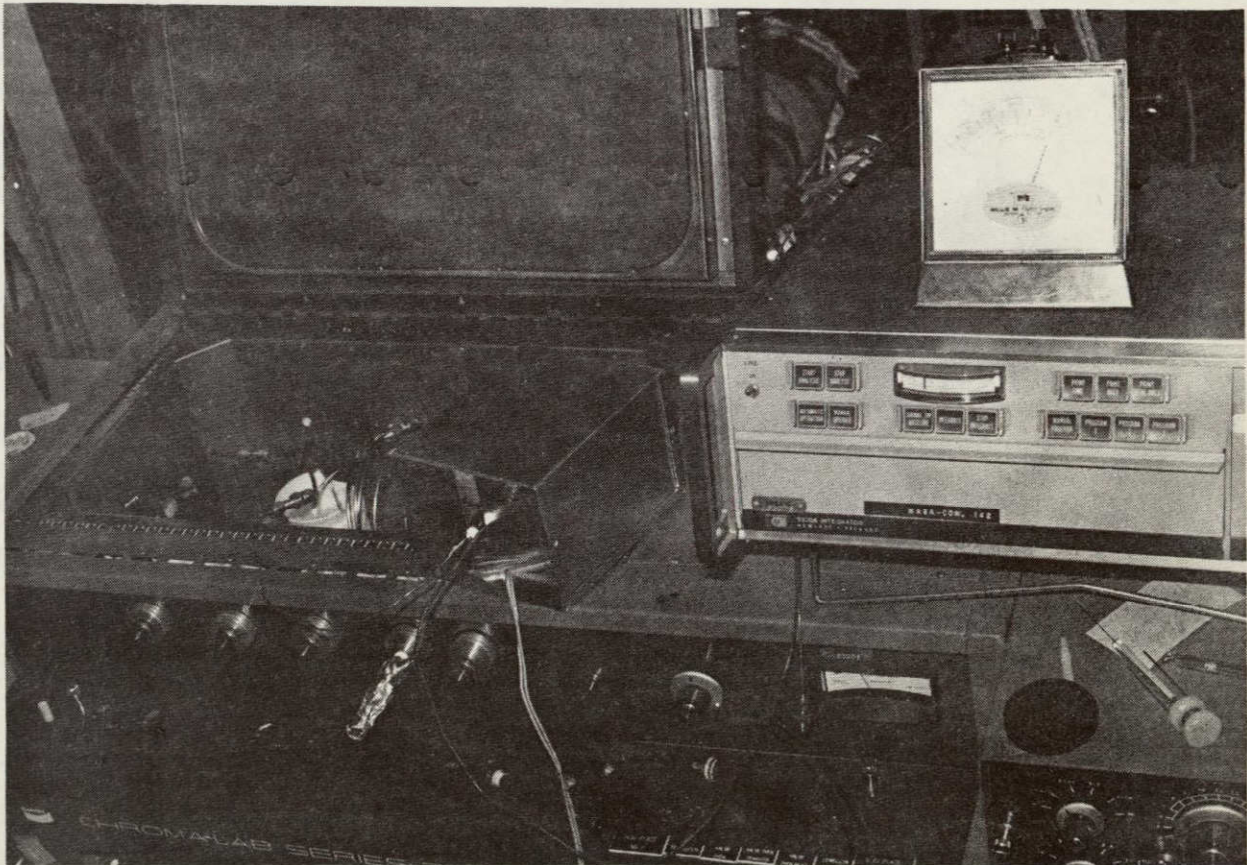
2.3 Chemicals

The gases for the GC were supplied by a local vendor. Medical grade air, zero grade nitrogen and hydrogen were used throughout the study.

(a) Schematic Drawing



(b) Photograph of the System



REPRODUCIBILITY OF THE ORIGINAL PAGE IS POOR

FIGURE 3. The Analysis System

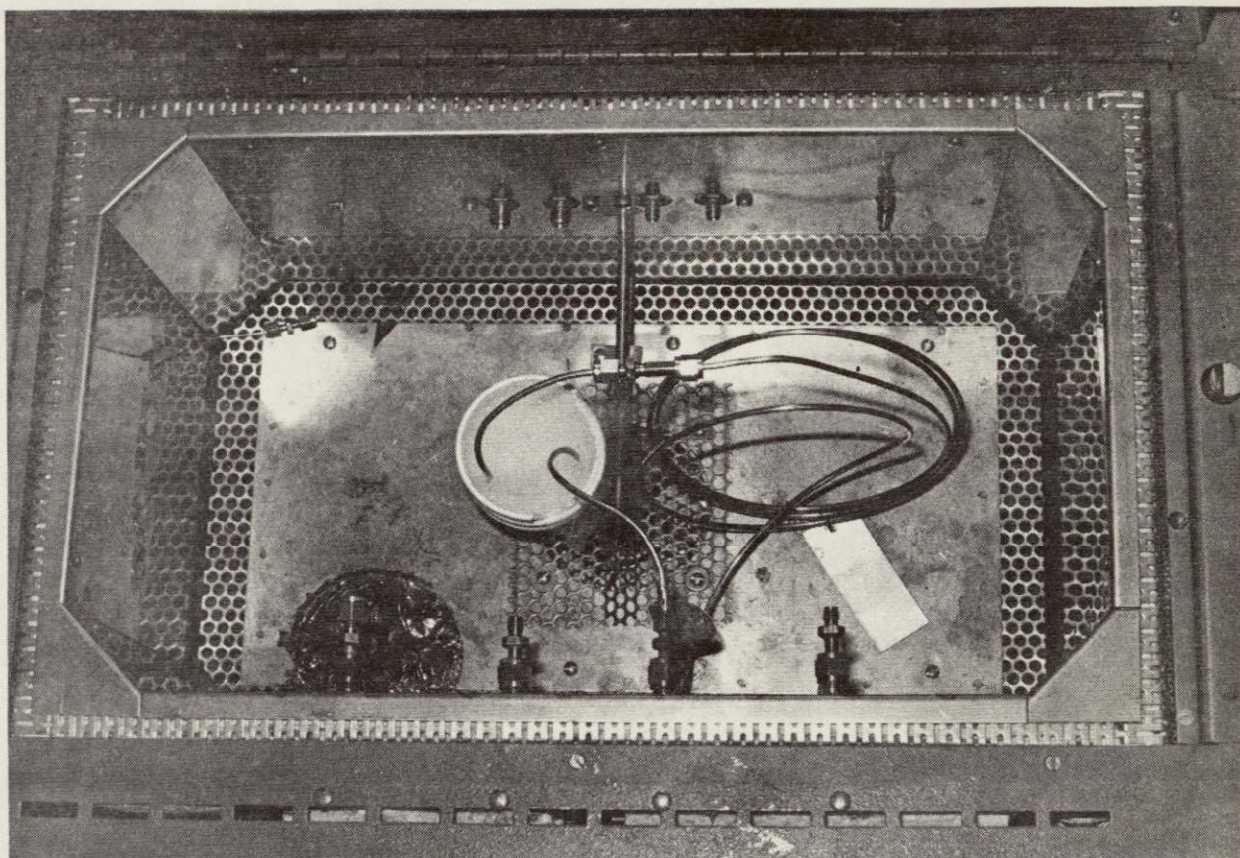


FIGURE 4. Close up of GC Oven with LN₂ Trap on Charcoal Column.

REPRODUCIBILITY OF THE
ORIGINAL PAGE IS POOR

All gases were run through a Silica Gel/Molecular Sieve trap to remove water and oils before use. The carrier gas also was passed through a short Molecular Sieve column immersed in an LN₂ bath to provide carrier gas stability during operation.

The calibration gases were supplied by Altech Associates in small aerosol type cans. These were off-the-shelf mixtures that were accurate to $\pm 2\%$. They proved to be a highly satisfactory method of compound identification and quantification.

The higher molecular weight liquid hydrocarbon compounds were supplied by Poly Science Corporation. Both straight and branched chain compounds were used to aid in the compound identification.

3.0 PROCEDURES

Hydrocarbons were analyzed utilizing a temperature-programmable gas chromatograph with a flame ionization detector. To insure separation and quantification of hydrocarbons in the range of C_1 through C_{19} the samples were separated into three molecular weight ranges using three selective adsorbents and analytical columns.

Gaseous samples were concentrated in an LN_2 cold trap at the head of the analytical column after desorption. Cryogenics were sampled as a liquid, allowed to vaporize and then treated as a gaseous sample.

3.1 Sampling

The sample bottle was used to transport a pressurized sample of the gas from the field sampling point to the laboratory for analysis. This was a simple procedure for the compressed gases in that a regulated pressure at the sample point of 800-1, 200 psi was used to pressurize the sample bottle. The bottle was disconnected and vented to the atmosphere to purge the bottle. The purge procedure was repeated twice before the actual sample was taken. Figure 5 illustrates a sample being taken from the high pressure nitrogen tank.

Cryogenics (LOX) were sampled by trapping a volume of the liquid sample. The liquid was then quantitatively expanded into the sample bottle as it warmed up to ambient temperature.

The sampler was attached to the LOX sample valve at point a. (See Figure 1). Valves 1 and 2 were opened to allow the liquid to flow

through the liquid trap until LOX flowed freely at the outlet (b). Valves 1 and 2 were then closed to trap a volume of liquid in the line. Valve 3 was opened to allow the liquid to vaporize into the expansion bottle as it warmed. The pressure in the bottle would increase to 200-300 psig from the trapped volume of liquid.

The bottle was filled and purged twice to remove all traces of previous gas in the bottle. This was accomplished by opening Valve 2 and venting the bottle to the atmosphere after the liquid had vaporized. Valve 3 was then closed, Valve 1 was reopened and the procedure was repeated to fill the liquid trap again.

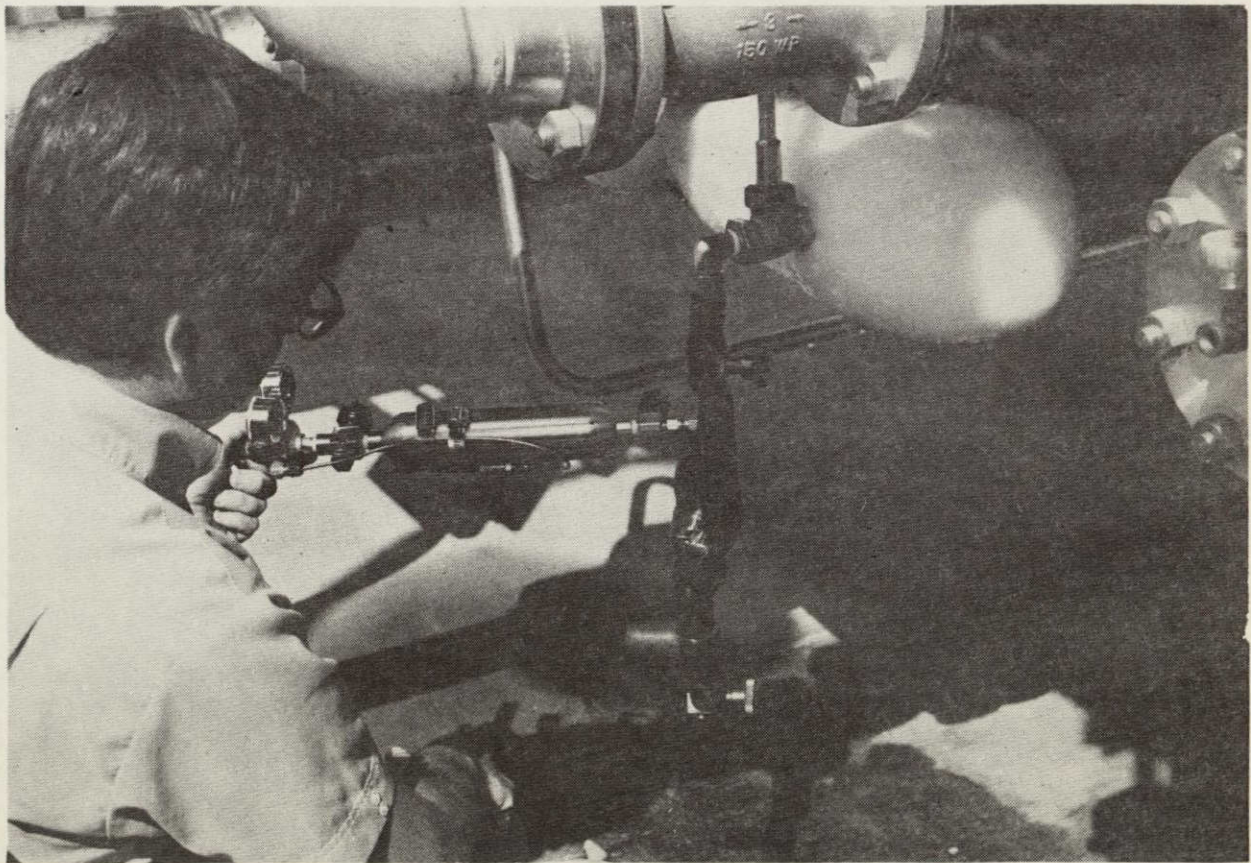
The pressure in the expansion bottle was increased to the critical pressure of oxygen by repeating the filling procedure. Normally three times of filling were required to increase the pressure in the bottle to approximately 800-1,000 psig. This pressure was sufficient for three 3-liter samples. Figure 6 shows a LOX sample being taken in the LOX storage facility at Building 4659.

3.2 Separation and Concentration

After returning the filled sample bottle to the laboratory, the adsorbent tubes were attached in series to the outlet of the micrometer valve. The gas was first passed through the Tenax tube to remove the C_6 and heavier compounds. A fraction of the C_4 and C_5 compounds were also adsorbed on the Tenax. The $C_2 - C_5$ compounds were trapped on the Molecular Sieve 5A tube. The final tube was a charcoal loop immersed in LN_2 to trap the methane. The methane concentration was high enough in the vaporized oxygen sample to be analyzed by direct injection into the GC without



FIGURE 5. Sampling at the High Pressure Nitrogen Tank



REPRODUCIBILITY OF THE ORIGINAL PAGE IS POOR

FIGURE 6. Sampling from the LOX Storage Tank

trapping a large volume of sample as described below.

The flow through the Tenax and Molecular Sieve tubes was adjusted to 50-70 ml/min using 10 psi regulated pressure and the micrometer valve. The exact flow was measured each time with a soap bubble flow meter. This was necessary since the tubes were not packed exactly the same and the flow coefficient would vary slightly from tube to tube. The flow rate and the time were used to calculate the volume of sample. One to three liters of sample provided a large enough concentration of the contaminants for detection.

After the flow was adjusted properly, the precooled charcoal loop was attached to the outlet of the Molecular Sieve column. Approximately one liter of the sample was used to trap methane and then the charcoal loop was removed. A larger sample was trapped each time on the Tenax and the Molecular Sieve than on the charcoal.

Once the contaminants were trapped on the adsorption tubes, the ends were capped and the samples could be stored. No lengthy study was done to determine how long a sample could be stored. Those that were stored for 1 week gave the same results as those analyzed immediately after being trapped. The methane was concentrated on the LN₂ cooled charcoal loop. The column could not be stored before analysis. It was inserted immediately into the GC for analysis.

The Molecular Sieve and the Tenax tubes required heating to 250°C for 30 minutes to desorb the trapped compounds. As the tubes were individually heated in the bake-off oven with carrier gas flowing through

them at 30-50 ml/min the compounds were slowly desorbed. The outlet of the adsorption tube in the bake-off heater was attached to a precolumn immersed in LN_2 to concentrate the compounds for analysis. The precolumn was packed with the same material as the analytical column.

3.3 Analysis

The analysis of the compounds trapped on the different adsorption tubes was accomplished on different columns. The methane trapped on the charcoal was analyzed on a 6' activated charcoal column. The contaminants on the Molecular Sieve tube were separated on a 12' Silica Gel column. The compounds trapped on the Tenax were separated on a 10' column packed with Emulphor ON 870 on Chromsorb W. All quantification was done by comparing the area obtained from a compound with that obtained from a methane calibration curve run on the same column.

This analytical procedure requires precise timing for proper identification of the hydrocarbons. A uniform starting time must be chosen and all retention times must be known precisely. To quantify the hydrocarbons in the range needed, the area under the curve must be calculated rather than peak height comparison. Due to the necessity of cold trapping on the column and slow warming necessary for proper separation, the peaks are often low in height and long in duration. The retention times must be reproducible for identification. By using an integrator the above difficulties were overcome. The areas of all peaks were compared to methane calibration standards. Therefore all quantities are expressed as an equivalent amount of methane. It would have been impossible to complete a study of this type without the use of an electronic integrator to determine concentrations and retention times.

3.3.1 Methane

The methane in the compressed gas was analyzed directly from the cold trapped loop. After being inserted at the analytical column inlet, the cold trap was removed to release the methane. The removal of the LN₂ trap caused a pressure surge and increased flow which blew out the flame in the FID. The flow subsided after 30-50 seconds and the flame could be relit.

Immediately after the removal of the LN₂ trap the oven door was closed and the temperature program was initiated. The normal program was to hold the oven at 25°C for 2 minutes and then increase the temperature to 200°C at 15°C/min. The temperature was held at 200°C for 20 minutes before cooling. The integrator was started (time = 0) when the recorder indicated the flame went out.

The methane in the LOX was analyzed by direct injection into the GC. The charcoal column was used as above but a 5-10 ml sample was removed from the sample bottle by using a gas-tight syringe. The charcoal will separate the methane from the oxygen thus allowing identification and quantification.

3.3.2 C₂ - C₅ Hydrocarbons

The C₂ - C₅ hydrocarbons that were trapped on the Molecular Sieve tube were desorbed and concentrated in a precolumn packed with Silica Gel. The same material was used as packing for the analytical column. The carrier flow rate was 30-50 ml/min. for the analysis.

After the LN₂ trap was removed, the same procedure was followed that was used for the methane analysis. The same temperature program was

routinely used. The GC reacted in the same way as with the methane analysis.

Part of the C_4 and C_5 compounds were trapped on the Molecular Sieve and part were on the Tenax. This meant that the total amount of the compound was the sum of those found during this analysis and the analysis of the higher molecular weight compounds.

3.3.3 $C_4 - C_{19}$ Hydrocarbons

Only a small part of the C_4 and C_5 hydrocarbons were trapped in the Tenax but 100% of the higher molecular weight compounds were present. The analytical column was a 10' column packed with Emulphor ON 870 on Chromsorb W. The temperature program used gave excellent separation of the entire range of compounds. The normal temperature program was to hold the column at 25°C for 2 minutes then increase the temperature at the rate of 15°/min. to 150°C which was held for 30 minutes. The temperature program was initiated immediately after the removal of the LN_2 trap from the precolumn.

After the removal of the LN_2 trap, the flame in the FID again went out due to the pressure surge. When the recorder indicated the flame was out, the integrator was started. A carrier flow of 30 ml/min. was normally used throughout the run although on occasion a 20 ml/min. flow proved to be useful.

4.0 RESULTS AND DISCUSSION

4.1 Reproducibility and Recoverability Studies

The complete method of analysis can be divided into three distinct parts - C₁ and C₂ unsubstituted hydrocarbons trapped on charcoal, C₂ - C₆ compounds trapped on Molecular Sieve 5A and C₄ and heavier compounds trapped on the Tenax. In addition, much time was spent checking the recoverability and the reproducibility of methane injections since all quantities were compared to methane standards.

The method of calibrating all compounds with methane is a convenient method of quantification since only one series of standards must be run to prepare a calibration. Throughout this study, all concentrations are expressed in ppm_{v/v} or µl contaminant/l of gas at room temperature and pressure (RTP). When discussing quantities of compounds the term ppm-ml will be used. One ppm-ml is the volume of a compound at RTP that would be found in one ml of a one ppm solution. By using this term it was possible to calibrate using different volumes of a single concentration mixture and then relate that quantity to the samples. For instance, the area of the GC signal obtained from 1 ml of a 100 ppm mixture of methane (100 ppm-ml) is equivalent to that obtained for 1,000 ml of a 0.1 ppm mixture.

4.1.1 Calibration and Reproducibility of Standards

After each batch of samples were analyzed on a particular column, a series of methane standards were analyzed to obtain a calibration curve for comparison purposes. A typical curve is shown in Figure 7.

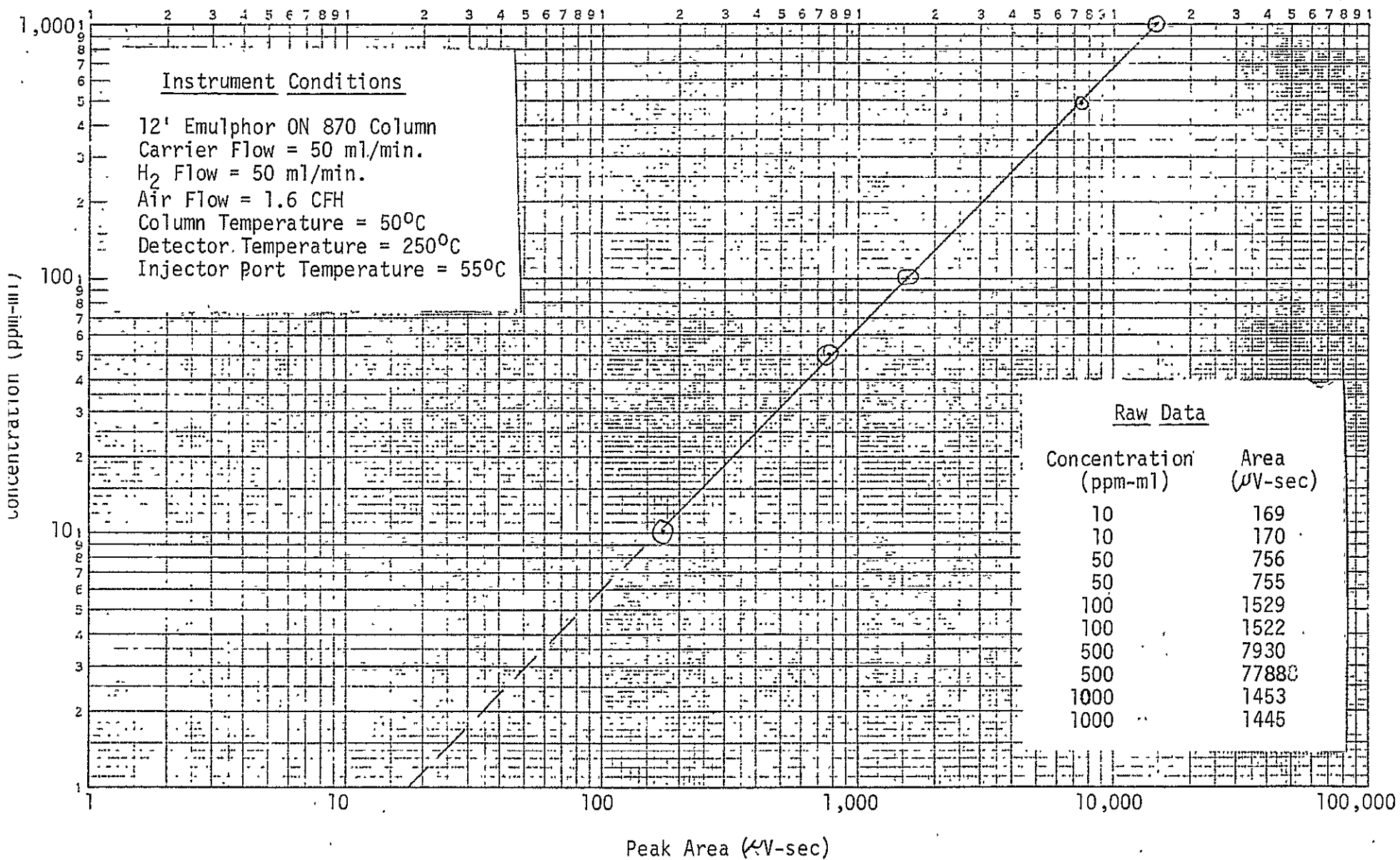


FIGURE 7. Sample Calibration Curve for Methane

A standard mixture of 100 ppm methane in nitrogen was chosen for calibration use. The volume of the mixture was varied to obtain the relationship between the peak area and the number of ppm-ml.

The reproducibility of the methane calibration is shown in Table 1 below. These injections were made consecutively. The response was found to vary slightly from day to day due to variations in the hydrogen flow. The response also varied from column to column due to the changes in carrier flow. The response throughout the day for a given column was extremely reproducible. To insure that the response was the same, methane standards were analyzed after each sample.

TABLE 1
REPRODUCIBILITY OF METHANE ANALYSES ON DIFFERENT COLUMNS

Injection #	12' Emulphor ON 870	6' Charcoal	12' Silica Gel	
	30 ml/min	10 ml/min	60 ml/min	30 ml/min
1	3260	899	4888	3347
2	3396	896	4908	3238
3	3323	939	4952	3280
4	3280	959	5003	3348
5	3234	947	4939	3438
6	3393	955	4962	3288
7	3439	943	4926	3285
8	3296	962	4979	3241
Average ($\mu\text{V-sec}$)	3328	938	4955	3308
Std. Dev.	28	10	99	25
Relative Std. Dev.	0.8	1.1	2.0	0.8

Note: The values in the table are the peak areas expressed in $\mu\text{V-sec}$. for 100 ppm-ml. The flow rates shown at the top of the table are the carrier flow rates.

Many standard mixtures of different hydrocarbons were analyzed on the columns that were routinely used. The retention times are normally approximately the same for the same type runs.

Table 2 contains calibration data for some $C_1 - C_6$ hydrocarbons on the Silica Gel Column. The volume concentration was obtained by the multiplication of the sample concentration by the volume of sample injected.

TABLE 2
HYDROCARBON CALIBRATION DATA

Compound	Retention Time (sec)	Sample Concentration (ppm)	Volume Concentration (ppm-ml)	Peak Area V-sec	Methane Equivalent
methane	114	18	270	9525	1.00
ethane	382	17	255	19360	2.15
ethylene	523	-	-	-	-
propane	613	17	255	29190	3.25
acetylene	659	-	-	-	-
butane	806	16	240	38460	4.54
pentane	987	20	300	53140	5.02
hexane	1272	21	315	60680	5.46

Note: These data were obtained by trapping a volume of the standard gas on the Silica Gel column with the LN_2 trap. The temperature program was the same as all the Molecular Sieve Analyses.

The methane equivalent shows the relationship between the methane signal and that for the different hydrocarbons. This means an actual pentane concentration of 1 ppm would have a methane equivalent concentration of 5 ppm. This is due to the number of ionized particles produced upon combustion. Thus one pentane molecule containing five carbon atoms produces approximately five times the number of ionized particles as methane with its one carbon atom.

Table 3 gives the retention time and calibration data for the higher molecular weight hydrocarbons on Emulphor ON-870. These data were used to identify the individual compounds. No methane equivalent is available for the higher molecular weight compounds since they are liquids and no calibration gases were available. To determine the retention times, vapor from a liquid sample was trapped and handled exactly as the samples were.

Figures 8 and 9 show typical analyses of standards on different columns. The retention times on the runs will vary slightly from run to run due to the heating rate and the exact time the integrator is started.

TABLE 3
RETENTION TIMES OF HIGHER MOLECULAR WEIGHT HYDROCARBONS

Compound	Retention Time Run #1 Seconds	Retention Time Run #2 Seconds	Retention Time Run #3 Seconds
isobutane	48	50	52
2-methyl butane	49	53	56
2,2-dimethyl propane	59	63	65
2,2-dimethyl butane	73	77	80
2-methyl pentane	89	92	95
3-methyl pentane	98	99	102
n-hexane	102		
n-heptane	183	181	
n-octane	289	287	
n-nonane	385	384	
n-decane	469	468	
n-undecane	546	549	
n-dodecane	620	622	
n-tridecane	697		
n-tetradecane	766		

Note: Temperature program was 25°C for 2 minutes then increased at 15°C/minute to 150°C and held for 20 minutes before cooling. The carrier flow was 30 ml/min. initially and then it decreased to 20 ml/min. as the temperature increased to 150°.

Standards

Silica Gel Column

H₂ Flow = 50 ml/min

Carrier Flow = 30 ml/min

Temp Prog = 25° for 2 min. then rise at 15°/min. to 200°, hold at 200°
for 20 min.

Sample Size = 2ml

Peak #	Compound	Concentration (ppm)	Retention Time (sec)	Peak Area (μV-sec)
1	methane	18	78	1142
2	ethane	17	333	2236
3	propane	17	609	3443
4	butane	16	805	11220
5	pentane	20	993	9729
6	hexane	21	1290	6708

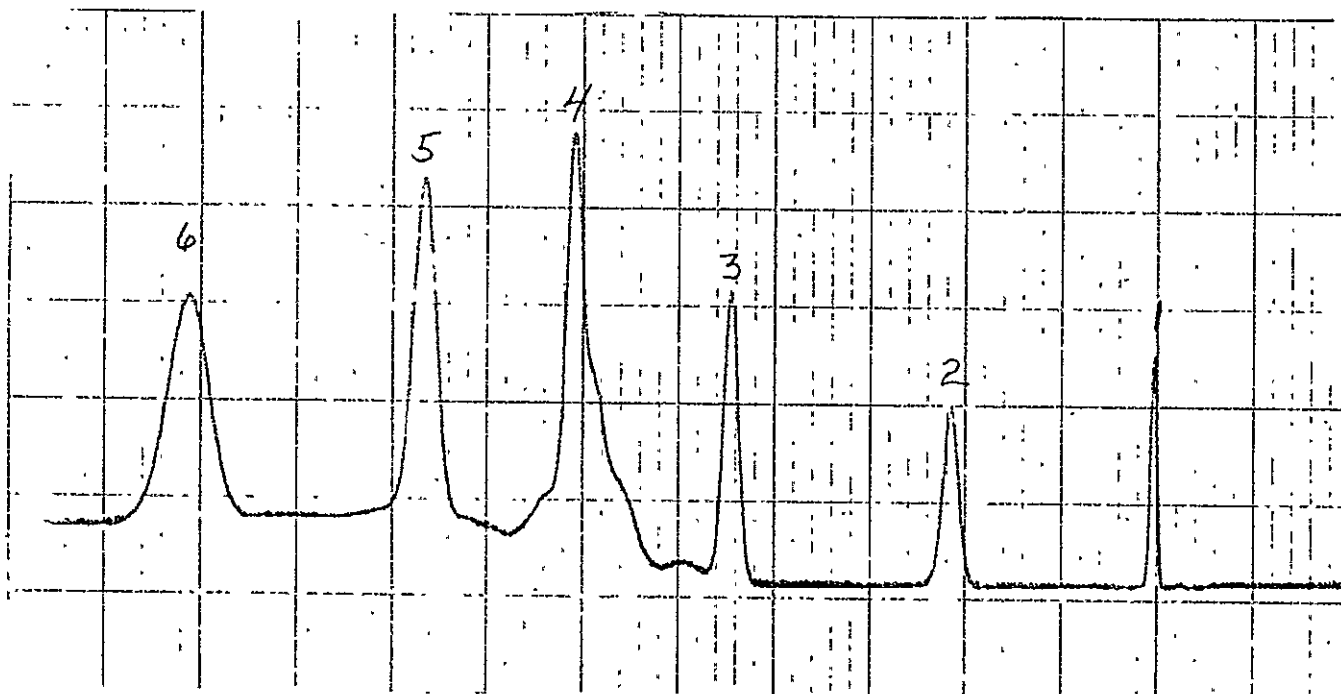


FIGURE 8. Normal Alkanes Analyzed on a Silica Gel Column.

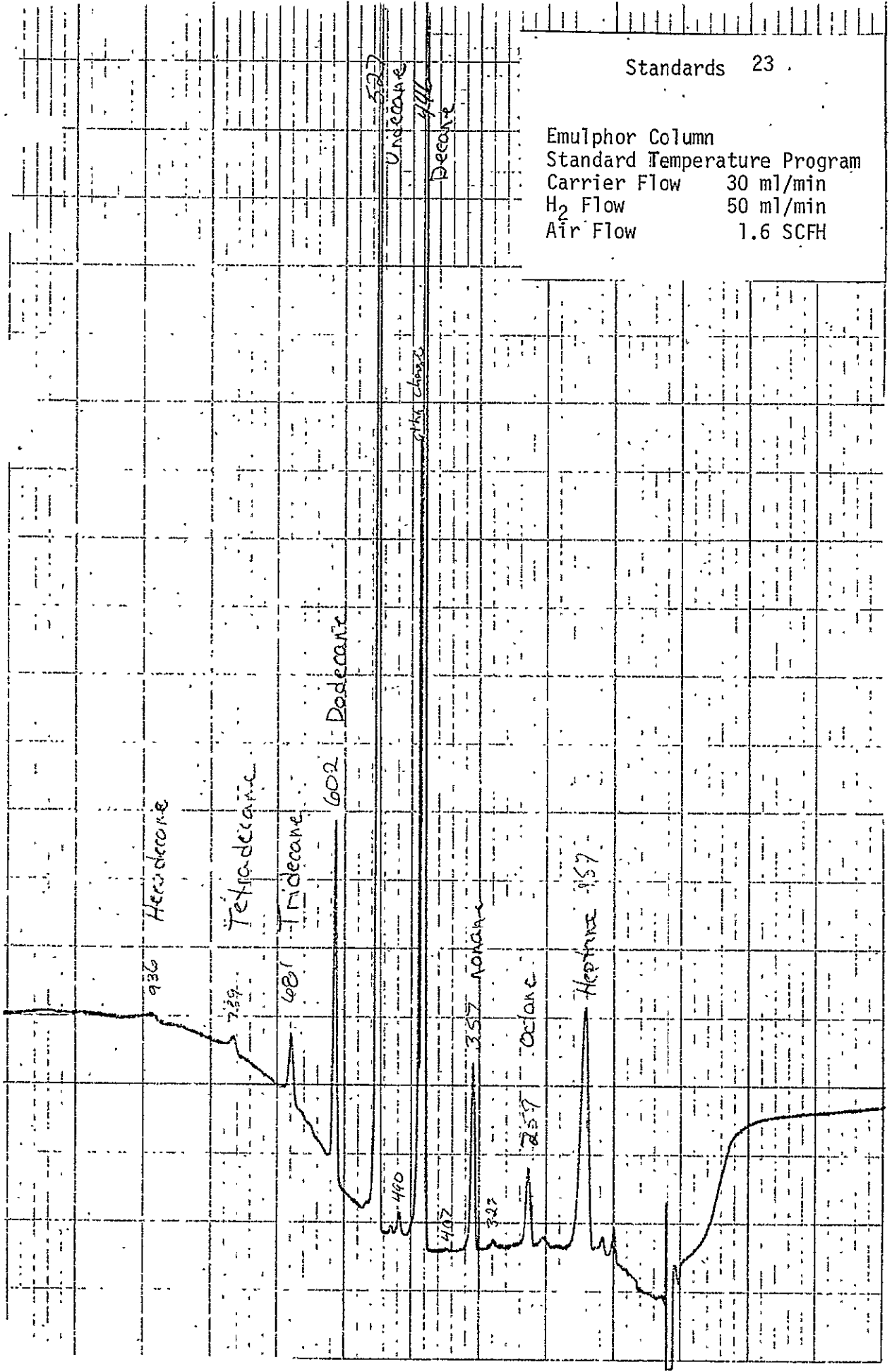


FIGURE 9. Hydrocarbon Analysis on Emulphor ON 870 Column.

4.1.2 Recoverability of Standards

The recoverability studies were accomplished using the exact procedure that was used to analyze the samples. Figure 10 shows a schematic drawing of the apparatus used for the recoverability work.

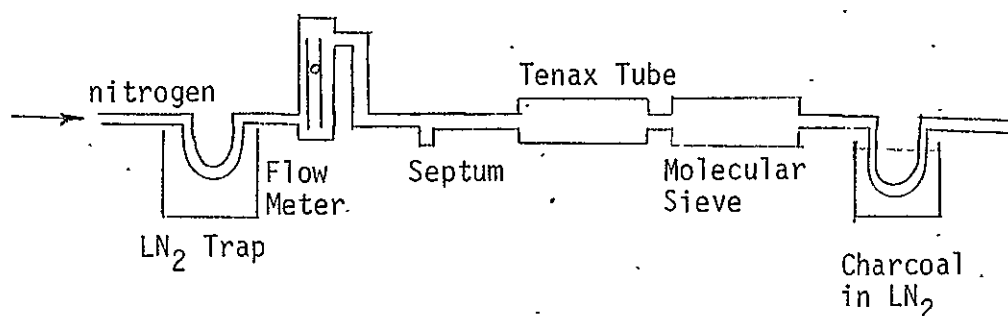


FIGURE 10. Schematic Drawing of Apparatus Used for Recoverability Studies

The nitrogen used was run through a Molecular Sieve 5A trap immersed in LN_2 to remove all traces of impurity before known amounts of standards were added to it. The flow rate was monitored to insure that it was in the same range as the sampling. Quantities of the certain standard gases were injected as the carrier flowed through the traps. Only the most important representative hydrocarbons were checked for recoverability. After the compounds were trapped, they were baked off and analyzed as the samples were.

The data in Table 4 shows the recoverability of some compounds that were found in the gas systems analyzed. Larger quantities of compounds were used in the studies to obtain more accurate information about the amount expected to be recovered from actual systems. The quantities of contaminants found in the samples many times were near the lower limit of the instrument sensitivity and therefore, it would be impractical to attempt recoverability studies at these levels.

TABLE 4
RECOVERABILITY OF SELECTED COMPOUNDS

Compound	Quantity Injected (ppm-ml)	Mean Percent Recovered
methane	100	115
acetylene	100	98
butane	32	80
pentane	40	97
hexane	42	99

The methane proved extremely difficult to obtain reproducible results. Since the methane was trapped on LN₂ cooled charcoal, one would expect excellent recoveries. The greater than 100% recovery is due to the standards not being run at exactly the same conditions. As the sample, the standard was run at a column temperature of 200° which reduces the carrier flow thus reducing the FID sensitivity slightly. Since near 100 percent recovery was found on the other compounds, the same is expected with methane.

The relatively low recovery found for butane is partly due to the shape peak found for the butane. Figure 8 shows a run of C₁ - C₆ alkanes

on the Silica Gel column. Note the irregular shape of the butane peak. This is due to a mixture of butanes in the original sample. The effect is more pronounced after adsorption in the LN₂ cold trap. The integrator settings did not lend itself to starting and stopping integration at the proper times thus seemingly giving a low recovery.

The butane and pentane were split between the Molecular Sieve 5A and Tenax adsorption tubes. Eight percent of the recovered butane was trapped on the Tenax and 92 percent was on the Molecular Sieve. Twenty-two percent of the recovered pentane was on the Tenax and 78 percent was adsorbed on the Molecular Sieve.

No recoverability studies were performed on hydrocarbons of higher molecular weight than hexane. The adsorption efficiency of these compounds on Tenax is well documented in the open literature. References to this work are listed in the Phase 1 report published earlier.

4.1.3 Sensitivity

The overall sensitivity of the method depends upon the volume of gas run through the traps. It was found that peaks with an area of 50 μ V-sec peak represents a concentration of 3 ppm-ml. If a 3 liter gas sample was run through the trap, then the concentration of the contaminant was 0.001 ppm or 1 ppb. This is well below the sensitivity required for this type work. The greatest sensitivity possible has been used throughout this work since it was not known what to expect in the gases. For routine sampling a sensitivity of 10 ppb would be sufficient.

4.2 LOX Analysis

4.2.1 Methane

The methane concentration is high enough in the LOX that a 10 ml sample is more than sufficient for analysis. Care must be taken to separate all oxygen from the sample during analysis. If the oxygen is not removed first the oxygen signal will interfere with the methane. The charcoal column proved sufficient to make the separation.

Table 5 shows the reproducibility of replicate analyses of a LOX sample. A much smaller volume of sample could be used and still obtain valid results.

TABLE 5
METHANE IN LOX

Analysis Number	Retention Time (sec)	Area (μ V-sec)	Concentration (ppm)
1	270	5219	23.8
2	270	5229	23.9
3	270	5201	23.8

Analysis Conditions: Sample 7
 Sample Volume - 10 ml
 Column Temperature = 50° isothermal
 Injector Port Temperature = 55°C
 Carrier Flow = 30 ml/min
 H₂ Flow = 50 ml/min
 Air Flow = 1.6 SCFH
 6' Charcoal Column

4.2.2 Molecular Sieve 5A Adsorption

The midrange hydrocarbons are adsorbed on the Molecular Sieve tube. The tubes were analyzed using the procedure described earlier. Figure 11 illustrates typical results for C₂ - C₅ hydrocarbons found in the LOX system.

The acetylene has been of particular interest throughout the study due to its explosiveness in LOX. Reproducible results have been obtained to verify its concentration. The 67 ppb value is typical of what was found on different days after deliveries to the storage tank.

4.2.3 Tenax Adsorption

Figure 12 indicates a strip chart recording of the higher molecular weight hydrocarbons that were found in a typical LOX sample. The extremely small concentrations of the higher (C₁₅ - C₁₉ hydrocarbons) are expected since the vapor pressure of these compounds is extremely low.

The retention times were used to identify the compounds. They may possibly be substituted hydrocarbons but the approximate molecular weight may be determined with relatively good accuracy. Many isomers of each compound were also present in the sample.

4.3 High Pressure Nitrogen

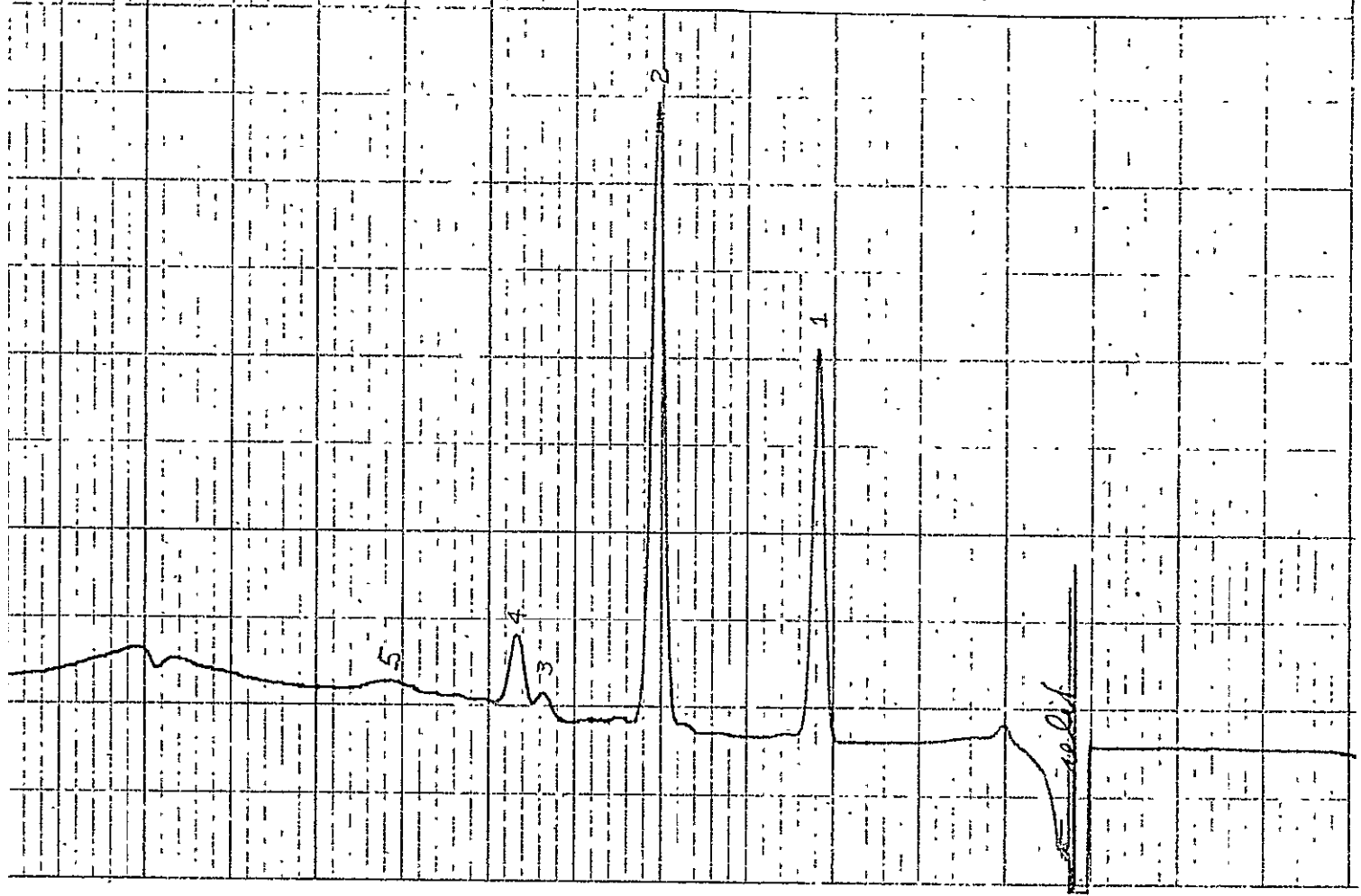
The high pressure nitrogen was sampled at the bottom of the 8,000 psi storage tank near building 4659. The pressure on the tank was less than 4,000 psi each time a sample was taken. There were no prospects of the pressure being increased during the time we would be sampling. The procedure for sampling and analysis was the same as if the pressure had been near 8,000 psi.

Sample 6 D

LOX
Molecular Sieve
Sample Volume 3000 ml
Carrier Flow 30 ml/min
H₂ Flow 50 ml/min
Air Flow 1.6 SCFH
Standard Temperature Program

Peaks

Number	Time (sec)	Area	ppb	Substance
1	378	4564	45	ethane
2	602	7523	67	acetylene
3	764	252	3	isobutane
4	798	774	8	butane
5	909	-	-	pentane



HEWLETT-PACKARD

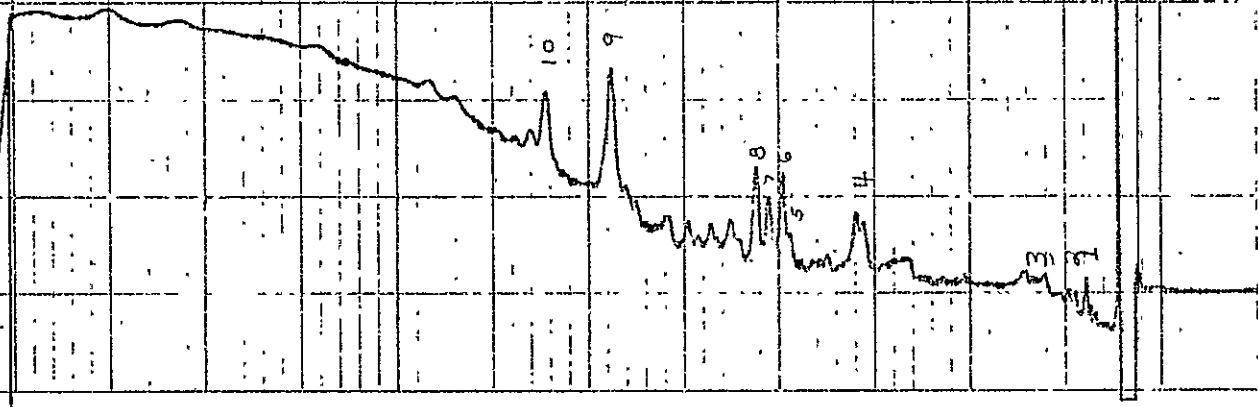
9270-1010

FIGURE 11. Midweight Hydrocarbons in LOX

Sample 7 A

LOX
 Tenax Trap
 Sample Volume 3000 ml
 Carrier Flow 30 ml/min
 H₂ Flow 50 ml/min
 Air Flow 1.6 SCFH

Peak #	Time (sec)	Area	ppb	Substance
1	74	51	0.5	2,2-dimethylbutane
2	82	74	0.7	2-methylpentane
3	114	78	0.8	n-hexane
4	342	590	5.7	nonane
5	432	140	1.4	decanes
6	441	409	4.0	
7	459	304	3.0	
8	474	520	5.1	
9	657	1291	12.6	tridecane
10	740	642	7.2	tetradecane



HEWLETT-PACKARD

FIGURE 12. Higher Molecular Weight Hydrocarbons in LOX

4.3.1 Methane

The methane in the high pressure nitrogen was found to be low during all analyses. Part of the methane was found to be trapped on the Molecular Sieve and the remainder was in the LN₂ cooled charcoal loop. The sum of the area of the two peaks yield a concentration of less than 20 ppb. This is such an insignificant amount that a great deal of emphasis was not placed on it.

4.3.2 Midweight Hydrocarbons

The C₂ - C₆ hydrocarbons in the nitrogen were trapped on a Molecular Sieve 5A as described previously. The results of a characteristic analysis are shown in Figure 13. The large peak present at 181 sec. should not be present in the apparant concentration. It was not present in other analyses and should probably be ignored at this point.

The results were as one would expect. That is, very small quantities of these volatile hydrocarbons would be picked up as contaminants. Also, very small quantities of these contaminants are present during the condensation process. The total concentration of the C₂ - C₆ trapped on the Molecular Sieve was less than 85 ppb expressed as methane. The actual concentration of individual compounds was much less than this.

4.3.3 Higher Molecular Weight Compounds

The C₆ and heavier hydrocarbons were trapped onto the Tenax tubes and baked off as described earlier. Figure 14 is a chromatogram of one of the samples. That sample was taken through a new regulator that had not been cleaned to MSFC-SPEC-164. Table 6 which follows the graph shows the retention times of the peaks and their tentative identification.

Sample 8 A

High Pressure N₂
 Molecular Sieve Trap
 Sample Volume 3000 ml
 Carrier Flow 30 ml/min
 H₂ Flow 50 ml/min
 Air Flow 1.6 SCFH

High Pressure N₂
 Sample 8 Molecular Sieve Peaks

Time (sec)	Area (μV-sec)	Conc (ppb)	Substance
181	app. 1000	10	methane
521	519	5	ethane
656	188	2	acetylene
733	120	1	
758	10	0.1	iso-butane
871	883	8	n-butane
943	79	0.8	
1184	4870	47	pentane
1252	714	7	pentene
1267	456	4	hexane

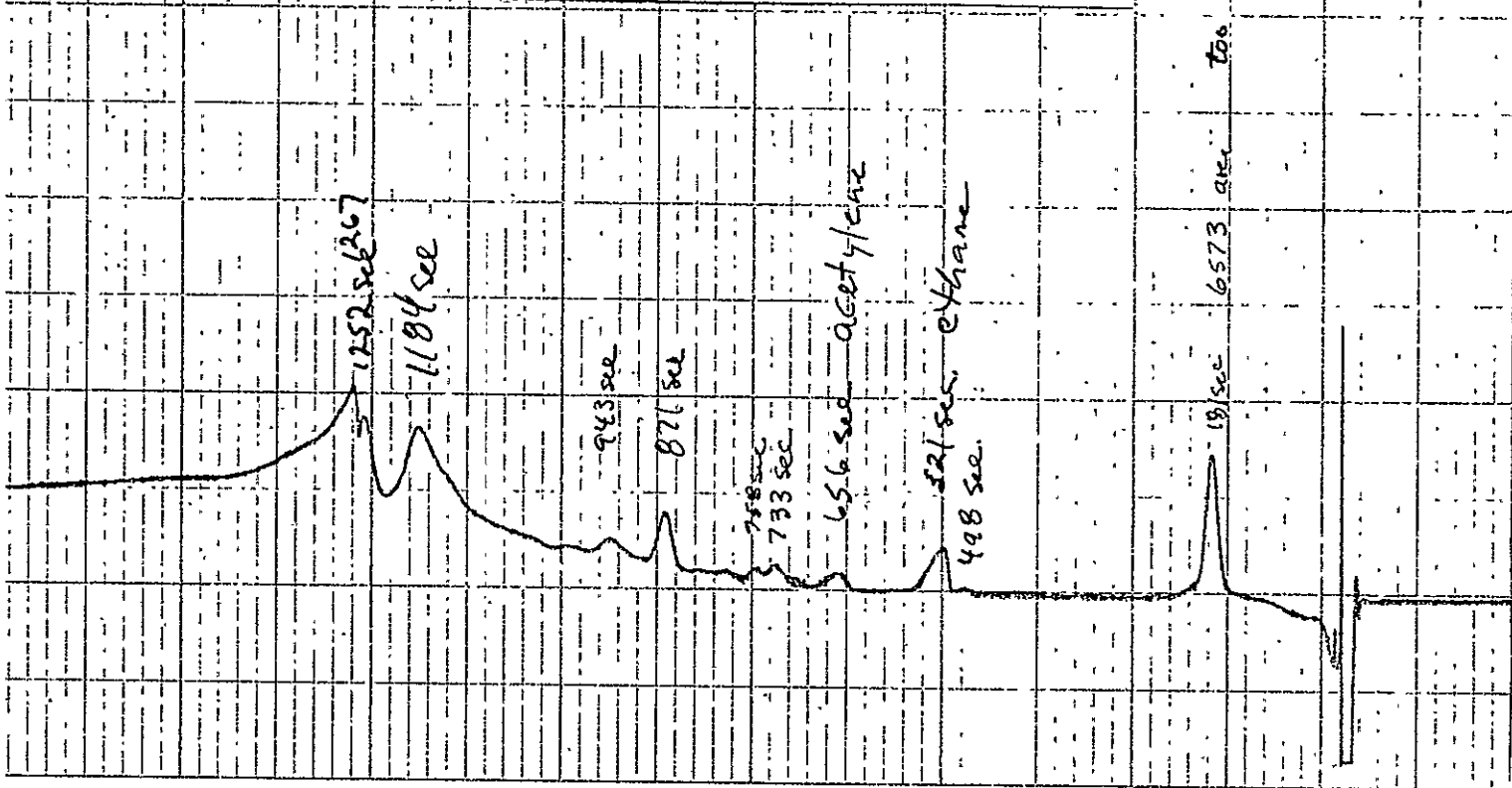


FIGURE 13. Analysis of Hydrocarbons in High Pressure Nitrogen Trapped on Molecular Sieve 5A

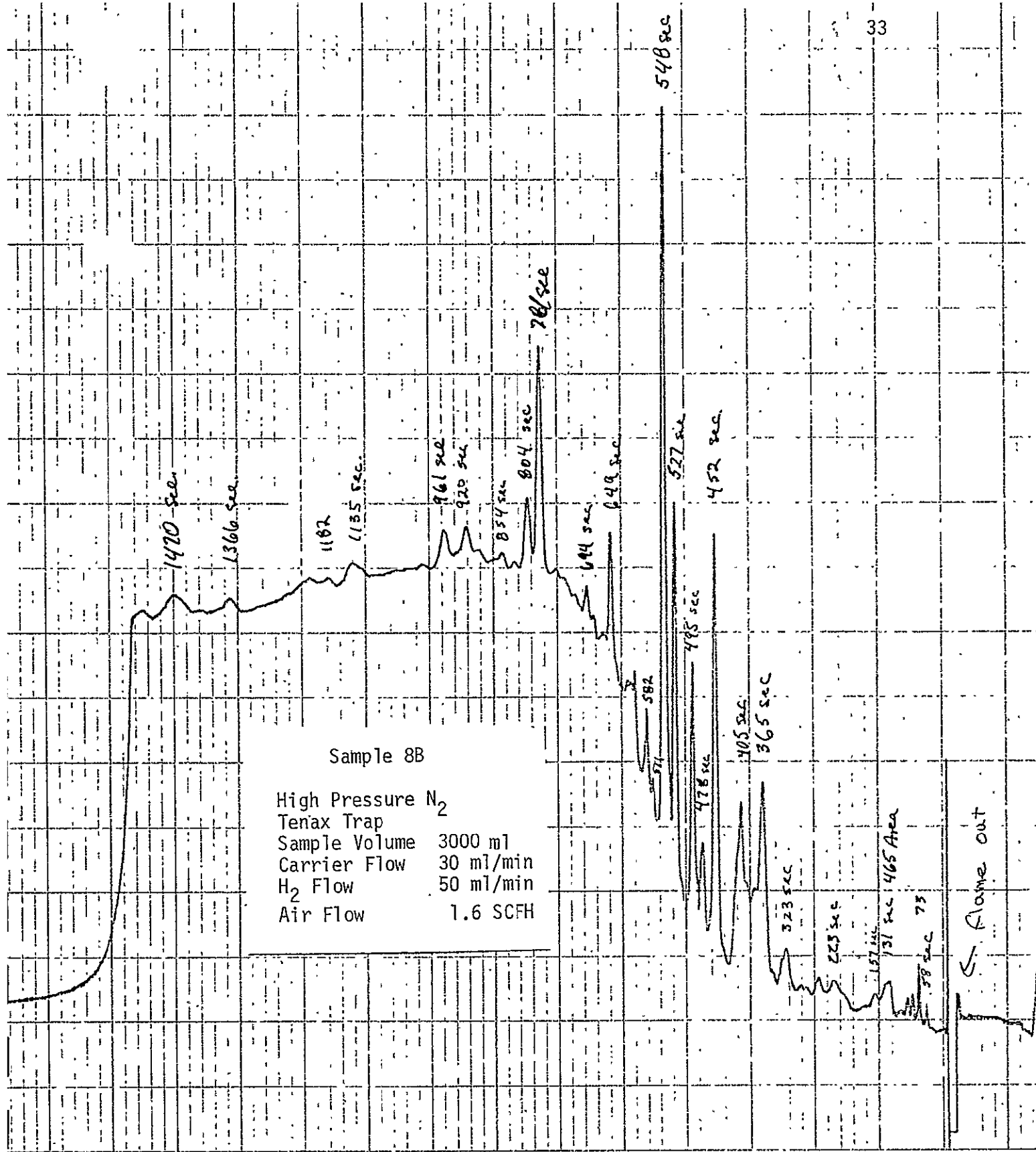


FIGURE 14. Higher Molecular Weight Hydrocarbons in High Pressure Nitrogen

TABLE 6
HIGH PRESSURE N₂, SAMPLE 8, TENAX PEAKS

Time sec	Area μV-sec	Concentration ppb	Substance
58	495	16	butane
73	192	6	pentane
131	465	15	hexane
233	599	20	heptane
296	100	3	
323	552	19	octane
365	432	14	
405	881	24	
452	3448	95	nonane
478	468	15	
495	1429	33	decane
527	2710	66	
548	4162	122	undecane
571	189	5	
582	513	17	
604	556	17	
649	1349	33	dodecane
694	202	6	tridecane
753	1014	27	
781	2026	52	tetradecane
804	374	12	
854	144	4	
920	226	8	
961	245	9	
1135	233	8	
1366	153	4	
1470	328	11	

The large number of peaks and their relatively large concentrations could possibly be due to a slight amount of contamination in the regulator or simply a collection of the hydrocarbons over a period of time. The difference could be resolved by using an extended routine sampling period and cleaning the valve.

It is interesting to note that many of the higher molecular weight compounds in the 8k nitrogen pressurization tank were also present in the LOX system. The small concentrations detected in the gas are not unexpected due to the high boiling point and the low vapor pressure of the compounds.

4.4 Low Pressure Nitrogen

The low pressure nitrogen distribution system was sampled at a use point in building 4653. The government owned distribution point was used to reduce the pressure. The quality of the nitrogen was, therefore, the same as would be expected for the use point.

4.4.1 Methane

The methane concentration was found to be less than 20 ppb in the gas stream. A trace was observed to be on the Molecular Sieve trap. This finding was consistent with expected findings and the concentration found in the high pressure nitrogen system.

4.4.2 Midweight Hydrocarbons

A representative analysis of a Molecular Sieve tube is shown in Figure 15. The compounds are present in extremely small amounts and a large sample volume was required to obtain the size peaks that are

Sample 13

Low Pressure N₂
Molecular Sieve Trap
Sample Volume 3000 ml
Carrier Flow 30 ml/min
H₂ Flow 50 ml/min
Air Flow 1.6 SCFH

Peaks

Time	Area	ppb	Substance
117	577	5	methane
656	282	2	acetylene
778	1158	10	butane
971	1241	11	pentane
1250	300	2	hexane

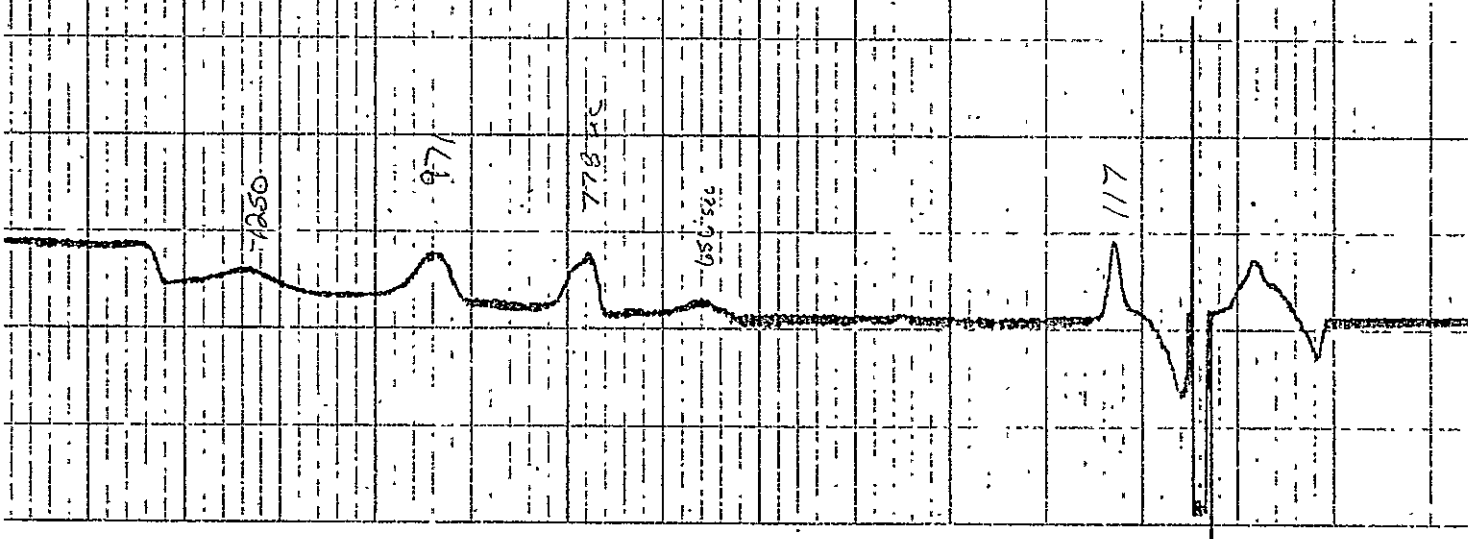


FIGURE 15. Midweight Hydrocarbons in Low Pressure Nitrogen

shown in the chromatogram. Nothing of real significance was found in the samples.

4.4.3 Heavier Molecular Weight Hydrocarbons

A chromatogram of the contaminants of the nitrogen system is shown in Figure 16. The system proved to be extremely clean (70 ppb total hydrocarbon expressed as methane). The results in the figure are self explanatory.

4.5 Missile Grade Air

The missile grade air was sampled at a use point in building 4653. Care was taken to obtain a sample that would be representative of the point. The same point was used each time the samples were taken.

4.5.1 Methane

The methane concentration was found to be less than 30 ppb in the samples. This concentration would be expected from the compressed air. Since it was such a trace quantity, it was not afforded a major amount of emphasis.

4.5.2 Midweight Hydrocarbons

The chromatogram shown in Figure 17 is symbolic of those obtained from the analysis of the Molecular Sieve Trap. This sample was only 1.1 liters but it was more than sufficient for identification and quantification.

4.5.3 Higher Molecular Weight Hydrocarbons

Figure 18 shows chromatograms and the results of duplicate analyses of the Tenax traps which had been used to trap the contaminants

Sample 13

Low Pressure N₂
 Tenax Trap
 Sample Volume 3000 ml
 Carrier Flow 30 ml/min
 H₂ Flow 50 ml/min
 Air Flow 1.6 SCFH

Peaks

Time	Area	ppb	Substance
61	145	3	butane
70	337	7	pentane
137	121	3	hexane
339	345	8	
374	128	3	nonane
646	120	3	dodecane
886	50	1	
947	54	1	
1005	276	6	
1112	96	2	

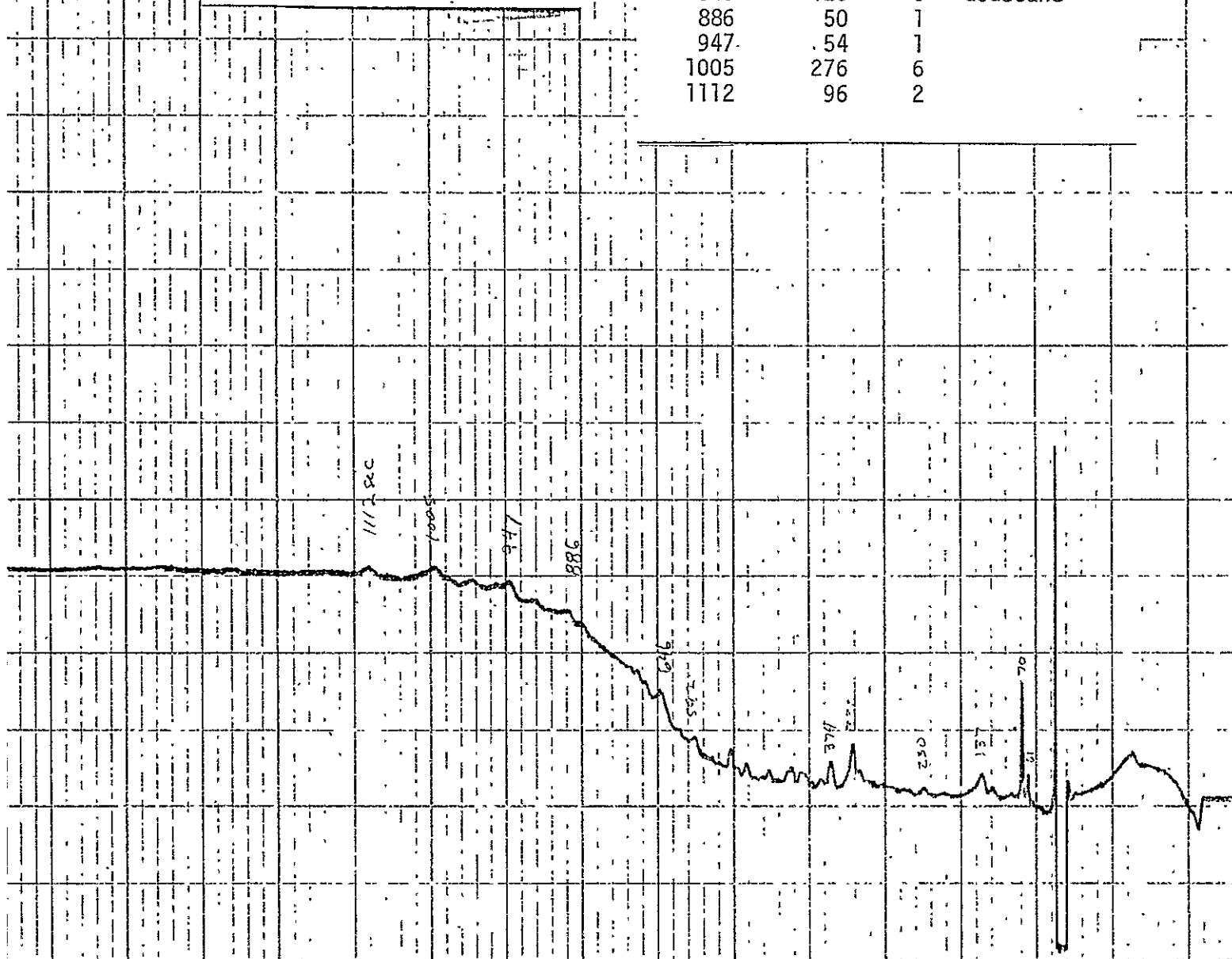
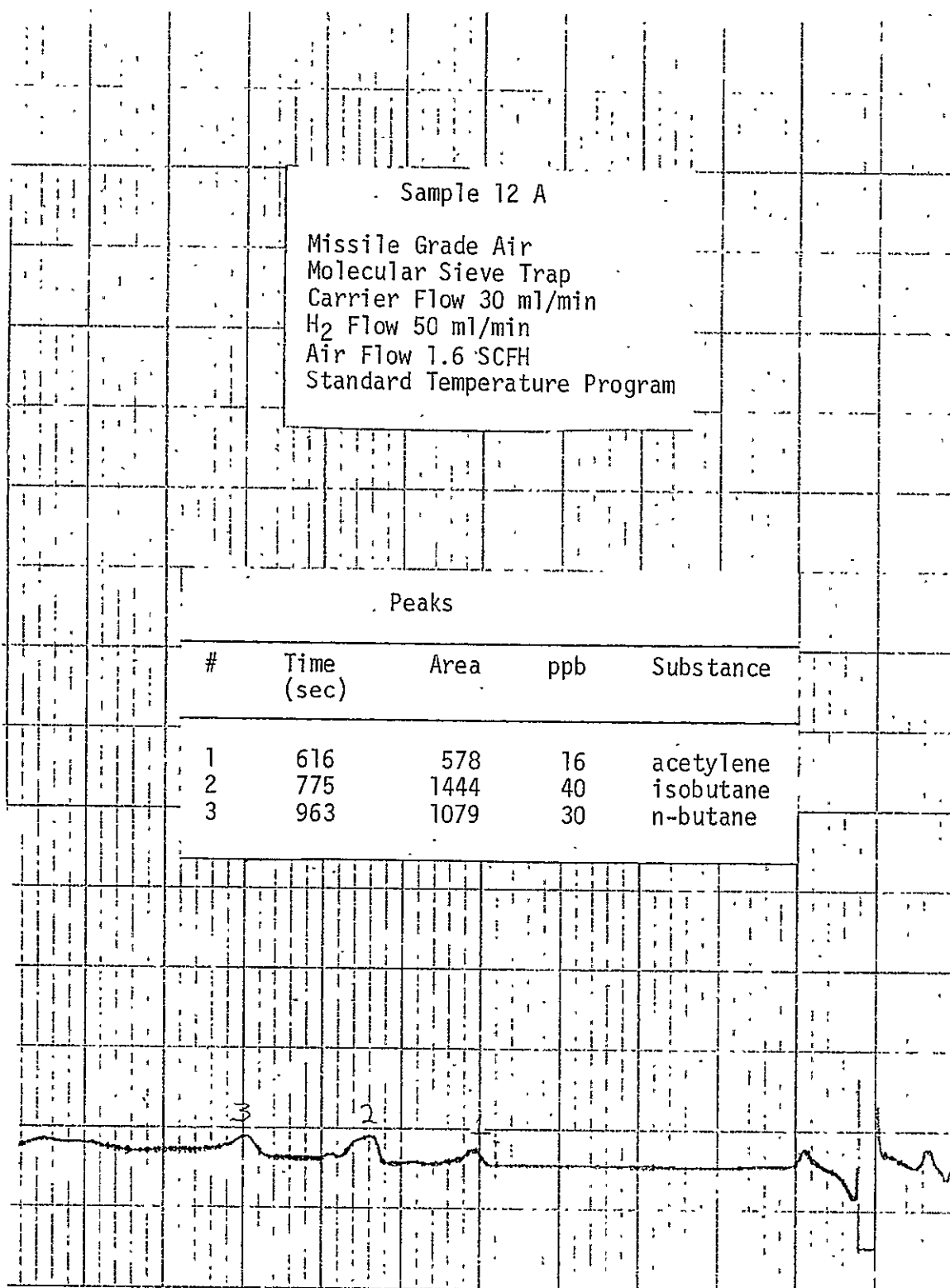
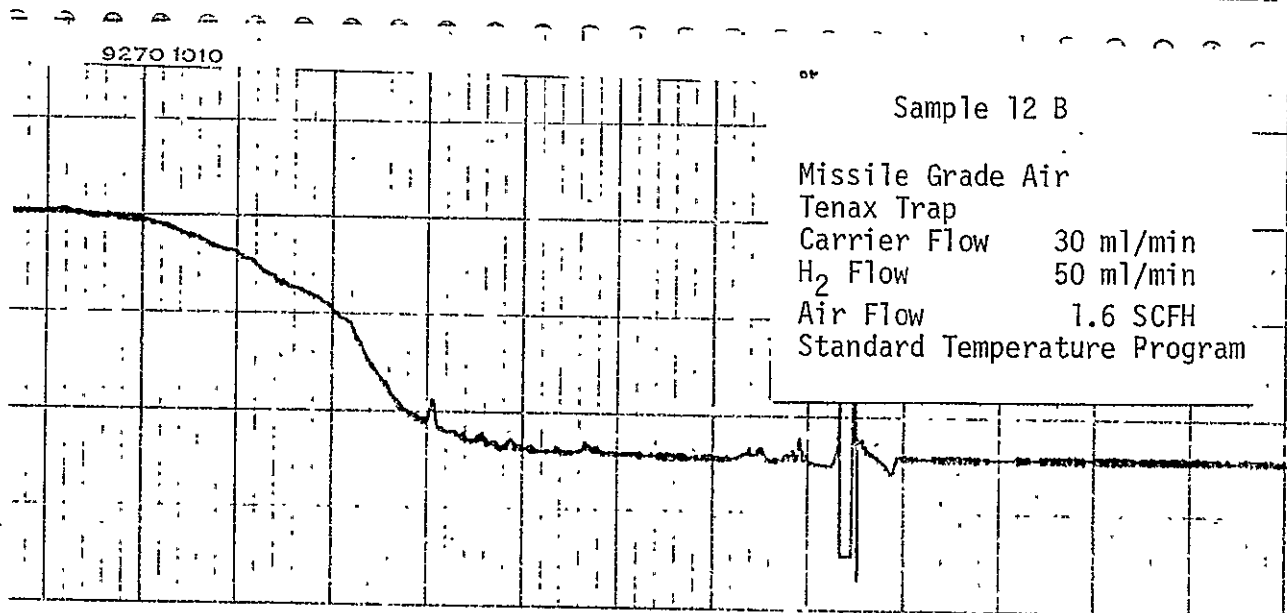
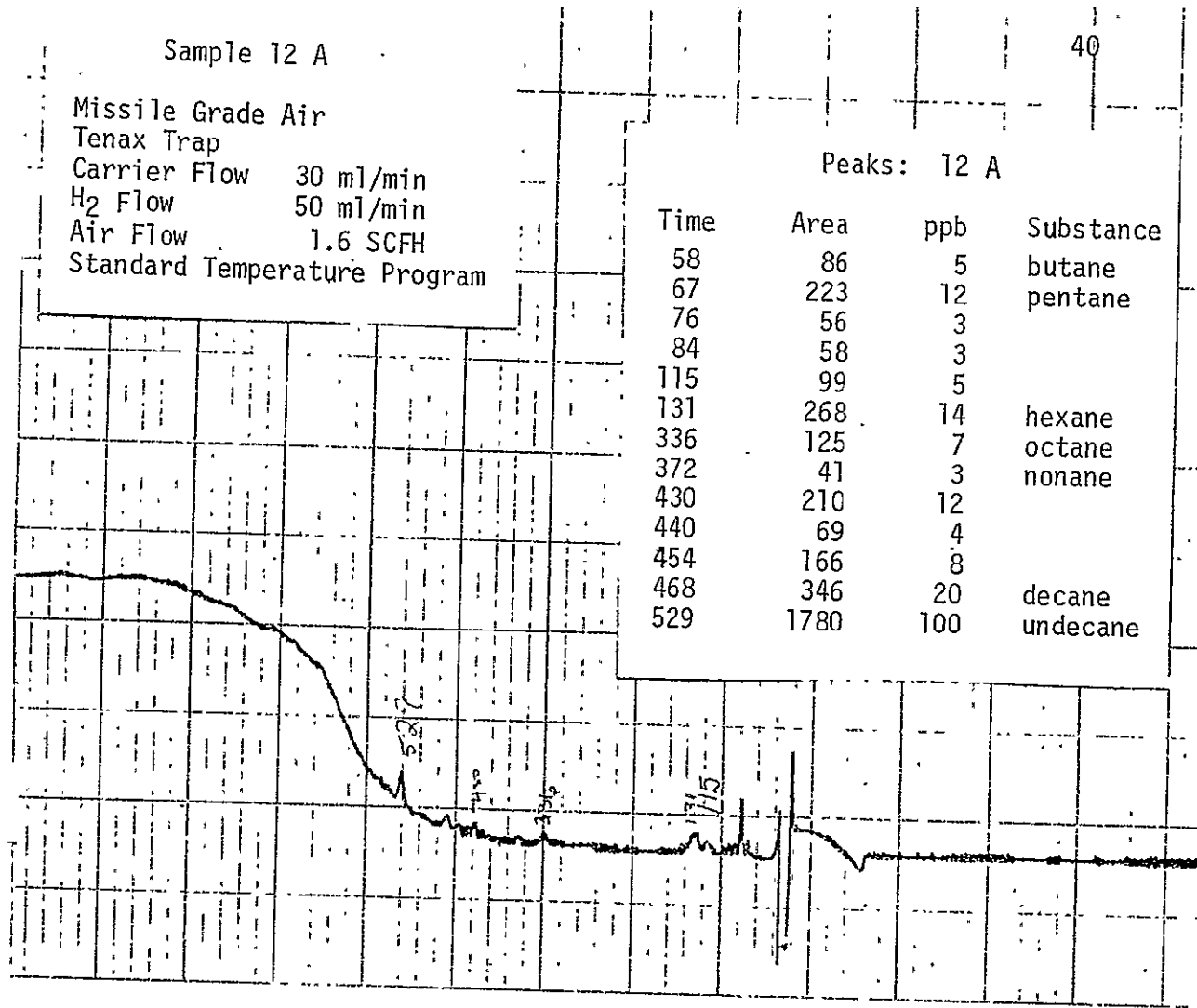


FIGURE 16. Higher Molecular Weight Hydrocarbons in Low Pressure Nitrogen



9270-1010

FIGURE 17. Midweight Hydrocarbons in Missile Grade Air



HEWLETT-PACKARD

9270-1010

FIGURE 18. Higher Molecular Weight Hydrocarbons in Missile Grade Air

from 1.1 liters of missile grade air. Both chromatograms are included to show the reproducibility of the actual analyses.

The baseline rise which begins after about 530 seconds is due to the bleed of the Emulphor column as the temperature rises during the temperature program. This rise is evident during each run and posed no problems in the analyses.

5.0 CONCLUSIONS

5.1 Current Hydrocarbon Monitoring

The current method of monitoring hydrocarbons is at best sensitive to 0.1 ppm total hydrocarbons expressed as methane. This is not sensitive enough to adequately monitor individual contaminants within a compressed gas.

5.2 Method of Analysis

The method developed during this study for sampling, concentration and analyzing hydrocarbons works extremely well. The method allows a large enough sample to be analyzed that will give a sensitivity of individual compounds of less than 0.3 ppb expressed as methane. This is much more sensitive than required for routine monitoring of the system.

5.3 Hydrocarbons in High Pressure Nitrogen

Exact limits for THC and individual compounds cannot be established until LOX compatibility studies have been completed by NASA. Many variables and assumptions must be made during the establishment of limits even when the explosion limits of the different compounds are known.

The graph and calculations in Appendix 1 indicate the complexity of the limits. The calculations were done for acetylene since it is the most sensitive to explosion in LOX.

The assumptions made for the calculations are as follows:

- 1) The acetylene concentration in the high pressure nitrogen was measured at ambient conditions as methane.
- 2) All acetylene in the GN_2 will be instantaneously transferred to the LOX upon pressurization.
- 3) The sphere is partially filled with LOX as indicated on the graph in Appendix 1.

The decision about maximum allowable individual compound concentrations must be made only after compound compatibility with LOX is known and after the assumptions are thoroughly evaluated to determine validity.

5.4 Condensable Hydrocarbons

The method developed during this study will allow the analysis of condensable hydrocarbons in compressed gases with greater accuracy and reliability than the present method described in MSFC-PROC-245. Individual compounds can be monitored by adsorption on Tenax tubes to give better control on the induced contamination.

5.5 LOX Filters

The analysis of the material on the LOX filters indicate a potentially hazardous situation since the high molecular weight hydrocarbons are solidified and concentrated on the filter. The present limits for system contamination do not adequately reflect the condition of the system since the filter is the worst possible case of system contamination. A more realistic approach would be to monitor the LOX itself with no filters installed.

5.6 Compatability Studies

Based on the analysis of the LOX and Freon wash from the LOX filter, compatability studies should be completed on all normal hydrocarbons C₆ - C₁₉. These will be representative of the full range of oils and greases that could be present. Due to the inadequate literature available on previous LOX compatability studies, acetylene should be studied. It appears to have the lowest solubility limit in the LOX and thus an extremely low compatability for the LOX without explosion.

5.7 Hydrocarbon Contaminant Limits

The maximum acceptable hydrocarbon limits for the LOX and the high pressure nitrogen will be governed by safety factors. The limits must be low enough that the possibility of an explosion can be precluded as determined by the LOX compatability studies.

The maximum allowable hydrocarbon concentration in the low pressure nitrogen and missile grade air must be set by user needs and must yet be established. The hydrocarbon concentration that can be tolerated by the specific applications is much less than the threshold explosion limits as reported in the open literature. No danger of explosion should exist until the user limits are exceeded by several orders of magnitude.

5.8 Applications

The analysis of contamination from a static distribution system provides information on the cleanliness of the distribution system surfaces. Hydrocarbons on the surface would diffuse into the static gas until the

vapor pressure reaches its saturation level. At this point diffusion would cease and a multiple phase system would exist. The analysis of this gas would show a maximum contamination at the saturated vapor concentration and therefore would not accurately describe the cleanliness of the system. For this reason each contaminant concentration must be checked against a table of saturated concentrations.

Analysis of a dynamic gas system would relate primarily to the concentrations of hydrocarbons in the gas originally, because of the short surface contact time. This would provide information on gas purity at the supply point rather than system cleanliness.

For "lock-up" testing the virgin lock-up gas contamination is determined and compared against the contamination of the gas after a specified "lock-up" period. The difference would indicate the cleanliness of the system.

6.0 RECOMMENDATIONS

As a result of the data obtained during the course of this study, we feel that further research should be conducted in certain areas. We also feel that a modification of the method of analysis developed in this study should be applied to the routine monitoring program for contaminants. Results from the present methods of analysis should be compared with those obtained from the before mentioned GC techniques.

6.1 Comparison of Methods for Determining Condensable Hydrocarbons

The present method for the analysis of condensable hydrocarbon contamination in compressed gases is specified in MSFC-SPEC-245. The method requires the scrubbing of 600 liters of the gas with carbon tetrachloride and then concentrating the carbon tetrachloride for quantitative analysis by infrared spectroscopy. The total amount of contaminants are calibrated against a pump oil standard. This method is plagued by lack of sensitivity and the possibility of many inherent errors.

A sample of the carbon tetrachloride used to scrub an air sample was analyzed by GC to determine what compounds were present in the gas. The chromatogram in Figure 19 shows the molecular weight range of the contaminants. Other peaks are probably covered up by the large solvent (CCl_4) peak. This sample indicates that the contaminants are in the range of those adsorbed by the Tenax.

The results from a modified adsorption method should be compared to those obtained using MSFC-Proc-245. Since only the compounds with

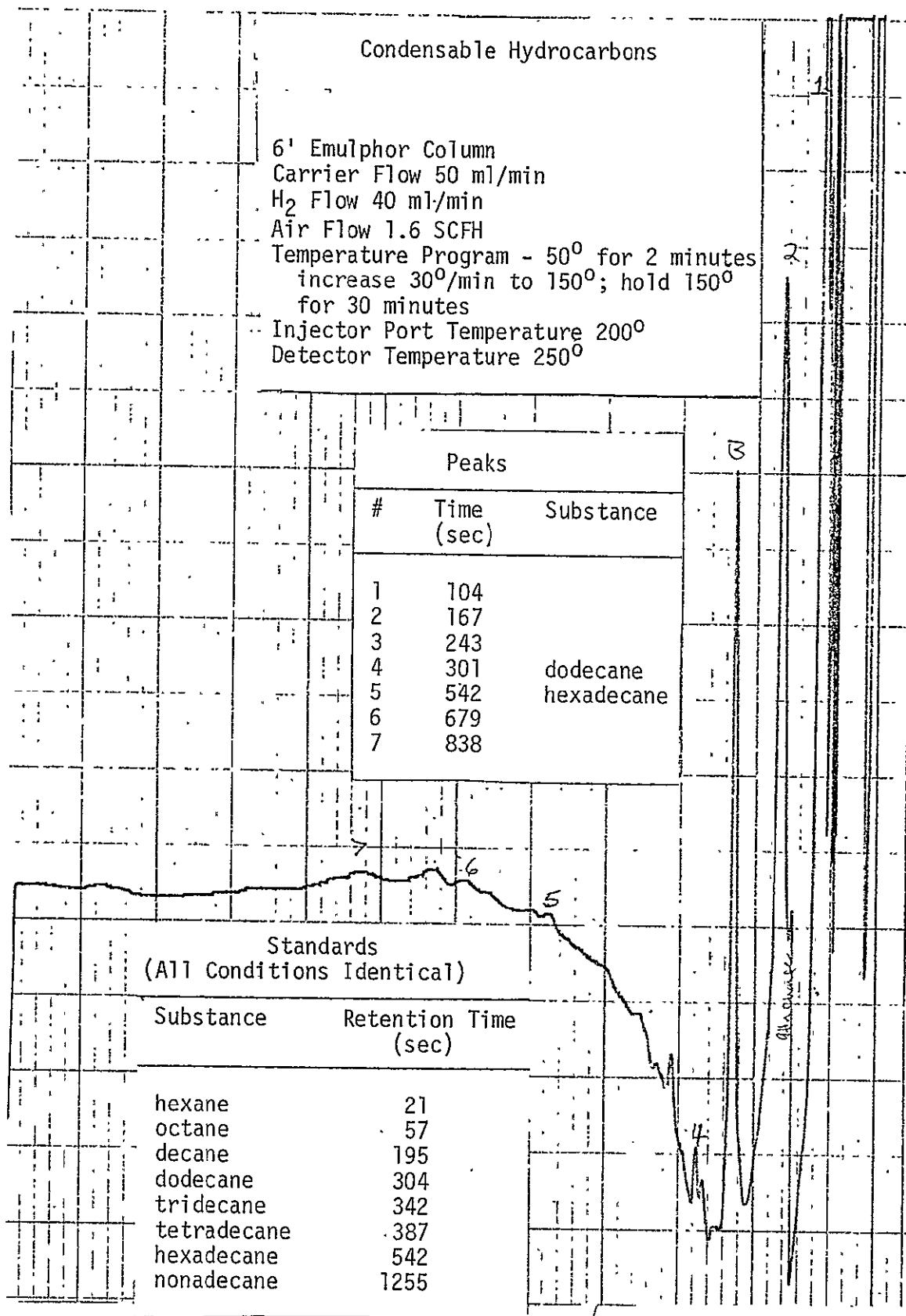


FIGURE 19. Chromatogram of Condensable Hydrocarbons

boiling points near and above that for carbon tetrachloride are trapped by the presently used method; adsorption on Tenax would be all that is required. Figure 20 shows a schematic of the sampling system that could be used on a routine basis to compare results.

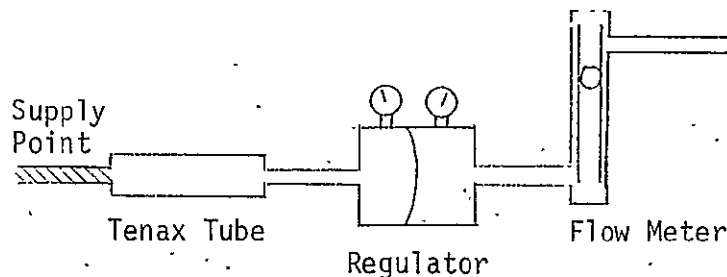


FIGURE 20. Schematic Drawing of Sampling System

The above system would prevent any possible contamination from the regulator and the flow meter and yet the flow could be adjusted and monitored as the sample was taken. The Tenax tube would be analyzed in the same manner as described earlier in this report.

Sampling and analysis by this proposed procedure would be more accurate and individual compound concentrations could be monitored to observe trends in the system. The total concentration could be determined and compared to methane or pump oil as desirable to isolate the source of contamination.

6.2 Sample LOX Routinely

Due to the explosive nature of LOX contaminated with hydrocarbons, the system should be monitored routinely. We feel that a complete analysis of the LOX storage tank should be performed weekly to obtain contamination trends. The methane and acetylene concentrations should be checked to

insure the quality of the liquid supplied. The heavy molecular weight compounds should be monitored to check the induced contamination within the system.

In addition to the LOX sampling reported earlier, a sample of the Freon used to wash an in-line filter was analyzed. Figure 21 shows the chromatogram of the wash solution and Figure 22 shows the standards run at the same time for comparison purposes.

Even though quantitative data was not available, the comparison of the chromatograms indicates that the high molecular weight compounds build up on the filter as LOX passes through. The Freon solution used to wash the LOX filters should be analyzed each time to correlate the amount and composition of the contamination with that found in the routine LOX analyses.

6.3 LOX Compatibility Studies

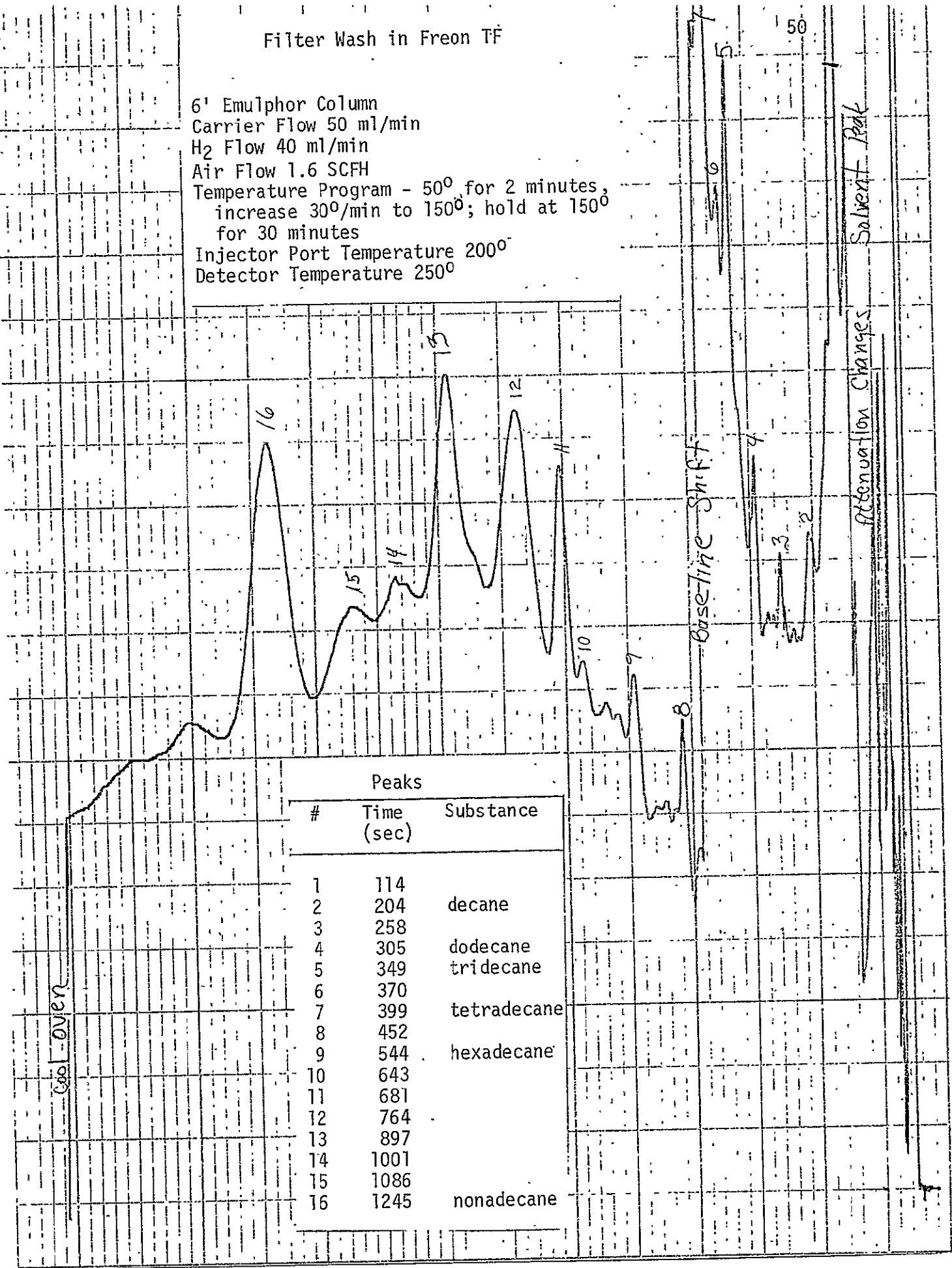
LOX compatibility studies should be completed on representative compounds found to be present in the LOX, on the LOX filters and the high pressure nitrogen. The results of those studies should be attached to this report as an appendix. Based on this information of compatibility and critical concentrations that would lead to explosion, limits on specific contaminants could be set keeping them below these critical points.

6.4 Routinely Sample High and Low Pressure Nitrogen Systems

The high molecular weight hydrocarbons should be routinely analyzed in the nitrogen distribution systems. This would allow a comparison of the contaminant levels and sources of contamination could be better isolated.

Filter Wash in Freon TF

6' Emulphor Column
 Carrier Flow 50 ml/min
 H₂ Flow 40 ml/min
 Air Flow 1.6 SCFH
 Temperature Program - 50° for 2 minutes,
 increase 30°/min to 150°; hold at 150°
 for 30 minutes
 Injector Port Temperature 200°
 Detector Temperature 250°

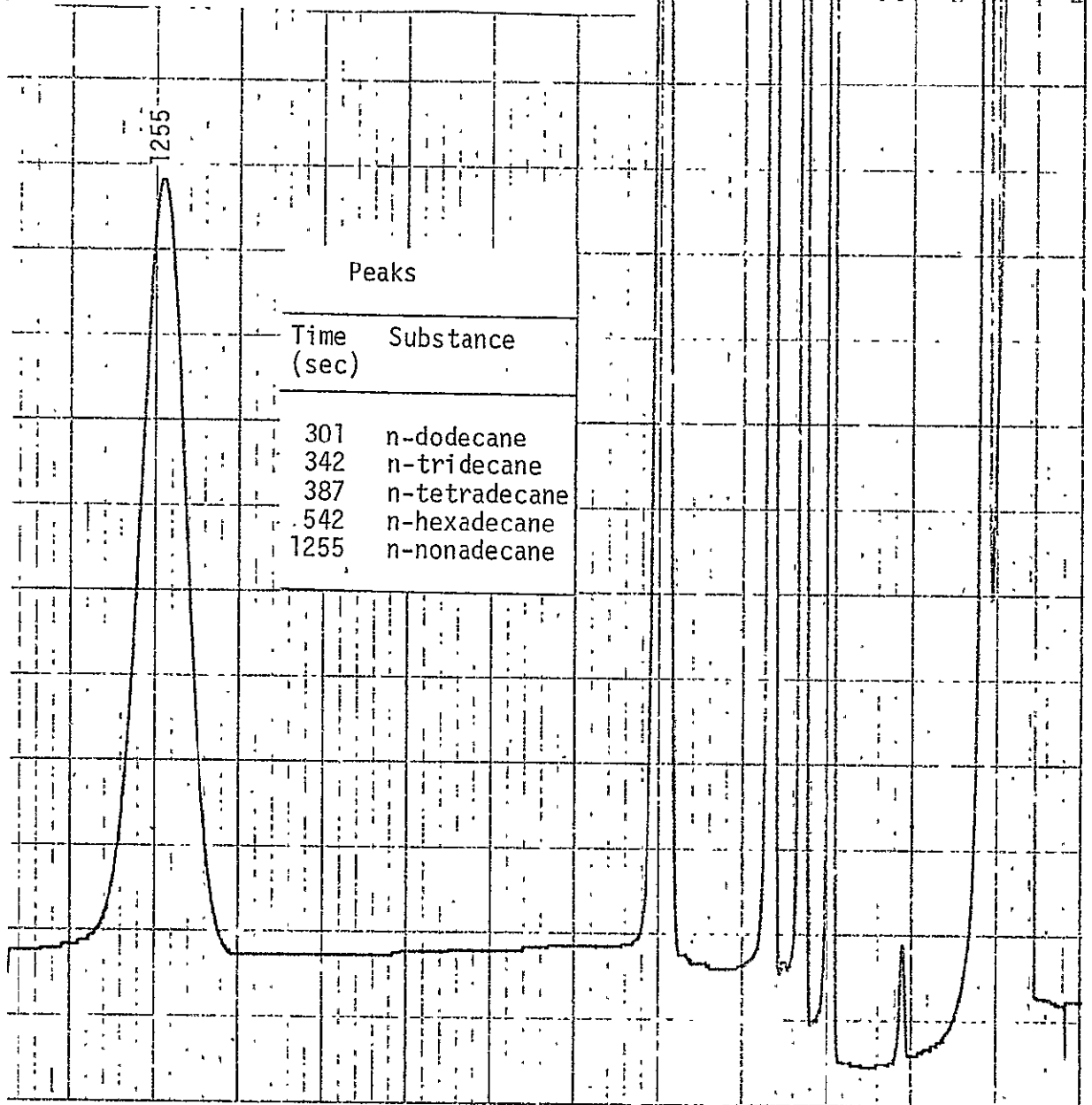


Peaks		
#	Time (sec)	Substance
1	114	
2	204	decane
3	258	
4	305	dodecane
5	349	tridecane
6	370	
7	399	tetradecane
8	452	
9	544	hexadecane
10	643	
11	681	
12	764	
13	897	
14	1001	
15	1086	
16	1245	nonadecane

FIGURE 21. Chromatogram of Freon TF Used to Wash LOX Filter

Standards in Freon TF

6' Emulphor Column
Carrier Flow 50 ml/min
H₂ Flow 40 ml/min
Air Flow 1.6 SCFH
Temperature Program - 50° for 2 minutes,
increase 30°/min to 150°, hold at 150°
for 30 minutes
Injector Port Temperature 200°
Detector Temperature 250°



HEWLETT-PACKARD

9270-1010

FIGURE 22. Chromatogram of High Molecular Weight Hydrocarbons

The sampline apparatus used can be the same as described for the condensable hydrocarbon analysis and as represented in Figure 20. The apparatus should be attached downstream of the high pressure regulator. The acetylene concentration in the high pressure nitrogen should also be periodically checked by inserting a Molecular Sieve tube in series between the Tenax tube and the regulator.

6.5 Routine Analysis of Missile Grade Air

The high molecular weight compounds in the air system should be checked routinely for contamination by the pumping station. The check would also show the efficiency of the filters and adsorbents downstream of the compressor.

The same apparatus could be used for sampling as for the nitrogen system. A total hydrocarbon (THC) analysis should be run at the same time to insure that upper THC limits are not exceeded.

6.6 Adsorbent Study

A separate study should be initiated to develop a series of adsorbents that would effectively trap the contaminants from Missile Grade air to use it as breathing air. The filters could be installed at the use points, immediately upstream of the attachment of the breathing apparatus hoses.

The use of this type filter and adsorbent would do much to preclude any contamination of the breathing air. The adsorbents should be evaluated for removal efficiency, removal rate, contaminate retention and contaminate retention selectivity. Adsorption of this type trap would insure maximum worker safety.

APPENDIX 1

APPENDIX 1 - Hypothetical Resulting Concentrations of Acetylene
in LOX from GN₂

Assume 1 liter N₂ at RTP with 5 ppm v/v acetylene
 $5 \text{ ppm}_{v/v} = 5.5 \text{ } \mu\text{g C}_2\text{H}_2/\text{l N}_2$

Compress to 5000 psig

Compression ratio = 1126:1

So $5.5 \text{ } \mu\text{g/l} \times 1126 = 6193 \text{ } \mu\text{g C}_2\text{H}_2/\text{l N}_2$

Density of C₂H₂ at 90°K = 620/l

Assume 100 liters total tank volume and assume tank is 90% full of
LOX, therefore it contains 10 liters of N₂

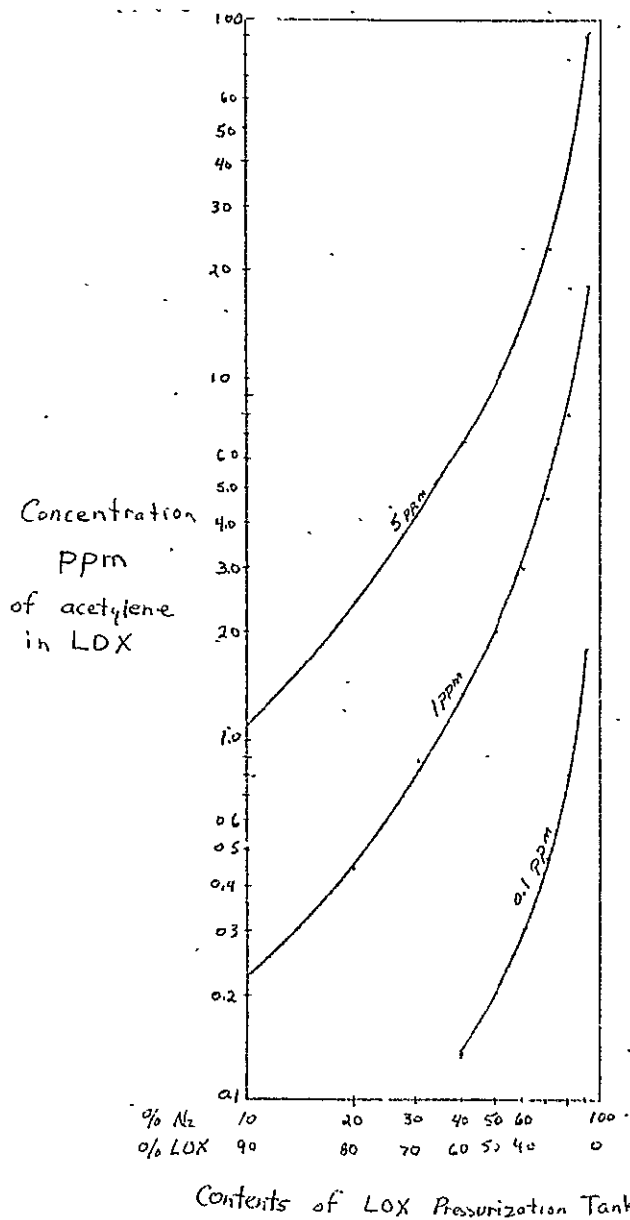
$6193 \text{ } \mu\text{g C}_2\text{H}_2/\text{l N}_2 \times 10 \text{ liters} = 61930 \text{ } \mu\text{g C}_2\text{H}_2 \text{ total}$

$61930 \text{ C}_2\text{H}_2 \div 620 \text{ g/l} = 1 \times 10^4 \text{ liters C}_2\text{H}_2$

Assume all of this acetylene is absorbed by LOX

$1 \times 10^{-4} \text{ liters C}_2\text{H}_2 \text{ in } 90 \text{ liters of LOX}$

$7.74 \times 10^{-5} \div 90 = 1.1 \times 10^{-6} \text{ l C}_2\text{H}_2/\text{l N}_2 = 1.1 \text{ ppm}$



This graph shows relationships between the concentrations of acetylene in GN₂ and the resulting hypothetical concentration of acetylene in LOX when the two are in contact. The concentrations of acetylene in GN₂ selected are 5, 1, and 0.1 ppm_{v/v}.