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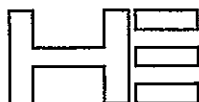
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NAS8-32200

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FOR HYDROCARBONS IN HIGH PRESSURE  
AIR AND NITROGEN SYSTEMS

Prepared For:  
NATIONAL AERONAUTICS & SPACE ADMINISTRATION  
MARSHALL SPACE FLIGHT CENTER, ALABAMA

MARCH 4, 1977



**HARMON ENGINEERING**  
**SCIENTISTS • ENGINEERS • SURVEYORS**  
AUBURN INDUSTRIAL PARK / BOX 2249 / AUBURN, ALA. 36830 / (205) 821-9250  
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## 1.0 INTRODUCTION

This report documents the results of Phase I of NASA Contract NAS8-32200. The first phase of this effort involved gathering the available information about state of the art procedures for the liquefaction and analysis of nitrogen and oxygen. This literature study involved locating the information regarding the safety limits of hydrocarbons (HC) in liquid and gaseous oxygen, the steps taken for hydrocarbon removal from liquefied gases and the analysis of the contaminants.

Very little recent literature was found about the desired information. Most of the work and information was done in the 1950's and much of that was by Russian authors. The work primarily involved means of preventing explosions of LOX plants. It appears that safe, workable HC limits were found and that recent work has not been required to try to raise the safety limits. Very little information could be found about systematic studies of HC compatibility with LOX and the explosion limits.

Recent literature was surveyed to find the state of the art in analysis and collection procedures for HC in gaseous samples. Based on that information, a detailed sampling and analysis plan is proposed to evaluate the MSFC high pressure GN<sub>2</sub> and LOX systems.

This study has been limited to the safety of hydrocarbons in gaseous systems. HC limits imposed because of various design criteria are beyond the scope of this project.



## 2.0 SUMMARY OF NASA & DOD GAS SPECIFICATIONS

The documents applicable to the specifications for nitrogen, oxygen and compressed gases have been reviewed to determine the maximum allowable concentration of selected impurities. The results of the document survey have been summarized in Table 1. Only the impurities that may be of interest in future study have been included in the table since extraneous data would serve no useful purpose.

TABLE 1  
SUMMARY OF NASA AND DOD GAS SPECIFICATIONS

<u>Gas Type</u>	<u>Class or Use</u>	<u>Standard Number</u>	<u>Purity Percent</u>	<u>Maximum Total Hydrocarbon (ppm v/v)</u>	<u>Maximum CH<sub>4</sub> (ppm v/v)</u>	<u>Maximum C<sub>2</sub>H<sub>6</sub> (ppm v/v)</u>	<u>Maximum C<sub>3</sub>H<sub>8</sub> HC (ppm v/v)</u>	<u>Maximum Alkynes as C<sub>2</sub>H<sub>2</sub> (ppm v/v)</u>	<u>Maximum Halogenated HC (ppm v/v)</u>	<u>Condensable Hydrocarbons (ppm v/v)</u>
Nitrogen Type I & II*	Grade A	MIL-P-27401C	99.5	58.3	NR	NR	NR	NR	NR	NR
	Grade B	MIL-P-27401C	99.99	5.0	NR	NR	NR	NR	NR	NR
	Grade C	MIL-P-27401C	99.995	5.0	NR	NR	NR	NR	NR	NR
	Instrument Grade	MSFC-SPEC 233A	99.99	3	NR	NR	NR	NR	NR	0.1
	Space Vehicle Grade	MSFC-SPEC 234A	99.99	5	NR	NR	NR	NR	NR	NR
Oxygen Type I & II	Grade A	MSFC-SPEC 399B	99.99	20.0	16.0	2.0	1.0	0.05	1.0	NR
	Grade B	MSFC-SPEC 399B	99.60	29.0	25.0	2.0	1.0	0.05	1.0	NR
	Grade C	MSFC-SPEC 399B	99.60	50.0	NR	NR	NR	0.25	NR	NR
Gas Bearing, Supply & Slosh Measuring System		MSFC-PROC 195A	NR	NR	NR	NR	NR	NR	NR	0.2
Drying & Preservative Gases		MSFC-PROC 404	NR	5.0	NR	NR	NR	NR	NR	NR
Compressed Gases		MSFC-PROC 245	NR	NR	NR	NR	NR	NR	NR	NR

\*Type I is gaseous and Type II is liquid

NR signifies no requirement for the particular parameter.

### 3.0 SELECTED GAS SUPPLIERS SPECIFICATIONS

Each supplier of compressed gases normally uses his own grade designation which is not necessarily standard for the industry. The specifications for the different suppliers' grade may also vary even if the grade name happens to be the same. In order to obtain a better understanding of the suppliers' grade specifications and methods of verification, a visit was made to the Airco research laboratory and telephone calls were made to the research facilities of several other companies. The results of the visit and the discussions with the suppliers' technical personnel will be discussed indirectly in the remaining sections of this report.

The data contained in Tables 2 and 3 were extracted from suppliers' catalogs and from conversations with technical representatives of the companies. The five suppliers listed are representative of those that routinely supply gases to NASA. The many blanks in the tables are due to the different ways that the gas suppliers report the specifications about their products. The blanks does not necessarily mean that a given gas is not analyzed for a parameter, but that the company has not reported the maximum concentration of the impurity that it will accept. Discussions with suppliers' technical representatives revealed that in most cases only semi-quantative work is done to maintain quality control in the lower standard gases. In most cases, the gas is only checked on a periodic basis to insure that the gas remains within their self-imposed

TABLE 2  
SELECTED GAS SUPPLIERS' SPECIFICATIONS FOR NITROGEN

<u>Supplier</u>	<u>Grade</u>	<u>Purity Min %</u>	<u>O<sub>2</sub> (ppm)</u>	<u>H<sub>2</sub> ppm</u>	<u>Ar ppm</u>	<u>H<sub>2</sub>O ppm</u>	<u>THC ppm as CH<sub>4</sub></u>	<u>Dew Point</u>
MG Scientific	MG5	99.999	<2	<1	<4	<1	<0.4	
	oxygen free	-	<0.2	-	-	-	-	
	ultra zero	-	-	-	-	-	<0.1	
	zero	-	-	-	-	-	<0.4	
	MG 4.8 prepurified	99.998						
Linde	Research	99.998	<1	<1	<20	<3	<1	
	ultra-high purity	99.999	<1	-	-	<3	-	
	prepurified	99.997	<5	-	-	<3	-	
	high purity	99.99	-	-	-	<3	-	
	extra dry	99.7	-	-	-	<8	-	
	oxygen free zero	99.99 99.9	<0.5	-	-	-	-	<0.5
Airco	4 (Prepurified)	99.99	<5					- 76°F
	4.8 (ultra-pure)	99.998						- 97°F
	5 (Research)	99.999						-105°F
	zero gas						<0.5	- 90°F
Air Products	zero	99.998					<0.5	
	ultra pure	99.999	<1	<1	<5	<1	<0.5	-105°F
	Research	99.9995	<1	<2	<5	<0.5	<0.5	-112°F
Matheson	Research	99.9995	<1	<1	<1		<0.5	-105°F
	Matheson purity	99.9995					<10	
	ultra-high purity	99.999					<0.5	
	zero oxygen free	99.998	<5				<0.5 <10	

TABLE 3  
 SELECTED SUPPLIERS' SPECIFICATIONS FOR OXYGEN

<u>Supplier</u>	<u>Grade</u>	<u>Purity Min %</u>	<u>N<sub>2</sub> ppm</u>	<u>Ar ppm</u>	<u>H<sub>2</sub>O ppm</u>	<u>THC (as CH<sub>4</sub>) ppm</u>	<u>Dew Point °F</u>
MG Scientific	MG 5.0, Scientific	99.999	<3	<5	<0.5		
	Ultra zero					<0.2	
	MG 4	99.99	<15	<50	<1	<12	
	MG 2.6 Extra dry	99.6					
Linde	Research	99.995	<15	<10	<3	<3	
	Ultra high purity	99.99			<3		
	Extra dry	99.6			<10		
	HC free UHP	99.99			<3	<0.5	
	Zero	99.6				<0.5	
Airco	USP	99.6					-76
	4 (Ultra-pure)	99.99					-97
	4.5 (Research)	99.995					-97
Air Products	Zero	99.9				<0.2	
	USP	99.994	10-40	15-20	<1	<1	-105
	Research	99.996	<15	<15	<0.5	<1	-112
Matheson	Research	99.99	<20	<20		<20	-85
	UHP	99.99				<20	
	Extra dry	99.6				<25	

standards and it is not routinely checked to know the quality of individual lots.

The information in the above cited tables is generally self-explanatory. The impurities listed are a combination of the suppliers' maximum limit and the reported typical amount found by analysis. It is difficult to decide which way a supplier reports his specifications. The main item that should be emphasized from the suppliers' information is the range of the impurity concentrations for the different grade gas.

The information supplied is for compressed gases rather than liquefied gases. This presents no real problem since the liquids were evaporated at the separation plant and the volume contaminant: volume gas ratio will remain very nearly the same upon vaporization.

## 4.0 REVIEW OF LATEST HYDROCARBON TEST EQUIPMENT AND METHODOLOGY

### 4.1 General Information

A survey was made of the latest instrumentation available for hydrocarbon analysis and of the methodology for sample concentration techniques. As a general rule there have been no major advances in hydrocarbon analysis instrumentation during the past ten years. There have been some improvements in the electronics, but the two types of instruments that are used are still gas chromatographs and infrared analysis. However, there have been major improvements and discoveries in trace contaminant concentration techniques.

### 4.2 Hydrocarbon Analyzers

Information was found on two hydrocarbon analyzers, the Beckman Model 400 and the AID Model 550. The Beckman has a range of 0-1 ppm as methane for low level monitoring. It operates in the same manner as a gas chromatograph with a short capillary column and a flame ionization detector (FID). The AID instrument is portable and has a minimum detectable concentration of .1 ppm. A copy of the manufacturer's literature is given in Appendix I.

### 4.3 Gas Chromatograph

A large number of manufacturers supply gas chromatographs equipped with FID's that may be used for hydrocarbon analysis. The packed column is simply replaced by a short capillary column that does not separate the mixture. A second column is used many times to separate the

compounds into different components. The price of the instruments varies from approximately \$1000 to greater than \$15,000 depending on the number of options and the complexity of the electronics. The sensitivity of these instruments with the FID is in the range of  $10^{-12}$  moles of hydrocarbon in a sample. This will normally be less than 1 ppm of the hydrocarbon when measured as methane.

#### 4.4 Infrared Analyzer

Infrared analyzers may be used to measure high concentrations of hydrocarbons, generally in the range of 1-100 ppm. Several companies manufacture infrared instrumentation, but the two that appear more oriented toward hydrocarbon contamination monitoring are Beckman and Wilkes. With a 127 mm cell the Beckman Model 365 can detect methane in the range of 0-2000 ppm, and with the 381 mm cell n-hexane may be detected in a range of 0-200 ppm. The Wilkes instruments have an optional gas cell with a series of mirrors to give a 20 meter path length. This long path length permits hydrocarbon detection to the 1 ppm range. It is, however, rather cumbersome to take samples from a high pressure gas line in the field. It is more suited for monitoring ambient conditions. Neither of these instruments appear satisfactory for extremely low level monitoring.

#### 4.5 Concentration Techniques

Several studies have been made in hydrocarbon contamination concentration techniques in recent years. Absorption techniques have not been improved to any great extent since absorption equipment of this type, with gas-liquid contact efficiencies greater than 90 percent, usually



has the disadvantage of relatively low flow capacities. Also when trace organic gases have been collected in the form of a very dilute solution in an organic solvent, the problem of recovery and analysis by GC techniques is still formidable.

#### 4.5.1 Low Temperature Condensation

The collection of vapor-phase organic air pollutants by condensation at low temperatures has at least two distinct advantages over other collection methods: (1) the collected organics are immediately available for analysis, without requiring either removal of solvents or desorption from an adsorbent; and (2) condensation is the most reliable method for preserving the organics without further occurrence of chemical reactions. The main disadvantages of collection by condensation are that large quantities of water will condense in the trap and the requirement for a cooling method in a field environment presents logistics problems.

#### 4.5.2 Cold-Surface Traps

Simple cold-surface traps have been used to condense organic gases. During the early investigatory period in the Los Angeles air pollution episodes, Cadle et al. (1), Haagen-Smit (2), and others (3, 4) reported that many volatile contaminants could be efficiently collected from the atmosphere with simple cold condensation surfaces. These simple open-bore, cold surface traps are now seldom used in air pollution studies unless there is a need to freeze out the water from the air to examine the organic materials dissolved in the water.

#### 4.5.3 Cryotraps

Rasmussen (5) reported the development of a portable air sampler that can collect and enrich large representative samples of atmosphere. The principle of the operation is the cryogenic technique of liquefying air. This straightforward approach is useful to obtain large samples of ambient atmosphere, but it does require liquid nitrogen for cooling.

#### 4.5.4 Packed Cold-Surface Traps

Packed cold-surface traps have made use of charcoal, silica gel, glass beads, stainless steel washers, porous polymers, and GLC substrates coated or bonded on refined solid support material. The proper selection of the packing material can give extremely good results even though some method of cooling the sample chamber is required. The details of some of these concentrating traps have been reported in the open literature (6-9).

#### 4.5.5 Adsorption Techniques

At ambient or subambient temperatures, gases adhere variably to solid surfaces; this phenomenon is called adsorption. The degree of adsorption depends on the relationship between pore structure and the size and shape of the contaminant molecules, as well as on the strength of molecular attractive forces. Some of these solids - activated carbon, silica gel, activated alumina and the porous organic polymer sorbents (Chromsorb and Porapak) used in gas chromatography - are practical adsorbents.

Recently, Kaiser (10) reported the use of a new type of porous carbon black (Carboseive) produced by thermal degradation of polymeric polyvinylidene chloride. This carbon black has both adsorbent and molecular seive properties and an extremely non-polar surface. Graphitized thermal carbon black has also been reported by Kalaschinikova et al. (11) to have excellent adsorption properties for C<sub>1</sub>-C<sub>6</sub> alkanes, alkenes, alkynes, alkadienes, cyclanes and cyclenes. Charcoal has also been used, but desorption is extremely difficult. Treated carbon such as Carboseive B has proven to be an efficient adsorbent, yet the contaminants may be readily desorbed with heat.

Hydrocarbons with more than five (5) carbon atoms have been very successfully adsorbed on Tenax GC, poly (p-2,6-diphenylphenyleneoxide). Bertsch and Zlatkis (12) have obtained a high degree of success using this adsorbent for a variety of organic volatiles (12-15). Ferguson (16) also obtained excellent results in concentrating volatile organic from industrial atmospheres on Tenax and then desorbing them for GC analysis.

From all literature thus far it appears that by selection of the proper adsorbent, or adsorbents, a wide range of volatile organics may be trapped and condensed for later analysis. This approach has the obvious advantage of not requiring any electrical power or LN<sub>2</sub> for field sampling, and it will be extremely simple when compared to other available techniques.

## 5.0 REVIEW OF NASA COMPRESSOR AND DISTRIBUTION SYSTEMS FOR POSSIBLE TYPES OF HYDROCARBONS PRESENT

Nitrogen is received at the MSFC in the form of a liquid delivered by insulated tank trucks. The tank trucks are not dedicated to the delivery of nitrogen only, so the nitrogen could become contaminated by liquids remaining in the tank trucks as a result of their use in other services. However, only liquid nitrogen and liquid oxygen are normally transported in these tank trucks, and the trucks are thoroughly purged between deliveries.

Liquid nitrogen is loaded into the tank trucks with centrifugal pumps equipped with mechanical seals, so no contamination should be introduced by the use of such pumps. During transport to the MSFC, the vapor space above the liquid nitrogen is maintained at a positive pressure of about 40 psig to prevent extraneous material from being introduced into the nitrogen during shipment. At MSFC, the contents of the tank truck are partially vaporized to maintain a positive pressure in the truck while the remaining nitrogen is pumped into storage tanks with centrifugal pumps equipped with mechanical seals. The storage tanks are maintained at an internal pressure of approximately 40 psig.

The liquid nitrogen is vaporized for use at the various locations in the MSFC. Positive displacement pumps increase the pressure of the liquid nitrogen to a value approximating that required for its use, pass the pressurized liquid through steam-heated vaporizers and deliver the vaporized material to storage tanks located at individual use points.

In general, nitrogen is delivered to use points at pressures of 200-8000 psig. The positive displacement pumps are fabricated from stainless steel, with Tylon seals, so the liquid nitrogen is in contact with only inert materials. The vaporizers are fabricated from stainless steel, and the vaporized nitrogen is pumped into storage tanks fabricated from carbon steel.

Oxygen is received at the MSFC in the form of a liquid delivered in the same type of tank trucks used for liquid nitrogen, as discussed above. The tank trucks are loaded by gravity flow from the manufacturer's storage tanks or with centrifugal pumps equipped with mechanical seals. The tank trucks are maintained under an internal pressure of 5-25 psig during transport to the MSFC. The tank trucks are unloaded by the pressure created by vaporizing a portion of the liquid oxygen. This pressure is used to force the remaining oxygen into a storage tank(s) which is generally located at the point of its use.

A review of the above information reveals that nitrogen can become contaminated during a number of operations:

1. Transfer from manufacturers' storage tank to tank trucks.
2. During loading of the tank truck, by materials remaining in the tank truck from other services.
3. Transfer from tank trucks to NASA storage.

4. By contact with contaminated pressurization gases.
5. By contact with less than perfectly clean component parts of the oxygen system.

Both products are analyzed by the suppliers to insure that purchase specifications are being met, but no sampling and analysis are performed during the delivery process to determine possible sources of contamination.

It is interesting to speculate that droplets of liquid or particles of solid hydrocarbons introduced into the nitrogen system during the loading and unloading of tank trucks or by contamination of the vaporizer system could be carried into the 8000-psig storage tank by entrainment. Using pumping rate data, information on the pipe size in the vaporizer system and the physical properties of nitrogen at 8000 psig, the mean velocity in the pipeline between the compressor station and the 8000-psig storage tank has been calculated to have a mean value of 11.5 ft/sec. Using the same input data in Soo's correlation (17), the minimum entrainment velocity was calculated to be 28.2 ft/sec, so the possibility of hydrocarbon transport into the storage tank by physical entrainment was ruled out.

Another interesting possibility to consider is whether hydrocarbons might be accumulating in the 8000-psig storage tank. The vapor pressures of the normal hydrocarbons from ethane through nonadecane were divided by system pressure and the quotient was multiplied by the number of carbon atoms contained in the hydrocarbons to obtain the vapor phase

content (as methane) of the hydrocarbon if it were present in the tank as a liquid at equilibrium conditions. (Methane was excluded from the calculation because its critical temperature is  $-82.1^{\circ}\text{C}$ , and it therefore cannot exist as a liquid in this system.) The results of these calculations are presented in Table 4.

Of all the analyses of the nitrogen in the 8000-psig tank over the past 1 1/2 years, only three have shown values of hydrocarbon content greater than 0.1 ppm, and these values were 0.11, 0.14 and 0.18 ppm. This information, considered together with the calculation results contained in Table 4, indicates no normal hydrocarbon lower than pentadecane can be accumulating in the storage tank. Octadecane has a freezing point of  $28^{\circ}\text{C}$ , and therefore normal hydrocarbons heavier than this would usually be present as solids, if at all. On the other hand, branched-chain hydrocarbons have lower melting points than the corresponding normal hydrocarbons, so some branched hydrocarbons heavier than octadecane could be present as liquids.

McKinley (18) has stated the following about the liquefaction procedure of oxygen:

To generalize, nearly all hydrocarbons up through butane and butylene (excluding butadiene and methyl acetylene) would enter the high pressure column, as would  $\text{NO}$ ,  $\text{N}_2\text{O}$ ,  $\text{CO}$ , ozone and hydrogen. Of these, hydrogen and some of the  $\text{CO}$  would leave the high pressure column with the relatively pure nitrogen overhead and the remainder leave in the crude oxygen bottoms which proceed to the low pressure column.

Therefore, the hydrocarbons which could be present in liquid oxygen and their vapor pressure) are compounds 1-4 and 20-37 listed in Table 5.

TABLE 4

## EQUILIBRIUM VAPOR PHASE CONCENTRATIONS AT 8000 PSIG

<u>Compound</u>	<u>Vapor Pressure @ 25°C, psi</u>	<u>Vapor Phase Content @ 8000 psig Volume Fraction</u>
Ethane	606	0.151
Propane	139	0.0520
Butane	41.3	0.0206
Pentane	10.7	$6.68 \times 10^{-3}$
Hexane	2.81	$2.10 \times 10^{-3}$
Heptane	0.83	$7.25 \times 10^{-4}$
Octane	0.25	$2.50 \times 10^{-4}$
Nonane	0.09	$1.01 \times 10^{-4}$
Decane	0.03	$3.74 \times 10^{-5}$
Undecane	$1.22 \times 10^{-2}$	$1.67 \times 10^{-5}$
Dodecane	$4.61 \times 10^{-3}$	$6.90 \times 10^{-6}$
Tridecane	$2.13 \times 10^{-3}$	$3.45 \times 10^{-6}$
Tetradecane	$6.78 \times 10^{-4}$	$1.18 \times 10^{-6}$
Pentadecane	$2.37 \times 10^{-4}$	$4.43 \times 10^{-7}$
Hexadecane	$8.86 \times 10^{-5}$	$1.77 \times 10^{-7}$
Heptadecane	$4.79 \times 10^{-5}$	$1.02 \times 10^{-7}$
Octadecane	$3.70 \times 10^{-5}$	$8.31 \times 10^{-8}$
Nonadecane	$1.22 \times 10^{-5}$	$2.89 \times 10^{-8}$



## 6.0 REVIEW OF BACKGROUND DATA FOR THE ESTABLISHMENT OF PRESENT HYDROCARBON SPECIFICATION LIMITS

Although we had access to the computer-based information-retrieval system at the Redstone Scientific Information Center during this study, we were not able to uncover any basic documents on the rationale used in establishing the present hydrocarbon specification limits.

A detailed search of the Chemical Abstracts from 1906 through 1975 revealed that Russian scientists have long been concerned with hydrocarbon limits; e.g. work on the solubility of acetylene, ethylene and propylene in liquid nitrogen, liquid oxygen and mixtures of the two were described in the late 1930's and early 1940's (19-21). In the United States, the American Institute of Chemical Engineers has been deeply involved in matters pertaining to air-plant safety; beginning with individual articles of interest and a detailed reporting of question-and-answer sessions on air-plant safety held at annual meetings. The Institute now holds annual symposia on "Ammonia Plant Safety (and related facilities)" and publishes the papers given at these symposia in a series of CEP technical manuals. Although the series primarily deals with ammonia plants now, it was formerly entitled "Safety in Air and Ammonia Plants," and early (late 1950's and early 1960's) issues dealt almost exclusively with air plants and their operation. The search of the Chemical Abstracts also seemed to indicate that the interests of engineers and scientists today have taken a turn similar

to that of the AIChE, i.e., not much work is presently being published on air-plant safety, hydrocarbon-liquid oxygen systems, etc.

Perhaps the most authoritative and informative publication we found on hydrocarbon-liquid oxygen systems was a paper by Karwat of the Linde Company of Germany (22). In the work described in this article, Karwat determined that : (1) the solubility of hydrocarbons in liquid oxygen at 90°K decreases as the number of carbon atoms increases; (2) the solubility of hydrocarbons with the same number of carbon atoms decreases as the hydrocarbons become more unsaturated; (3) the solubility of compounds with the same number of carbon atoms decreases as the number of double bonds in the compounds increases; and (4) compounds with triple bonds are less soluble than the corresponding compounds with double bonds. For example,

<u>Hydrocarbon</u>	<u>Solubility in LOX @ 90°K (ppm)</u>
Acetylene	5.6
Ethylene	20,000
Ethane	128,000
Propane	9,800
Butane	175

Karwat also determined that unsaturated solutions (of hydrocarbons in liquid oxygen) containing less than 1 mole percent of methane, ethylene or ethane could not be made to explode, even with primer caps as initiators, but rich solutions, especially stoichiometric mixtures, react

with velocities equaling explosion. Acetylene, the  $C_3$ ,  $C_4$  and higher hydrocarbons could not be made to explode as long as their concentrations did not exceed the limit of solubility. However, all two-phase systems liquid-solid or liquid-liquid brought about violent explosions. Solid or liquid hydrocarbons moistened with unsaturated liquid oxygen were just as dangerous as the two-phase systems.

Views presented in other papers by members of the air-separation industry are of interest. The hazards associated with acetylene are universally recognized and have been since the late 1930's and early 1940's.

Methane is considered relatively harmless. Kerry (23) stated that "Methane, because of its higher solubility limit, has little, if any, effect on the operation of oxygen plants." McKinley (18) indicated oxygen plant tolerance for methane is high indeed, since oxygen containing as much as several percent of methane is not explosive.

As for hydrocarbons heavier than methane, Kerry (23) indicated that such materials have been found in air plants but they were never analyzed quantitatively with any degree of accuracy. McKinley (18) hypothesized that, using the approximation that the lower flammable limit, expressed as methane or carbon atom equivalent; is reasonably constant at about 5 mole percent, a value such as 500 ppm (Safety factor = 100:1) may be adapted as a tolerable level for soluble contaminants. Karwat (22) stipulated ". . . as a general safety rule, that at no place in an air-separation plant should it be possible to form solutions that contain

more than one third of the solubility limit i.e., 6,600 ppm  $C_2H_4$  or more than 1 vol %  $C_2H_6$ . Hugill (24) specified that ethylene concentration could be permitted to rise to 300 ppm before it was necessary to shut the plant down. An explosion in a plant in which the presence of sufficiently large quantities of acetylene was definitely excluded led Karwat (25) to a renewed investigation of the behavior of  $C_2$  and  $C_3$  hydrocarbons. This investigation led to the conclusions that ". . . it would be best to keep  $C_3H_8$  away from  $O_2$ -rich liquids;" that  $C_4H_{10}$  would be ". . . in the same class as  $C_3H_8$  relating to its safe handling," but "focussing attention on  $C_3H_8$  does not mean we classify it as the number two enemy behind  $C_2H_2$ ."

Permissible concentration of hydrocarbons in air-plant streams was also discussed. Kerry (23) recommended that acetylene content in the main vaporizer be kept below 2 ppm. Hugill (24) indicated that "Some plants use a maximum allowable acetylene of 1 ppm, at which point they must carry out excessive purging. At 2 ppm, they must be shut down." Bollen (26) stated that "Our shutdown limit (for acetylene) at that time was set at 3 ppm" (the plant had an explosion). As for allowable total hydrocarbon concentration, McKinley (18) states "A total hydrocarbon level of 200 ppm is safe only if no hydrocarbons with a solubility below 200 ppm are present in excess of their individual solubility limits." Matthews (27) suggested that hydrocarbons concentrations of 30 ppm were "normal" while a concentration of 200 ppm would be "the shut down point."

McKinley (18), Karwat (22) and Reynolds (28) all stated that two-phase mixtures of hydrocarbons and liquid oxygen are explosive. It is conceivable that Karwat's work led to the formulation of the present specification limits for hydrocarbons in liquid oxygen. An acetylene concentration of 0.25 ppm in liquid oxygen systems is acceptable by current purchase specifications; this concentration, coupled with Karwat's value of 5.6 ppm for the solubility of acetylene, leads to a safety factor of about 22:1. Similarly, butene at 109 ppm was the least soluble of the other hydrocarbons Karwat studies; considering the specification limit of 50 ppm of hydrocarbon (as methane), and considering butene to be the equivalent of four methanes, leads to a safety factor of about 9:1.

## 7.0 PROPOSED SAMPLING AND ANALYSIS PROGRAM TO BE CONDUCTED IN PHASE II

### 7.1 Introduction

As indicated in earlier sections of this report, the major contaminants expected to be present in the liquid oxygen (LOX) and the liquid nitrogen (LN<sub>2</sub>) from the distillation process are low (C<sub>4</sub> and less) molecular weight hydrocarbons. Virtually all higher molecular weight compounds enter the system from contaminated connections, valves, pipes and other hardware. The proposed sampling and analysis for Phase II will mainly be concerned with the low molecular weight compounds that could possibly reach explosive concentrations but provisions will be made to analyze the higher molecular weight fraction to determine contaminant build up.

Table 5 lists the compounds that are known to be present in LOX and LN<sub>2</sub> as well as those that could possibly be present. The vapor pressure data shows that methane is the most likely to be present. Also methane and acetylene are most likely to be present from the abundance in the atmosphere which is liquefied. The exotic multiple double and triple bonded compounds are possible but not expected due to their rareness and greater reactivity.

Very small amounts of the C<sub>5</sub>-C<sub>8</sub> hydrocarbon- are expected to be found in the system since they do not normally go through the distillation process at the liquefaction plant and they are too volatile to remain

TABLE 5  
PHYSICAL PROPERTIES OF HYDROCARBONS

Compound	Boiling Point (oc)	Pressure (psi) @ 25° C	Compound	Boiling Point (oc)	Vapor Pressure (psi) @ 25°C
1 Methane	-161	4730	20 Ethylene	-104	1623
2 Ethane	- 88	606	21 Propylene	- 47	236
3 Propane	- 45	139	22 2-Methyl propene	- 66	53
4 Butane	- 1	41	23 1-Butene	- 6	52
5 Pentane	36	11	24 Cis 2-Butene	4	37
6 Hexane	69	3	25 Trans 2-Butene	1	39
7 Heptane	98	0.8	26 Acetylene	- 84	3163
8 Octane	126	0.3	27 Propyne	- 23	118
9 Nonane	150	0.09	28 1-Butyne	8	30
10 Decane	174	0.03	29 2-Butyne	27	16
11 Undecane	194	$1 \times 10^{-2}$	30 Allene	- 34	173
12 Dodecane	215	$5 \times 10^{-3}$	31 1, 2-Butadiene	18	20
13 Tridecane	234	$2 \times 10^{-3}$	32 1, 3-Butadiene	- 4	48
14 Tetradecane	252	$7 \times 10^{-4}$	33 Butadiyne	10	37
15 Pentadecane	270	$2 \times 10^{-4}$	34 1-Buten-3-yne	5	36
16 Hexadecane	288	$9 \times 10^{-5}$	35 Cyclo butene	2	36
17 Heptadecane	303	$5 \times 10^{-5}$	36 Cyclo propane	- 33	189
18 Octadecane	317	$4 \times 10^{-5}$	37 Methyl-cyclopropane	5	36
19 Nonodecane	330	$1 \times 10^{-5}$			

on parts if the system were contaminated with a mixture of hydrocarbons in some type oil.

## 7.2 Evaluation of the Present Sampling System

At present the LOX is not being analyzed for hydrocarbon content after it arrives at MSFC. The filters in the incoming and outgoing LOX lines are periodically removed and washed with a solvent to remove any collected oils (higher molecular weight compounds) and then an analysis is made by infrared spectroscopy to determine the status of the system (clean or dirty). Analysis data sheets are supplied with each lot of LOX that arrives but the analysis was performed before loading for transport. Typical results indicate an extremely low total hydrocarbon content which will not explain the hydrocarbon accumulation in the filters over a period of time.

The GN<sub>2</sub> is being routinely checked for total hydrocarbon content at several use points and from the 8000-psig storage tank. Only three results for the 8K tank have been greater than 0.1 ppm (0.11, 0.14, 0.18). The 0.1 ppm value is the limit of sensitivity on the instrument so the actual THC is not known. Two of the high readings were obtained in July - as would be expected if the actual hydrocarbon concentration was at or approaching instrument sensitivity level, but the highest reading (0.18 ppm) was observed in January so it is possible that the three elevated values were really just erratic readings.

The actual sampling procedure used does not necessarily lend itself to obtaining representative results of the THC of the system. Before



sampling from a valve, the stream is allowed to flow for several minutes to purge the line. This will blow out any condensed hydrocarbons that may be present near the outlet. This is especially important on the 8K tank since the sample part is located near the bottom of the tank where hydrocarbons might possibly condense. If droplets were present during analysis it would not reflect the gas phase concentration, but the high results would indicate the presence of the condensate.

Another important factor in the present analysis scheme is the volume of sample taken. A 1 ml sample loop is being used to determine the THC concentration. Two factors should be noted here: (1) the 1 ml sample does not contain enough THC to be above the minimum detectable limit and (2) the sample analyzed is not representative of the concentration in the tank. The first factor could be solved by taking a 10 or 100 ml sample, at which time analysis by GC becomes impractical. An instrument with a lower detection limit could be used, but instrument portability prevents optimization of all parameters of analysis and also movement reduces the stability of the electronics package. Some method of contaminant concentration is needed.

The second factor discussed above (representative sample) requires some thought and discussion at this point. The method of measuring concentration as ppm (v/v) as methane is extremely misleading. The term ppm (v/v) is defined as the ratio of parts contaminant per million parts solvent. That is, a 1 ppm THC in nitrogen is  $10^{-6}$  liter THC in 1 liter of nitrogen. In the case where a high pressure gas is being analyzed

at a low pressure the ppm concentration calculated at the low pressure is not representative of the actual concentration in the 8000 psig tank.

Assume that a 1 ml sample was analyzed and found to contain 0.1 ppm THC as methane. Then the instrument was able to detect  $4.1 \times 10^{-12}$  moles or an apparent concentration of  $4.1 \times 10^{-9}$  moles/liter with respect to the fixed 1 ml volume at RTP. But since the gas in the tank is compressed to approximately 533 atmospheres the concentration of THC with respect to fixed volume is  $3.2 \times 10^{-6}$  moles/liter - almost a factor of  $10^3$  difference

$$4.1 \times 10^{-9} \text{ moles/liter} \times \frac{1 \text{ atm}}{533 \text{ atm}} \times \frac{1}{1.42} = 3.2 \times 10^{-6} \text{ moles/liter}$$

where 1.42 = Compressibility factor of  $N_2$  @ 533 atm

Therefore a concentration analyzed at 0.1 ppm @ RTP would be approximately 100 ppm at 8K. The fact is important because the contaminant vapor pressure and the amount of hydrocarbon in contact with the LOX and the surfaces are not dependent upon the pressure of nitrogen present, but simply the partial pressure of the THC. The partial pressure of the THC is dependent upon temperature and not on the partial pressure of other gases present. More detailed calculations are given in Appendix IIa.

### 7.3 Determination of Required Volume of Gas for Analysis

The situation of saying that the THC concentration is less than the detection limit of the instrument still does not exactly define the concentration. The obvious solution is to take a larger sample and concentrate the THC to get a quantity large enough to determine the

concentrations of the individual hydrocarbons. Assuming that an instrument can detect absolutely  $5 \times 10^{-12}$  moles of a hydrocarbon, in order to have enough material to detect the different compounds we estimate that  $10^{-9}$  moles will be required. Methane will probably be more than half this amount, but as much as  $10^{-10}$  moles of other hydrocarbons should be available for analysis. Appendix IIB gives a calculation of the amount of  $\text{GN}_2$  that will be required to give the necessary amount of THC. On the assumption that the incoming  $\text{LN}_2$  has a THC concentration of 1 ppm, for the desired accuracy at least a 60 ml sample @ RTP should be taken for analysis. If the THC concentration in the 8K tank is in the  $10^{-6}$  mole/liter range as indicated by the calculations in Appendix IIB, this means that a 60-100 ml sample at RTP should be analyzed.

The same procedure must be followed to determine the sample size of the LOX to take for analysis. The calculation has been made to find what volume of LOX must be trapped and then allowed to expand at RTP for analysis. Again if  $10^{-9}$  moles of THC is required for a GC analysis and a 10 ml sample of LOX is taken then the minimum concentration detectible in the LOX would be  $10^{-7}$  moles THC/liter LOX; or if the THC was all acetylene with a density of 0.62, the minimum detectable concentration would be 0.04 ppm (v/v). This limit would be sufficient to identify and quantitate the individual hydrocarbons that might be present.

#### 7.4 Hydrocarbon - Liquid Oxygen Compatability

McKinley (18) is one of the several individuals who discussed the

acceptable hydrocarbon content in liquid oxygen as it comes from air-separation plants. All reports found discuss the hazards of hydrocarbons in liquid oxygen during separation since numerous explosions have taken place at these plants over the years. A hazard is normally produced when the hydrocarbon begins to separate from the solution as a solid. Table 6 shows that only acetylene is likely to be present in quantities that will produce such a hazard.

Table 7 gives more detailed information about the concentration required for explosive propagation at  $-183^{\circ}\text{C}$  for acetylene, ethylene and methane. Hydrocarbons are removed in the air-separation plants by their adsorption on a silica-gel bed. It is not unusual for the liquid oxygen to contain as much as 200 ppm THC and up to 0.2 ppm acetylene. The Government standards under which LOX is purchased are much more stringent than this and also the lot analysis shows a very small amount of THC present.

#### 7.5 Recommended Sample Points

The location of representative supply points will determine whether or not valid, useful results may be obtained. The locations that are proposed herein were selected with the idea in mind of not only being able to know the status of the system contamination, but also to determine the source of the contamination. These tentative sample points have been selected based on expected contamination sources and may require some changing in Phase II. These points may also be changed after discussion with the COR if he feels that more representative samples may be obtained at other points.

TABLE 6

## SOLUBILITIES OF VARIOUS HYDROCARBONS IN LIQUID OXYGEN

<u>Compound</u>	<u>Solubility in ppm (1)</u>	<u>Solubility in ppm (3)</u>	<u>Solubility in ppm (4)</u>	<u>Solubility in ppm (5)</u>
Methane	$7.4 \times 10^5$			
Ethane	$9.2 \times 10^4$	$5.6 \times 10^4$		$1.3 \times 10^5$
Propane	$4.5 \times 10^4$			$9.8 \times 10^3$
Butane	150			175
Pentane	20			
Hexane	2			
Decane	0.6			
Acetylene	1.7	5	1.0	5.6
Ethylene	1800	$1.3 \times 10^4$		$2 \times 10^4$
Propylene	2500	$6.6 \times 10^3$		
Benzene	4			

(1) Air Products, Inc. Research Laboratory, as reported in (2) below.

(2) Chem. Engr. Prog., 53 (3), 112 (1951).

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TABLE 7  
 POSSIBLE CONCENTRATION OF ACETYLENE,  
 ETHYLENE AND METHANE IN LOX

<u>Hydrocarbon</u>	<u>Concentration Required For Explosive Propagation</u>	<u>Possible Concentration in LOX From Air-Separation Plant (ppm)**</u>
Acetylene	5 ppm*	0.2 (safe)
	0.005 gm/l of LOX	0.5 (doubtful)
	$4 \times 10^{-5}$ lb/gal of LOX	2.0 (dangerous)
Ethylene	3000 ppm	
	15 gm/l of LOX	200 (safe)
	0.124 lb/gal of LOX	
Methane	8000 ppm	
	40 gm/l of LOX	200 (safe)
	0.33 lb/gal of LOX	

\*ppm = parts per million

\*\*McKinley, Chemical Engineering Progress; 53 (3), 112 (1957).

The sampling will be divided into two distinct parts - the high pressure GN<sub>2</sub> system and the LOX system. The combination of the results from the two systems should indicate if contamination levels in the LOX system could possibly reach explosive levels.

The GN<sub>2</sub> system status can be monitored at the same point as it now is, at the 8000 psig reservoir tank. If liquid hydrocarbons are collecting in the tank, the sample point at the lower end of the tank will indicate the worst possible conditions. The vapor phase hydrocarbons will be in concentrations in this tank that will be representative of those that will be exposed to the LOX upon pressurization in the spherical tank. If high hydrocarbon concentrations are found in the 8K tank, the sample points upstream will be selected to attempt to isolate the problem. These points have not now been selected since a contamination problem is not anticipated in the GN<sub>2</sub> system.

The LOX system is known to accumulate hydrocarbons over a period of time. The source is not known exactly, but it is anticipated that the LOX is contaminated at the time of delivery. The sample points proposed should aid in the isolation of the source of the contamination.

The first sample point should be as the LOX leaves the truck before it comes into contact with any valves or filters and after contact with a minimum amount of the lines. Periodic sampling should be accomplished here to determine the purity of the incoming LOX. This sampling would not be done each time a truck unloads, but simply on a random basis to get a general idea of the purity of the incoming product.

The LOX storage tank should be routinely monitored to determine if any buildup of hydrocarbons is experienced and also to help pinpoint any contamination increase from dirty system hardware and components. This THC concentration should vary with the system contaminants until such time that the hydrocarbons begin to become insoluble in the LOX and form a two-phase system.

The GN<sub>2</sub> blanket in the spherical LOX pressurization tank will also be sampled before LOX is put into the tank. This low pressure GN<sub>2</sub> sampling will indicate possible hydrocarbon accumulations in the tank. LOX is added to the spherical tank for pressurization with the 8K GN<sub>2</sub>.

Other sampling points may be required as the second phase progresses. The sample points designated will also serve to check the methods of analysis that we propose so no time will be lost by possibly not having enough sample points designated at this time.

## 7.6 Recommended Analysis Procedure

### 7.6.1 Introduction

The proposed method of analysis is modification of the technique used by Zlatkis and his co-workers (13). The basic method has since been used by several investigators for a variety of applications and it has been found to be extremely effective. This method uses porous polymer solid adsorbents to trap organic volatiles at ambient temperatures. Heat is then used to desorb the trapped volatiles for analysis by gas chromatography. The modification for this work will require the selection of the proper adsorbents that will be compatible with oxygen



and yet adsorb a full range of hydrocarbon compounds.

### 7.6.2 System Hardware

A schematic drawing of the basic hardware and system design is shown in Figure 1. The detection system makes use of a GC equipped with a FID that has been modified with a heater to desorb the trapped organic compounds. The mass spectrograph shown in the system is optional and is only needed to initially identify the components present. After initial identification, the mass spectrograph will be bypassed and the quantitative analysis will be accomplished using the FID.

The LN<sub>2</sub> cold trap (Figure 1 (a)) on the nitrogen supply line is to remove all traces of moisture or other contaminants that would be trapped in the LN<sub>2</sub> cold trap (b) on the column and then released when the cold trap is removed and analysis begun. The regulator (c) is used in conjunction with the restrictor (d) and the micrometer valve (e) to regulate the flow through the collector heater (g).

Figure 2 illustrates the usefulness of the 6-part valve to switch the gas flow away from the collector tube for analysis. The restrictor on the 6-part valve reduces the carrier flow to the 4-10 ml/min range for use with SCOT capillary columns.

Figure 3 shows a cross-sectional view of the collector heater with a collector tube inside. The carrier gas flows beside the tube, through the slotted washer and through the collector tube. The system at the top allows injection of known volumes of gas for calibration purposes.

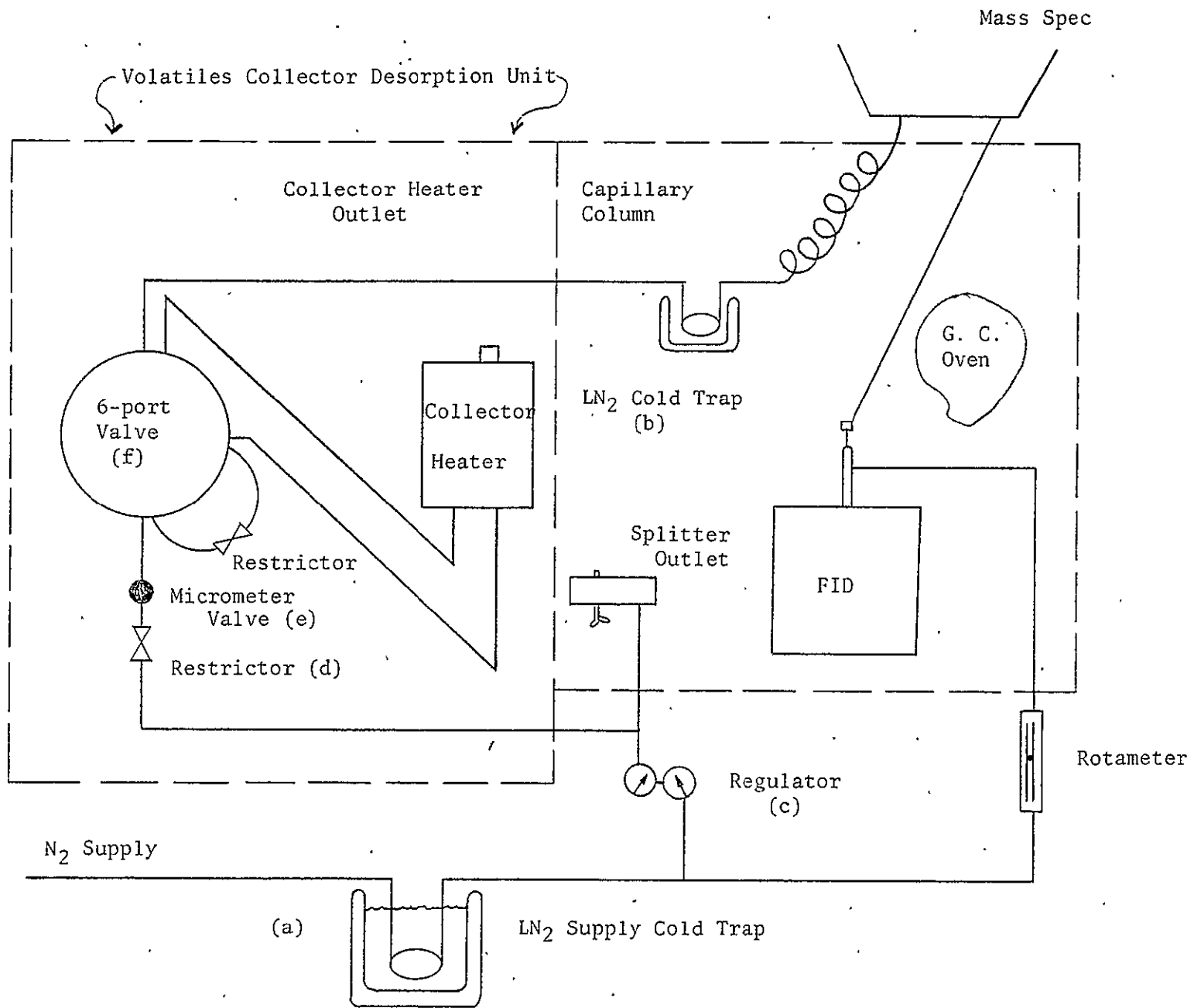


Figure 1. Schematic Outline of Integrated AVC Heater System.

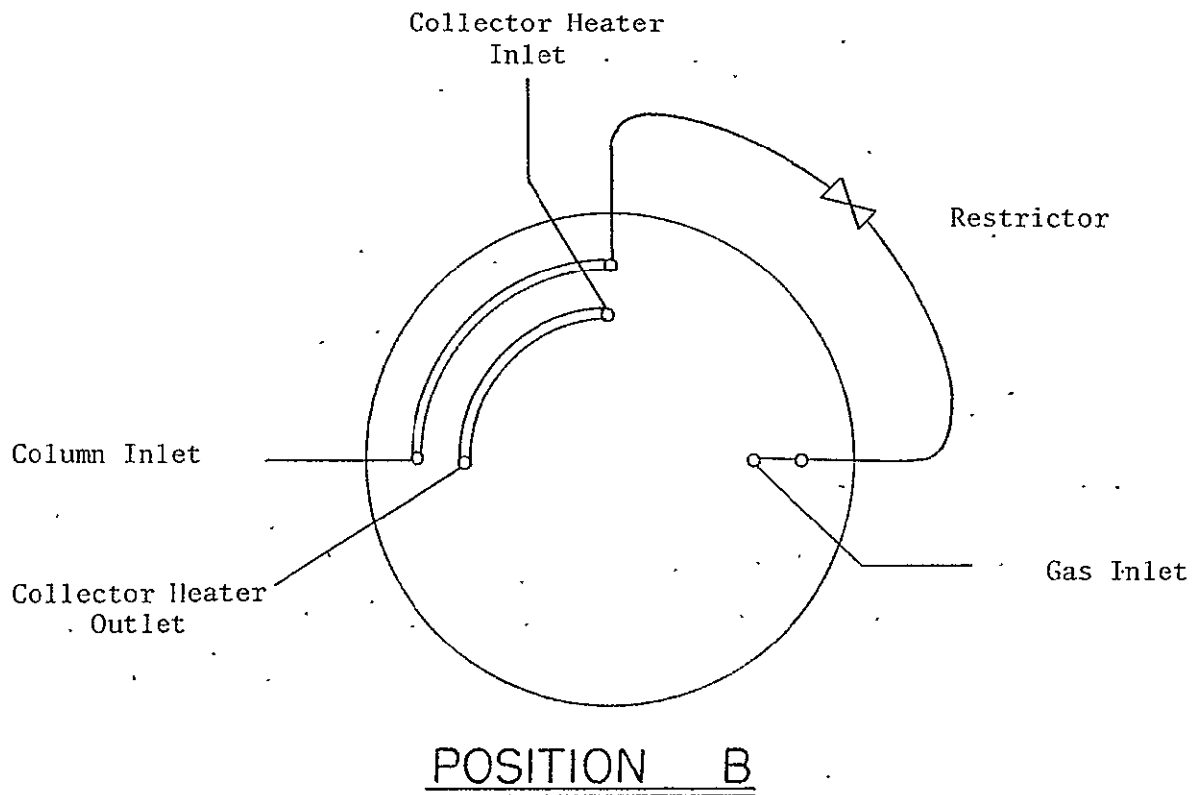
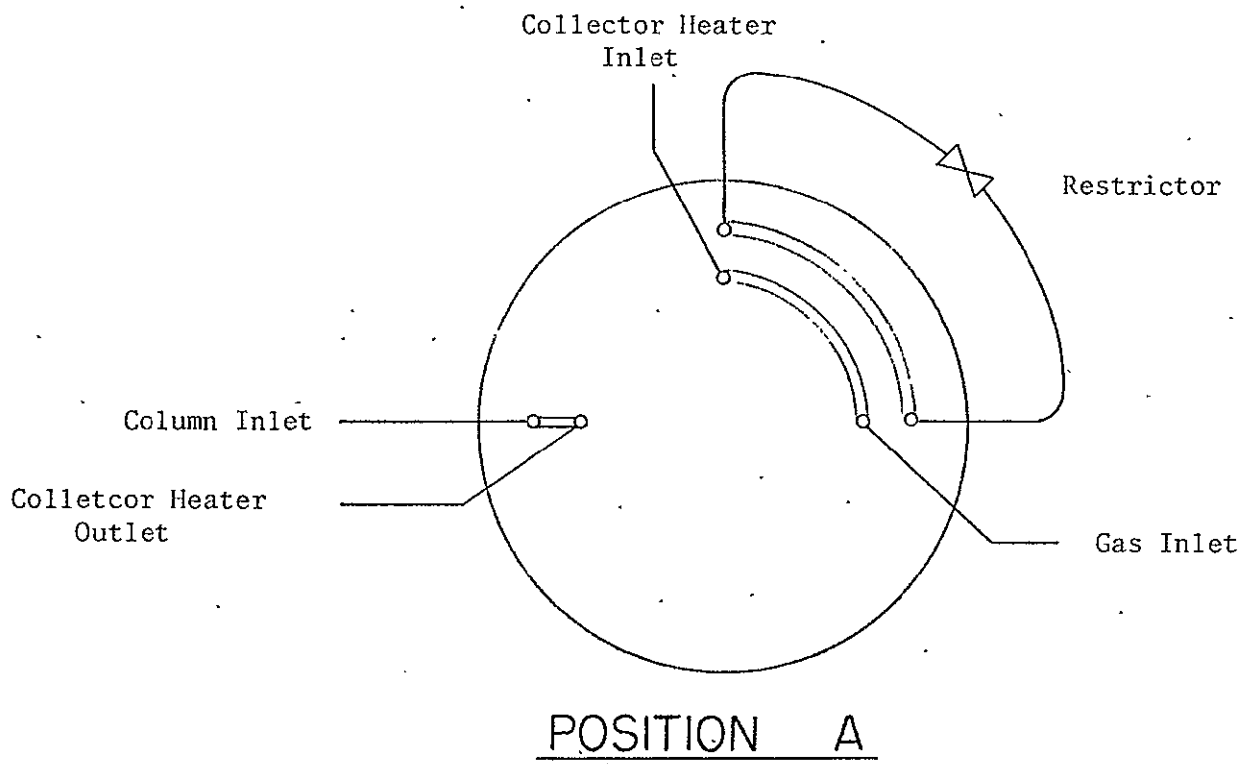


Figure 2. Schematic Diagram of the 6-Port Valve.

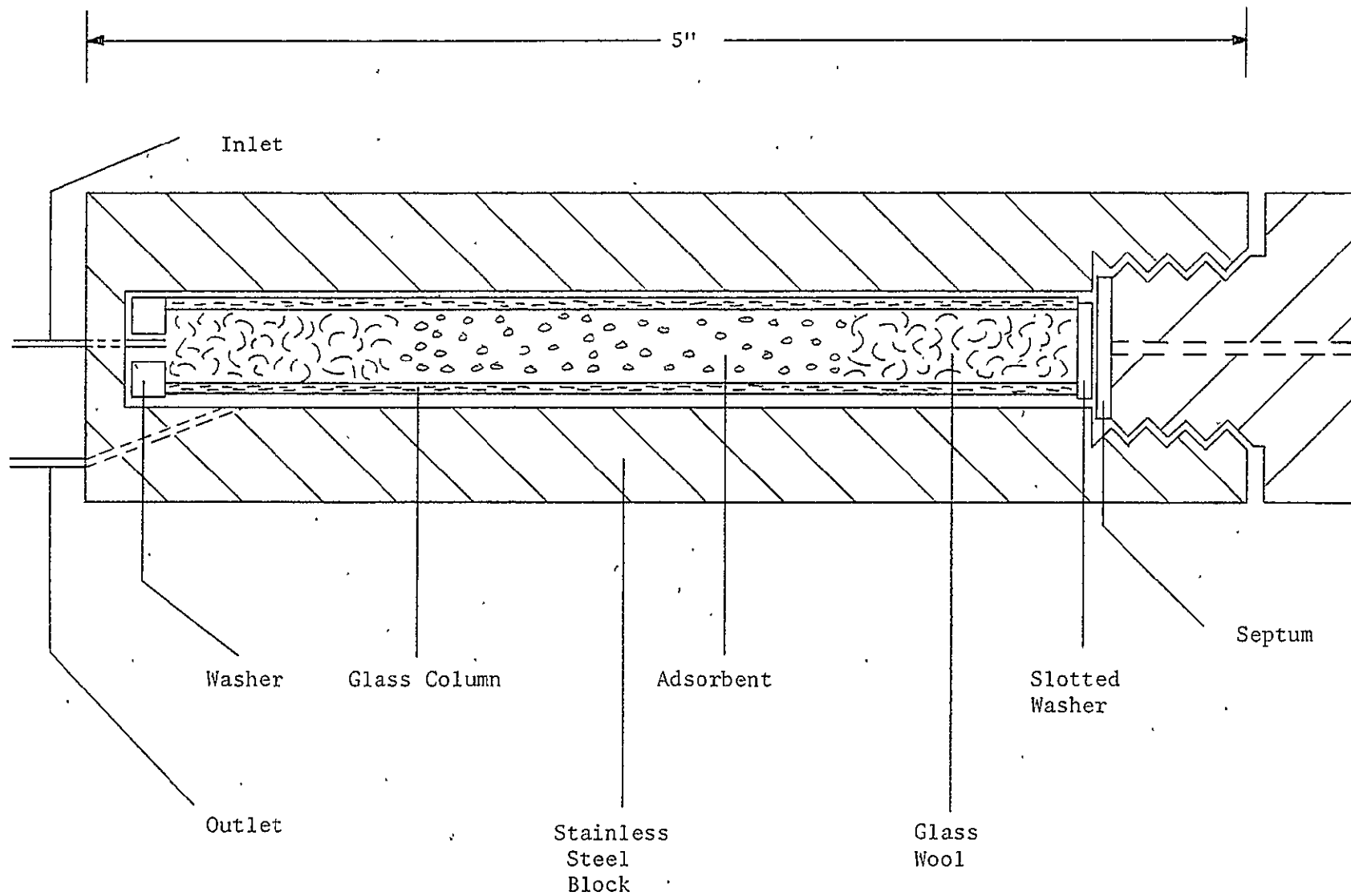


Figure 3. Cross Section View of Sample Tube in the Collector Heater Block.

Figure 4 represents the arrangement of the sample collection tubes in the sampling holder. Two different types of adsorbents will be required to trap all the hydrocarbons. The first adsorbent will trap all the high molecular weight compounds and the second tube will adsorb those that pass through the first tube. This collecting tube holder will be attached to different type devices depending on whether  $\text{GN}_2$  or LOX is being sampled. The collection tube holder and the collection tubes will all be interchangeable for use with either the LOX or the  $\text{GN}_2$  system.

### 7.6.3 Adsorbents

The adsorbents that will be used to trap the hydrocarbons will require evaluation to determine which are the most appropriate for use. From results reported in the literature and supplier's brochures, several adsorbents are promising for use. Several of these adsorbents will be purchased and adsorbent efficiencies will be evaluated to select the most efficient ones for further testing.

The adsorbent to trap the high molecular weight will almost certainly be Tenax-GC, a porous polymer that is based on 2,6-diphenyl-p-phenylene oxide. Several investigators have found this adsorbent to be extremely effective in trapping hydrocarbons with 5 or more carbon atoms. This polymer will, of course, be evaluated for efficiency in this application.

The choice for an adsorbent that will trap the  $\text{C}_1\text{-C}_4$  hydrocarbons is not nearly so clear cut. Several possibilities are available including

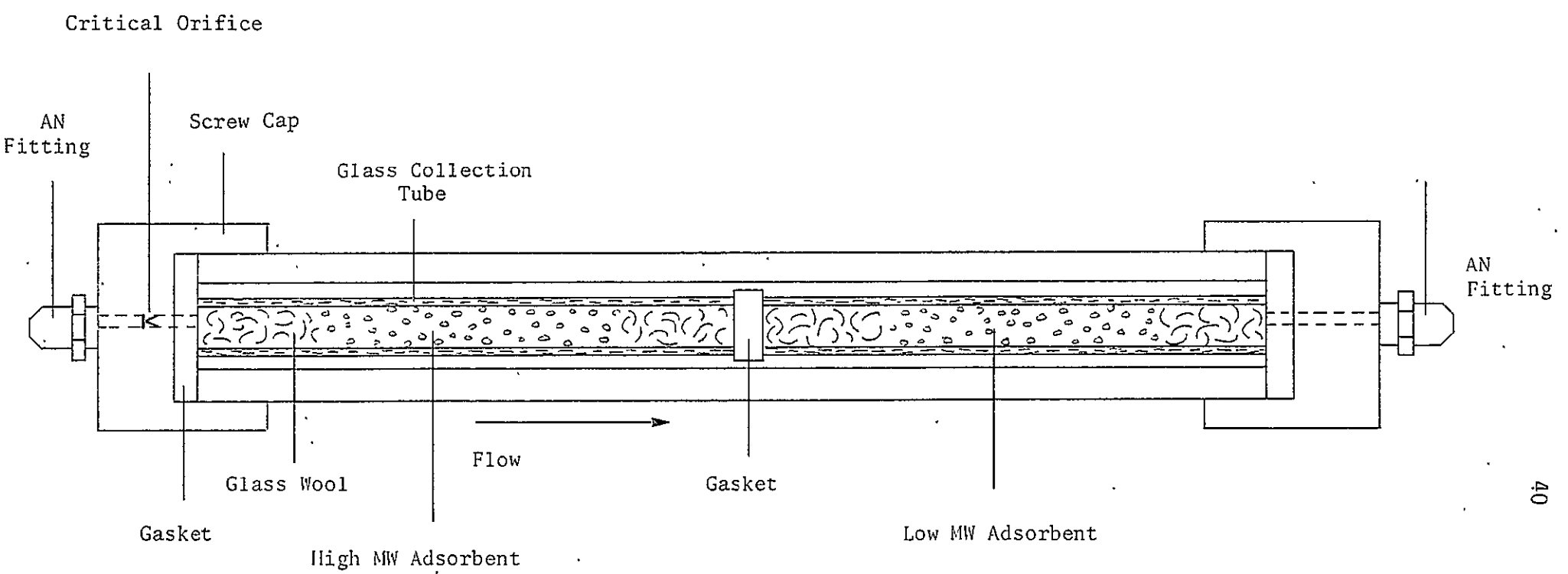


Figure 4. Collection Tube Holder.

Carbosieve-B, Carbosieve-S, Molecular Sieve 13X, Spherocarb, Carbopak C, Chromsorb 102, and Porapak Q. The carbonaceous adsorbents will not work on the LOX system since they are degraded by oxygen. If the Porapak or Chromsorb is used, it may be necessary to use subambient cooling to cause compound adsorption. Further speculation about adsorbent type or conditions would be useless since only experimental results will define the best choice.

#### 7.6.4 Sampling Procedure

The method of sampling will vary between the LOX and the high pressure GN<sub>2</sub> system. The presently used sampling port on the GN<sub>2</sub> will be modified by the addition of another valve to give a chamber of known volume for sampling. Figure 5 represents a schematic of this proposed system. The system will be purged by opening both valves for a few seconds before the collector tube holder is attached. After purging, both valves are closed (#2 first) and the collector tube holder is attached. Valve #2 is then opened and the known volume of gas trapped between the two valves is allowed to bleed through the collection tube. The flow through the tube will be regulated to between 50 and 200 ml/min by the critical orifice. The known volume will be a function of temperature and pressure of the gas and, therefore, those values must be recorded each time.

The LOX will be sampled with an apparatus similar to the one diagrammed in Figure 6. The apparatus will be attached to the valve on the LOX storage tank and valves #1, #2, and #4 will be opened to purge the system with LOX before the concentrator tube holder is attached. When the system has

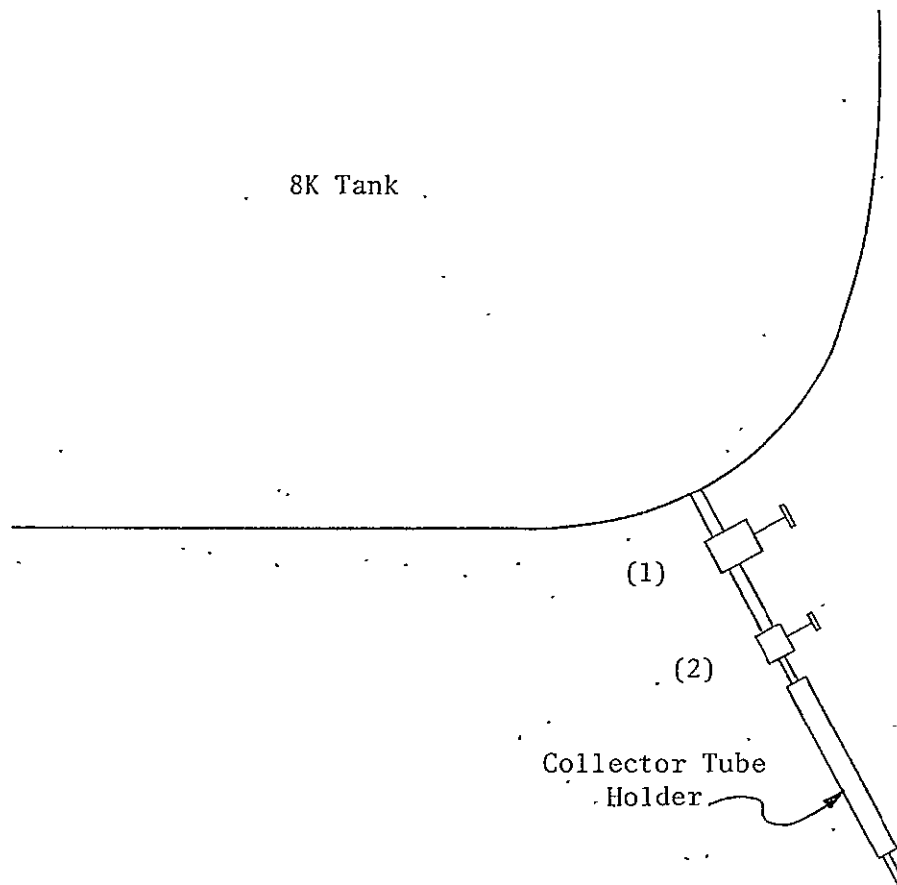


Figure 5. Sampling System on the 8000 psi Tank.



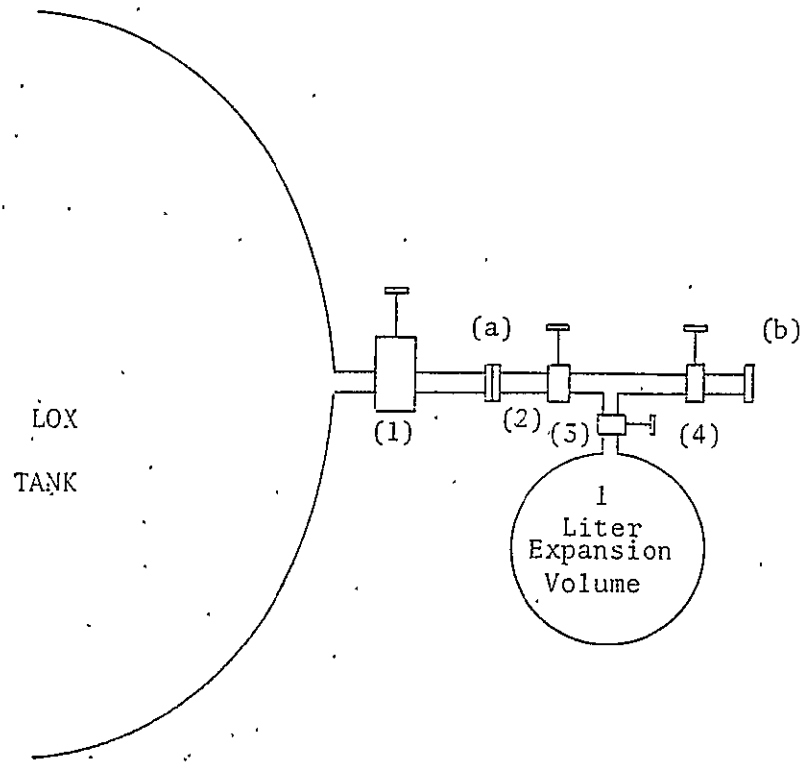


Figure 6. Sampling System for LOX System.

purged a few seconds, the valves will be closed in the order #4, #2, and #1 to trap a known volume of LOX in the line. The #3 valve will then be opened to allow the LOX to vaporize and expand into the bottle. After expansion, valve #4 will be opened to allow the expanded gas to purge the system and leave pure O<sub>2</sub> in the 1 liter volume. Valve #3 will be closed and valves #1 and #2 will be opened until the line cools and LOX is being vented to the atmosphere. After LOX flows freely, the valves are closed in the order #4, #2, and #1. Valve #3 is opened to allow the LOX to expand and the apparatus is detached at point (a) and transported to a convenient location to remove the gas. After all LOX has vaporized and the temperature has stabilized, the concentrator tube holder is attached at point (a) or (b) and the appropriate valve is opened to allow the gas to pass through the collector tubes in the same manner as for the GN<sub>2</sub> samples.

## 8.0 LOX COMPATABILITY STUDIES

The samples of the  $\text{GN}_2$  and LOX will reveal the hydrocarbon components that are excessively high or that appear to be concentrating in the systems. It would be possible for the  $\text{C}_1$ - $\text{C}_3$  hydrocarbons to accumulate slightly over the years simply from the replacement of evaporation losses with fresh gases. This concentrating rate would be a function of the evaporation rate and the use rate. The rate should be extremely small since the gases are removed in liquid form from time to time and not allowed to just sit and evaporate. Figure 7 was taken from a study done by Arthur D. Little, Inc. (29) about the long term storage of liquid oxygen. The graph indicates the rate of accumulation of acetylene in LOX storage tanks at missile silos which experience an evaporation rate of 0.4% per day.

The higher molecular weight compounds ( $\text{C}_8$ - $\text{C}_{18}$ ) could possibly accumulate due to contamination of the lines from induced contamination; this means the HC's that are present on dirty parts installed, dirty hose connections, etc. These higher molecular weight compounds will not evaporate and since they are very slightly soluble in the LOX, will tend to accumulate on the surfaces. When this two-phase system forms in the LOX system, potential problems exist with explosions.

After evaluation of the systems, further discussion with the COR will take place about the compounds present in the highest concentration. If he feels that the concentrations are in the range that warrant further

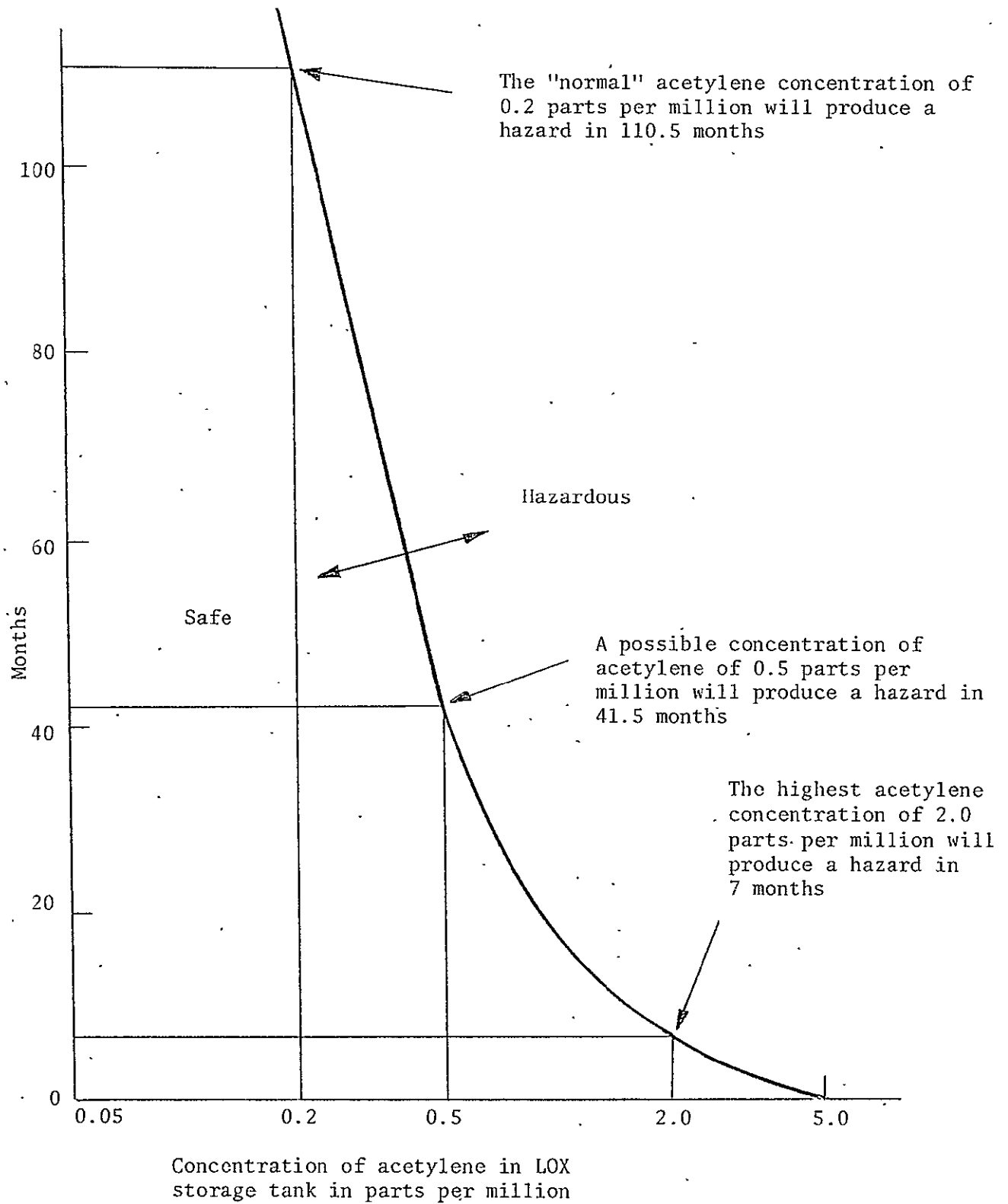


Figure 7. Accumulation of Acetylene in LOX Storage Tanks

work, then samples of the pure hydrocarbon will be supplied by Harmon Engineering to the COR for LOX compatibility studies. The HC will be supplied in its normal state at RTP in quantities necessary for a full series of tests as specified in the ASTM.

This part of Phase II will be more or less a culmination of the work and evaluation of the systems. It could possibly even be considered another phase since no real decisions about the nature of the HC to be supplied can be made until the analysis indicates the specific problem areas. It will be necessary to wait until nearer the end of the contract to make recommendations and supply the samples.

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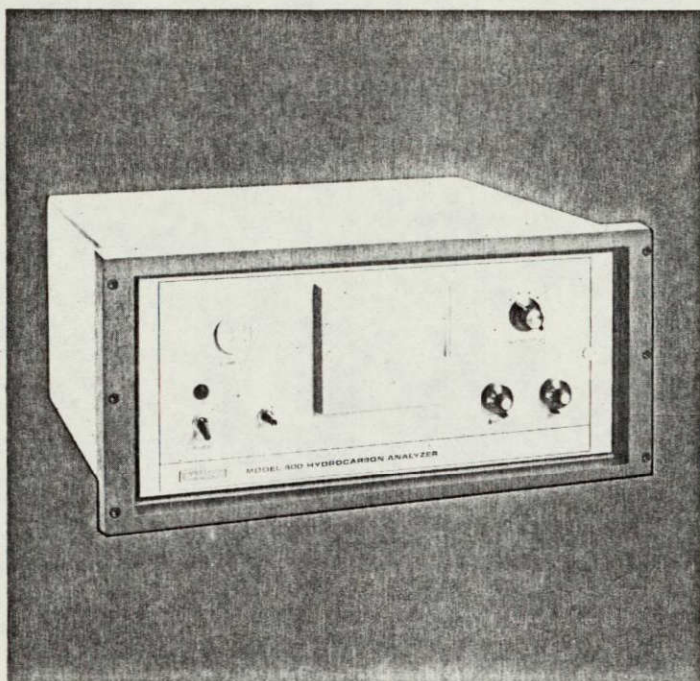
## APPENDICES



APPENDIX I

BECKMAN 400  
AID 550

# Model 400 Hydrocarbon Analyzer



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- FULL SCALE SENSITIVITY 0-1 ppm (P/10<sup>6</sup>)
- ELECTRONIC STABILITY WITHIN 1%
- FAST RESPONSE, 90% WITHIN ONE SECOND
- SOLID STATE RELIABILITY
- LOW MAINTENANCE

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The Model 400 has been specifically engineered to improve the stability and speed of response capabilities of existing units. High-level performance is attained in this temperature-controlled unit with advanced, electronic circuit design and rapid-response sample-flow system. The result: maximum stability for low-level ambient-air monitoring and accelerated speed of response for automobile-exhaust analysis.

In addition, the instrument features solid-state reliability, operational ease, and maximum safety devices.

## PRINCIPLE OF OPERATION

As its principle of operation, the Model 400 utilizes the flame ionization method of detection to determine the concentration of hydrocarbons present in a gas stream or ambient air. The flame formed when hydrogen burns in air contains a negligible number of ions. Introduction of mere traces of hydrocarbons into the flame results in a complex ionization, producing a large number of ions. A polarizing voltage applied between the burner jet and the collector produces an electrostatic field in the vicinity of the flame. The electrostatic field results in an ion migration whereby the positive ions are attracted to the collector and the negative ions to the burner jet. Thus, a small ionization current is established between the two electrodes. It is this small current that is measured by an electrometer amplifier circuit and is directly proportional to the hydrocarbon concentration in the flame.

The amplifier circuit provides the driving voltage for an indicating meter and recorder. The magnitude of the electrometer amplifier signal is indicative of the number of carbon atoms passing through the flame. The "carbon counting" characteristic of the detector is proportional to both the sample flow rate and the nature of the sample.

## APPLICATIONS

**Air Pollution:** Ambient air monitoring. Measuring combustion engine efficiency relative to the control of vehicle exhaust emissions. Determining muffler and afterburner effectiveness.

**Other Typical Uses:** Monitoring combustion efficiency. Monitoring for leakage in connection with aerosol packaging. Detecting hydrocarbons in drilling mud and in swamp seepage. Testing for refrigerant leakage. Analyzing brazing and annealing atmospheres. Leak detection in natural gas distribution systems.

**Safety:** Detecting explosive-level gas conditions in tunnels and garages. Measuring concentrations of hydrocarbons in fuel handling areas. Protecting against dangerous natural gas leaks. Controlling solvent recovery systems. Detecting hydrocarbons in mine atmospheres.

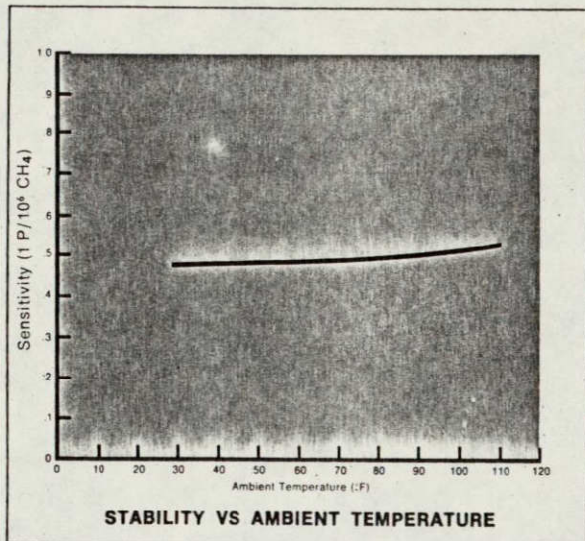
**Process Analysis:** Monitoring purity of inert gas streams. Monitoring controlled atmospheres in packaging and production lines. Transistor packaging-crystal growing.

BECKMAN®

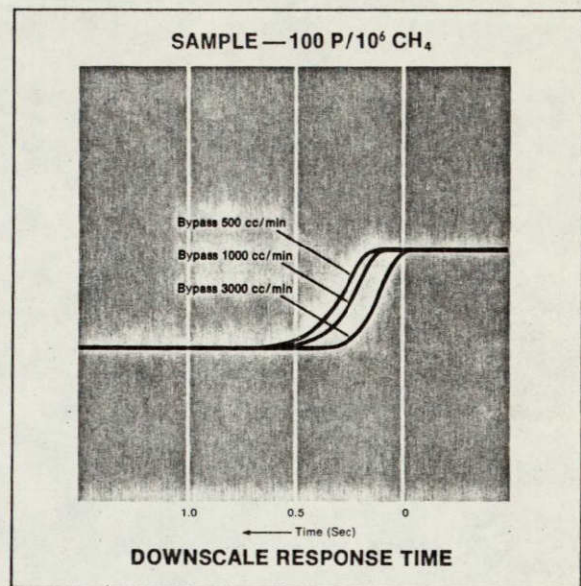
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(A) (B)



(C)



### FEATURES

Developed with the complex demands of the future in mind, the Model 400 features:

(A) **Sensitivity** — Full scale ranges from 0-1 P/10<sup>6</sup> as CH<sub>4</sub> for low level ambient air monitoring.

(B) **Stability** — Electronic stability within 1% full scale on most sensitive range over ambient temperature variations from 32°F to 110°F (0-43°C). Integral temperature control is employed to eliminate ambient temperature effects upon the flow control system.

(C) **Response** — 90% in less than 2-3 seconds for vehicle emission systems monitoring.

**Output** — 10 mV, 100 mV, 1 V and 5 V are standard. Optional 4-20 mA and 10-50 mA outputs provide compatibility with any recorder.

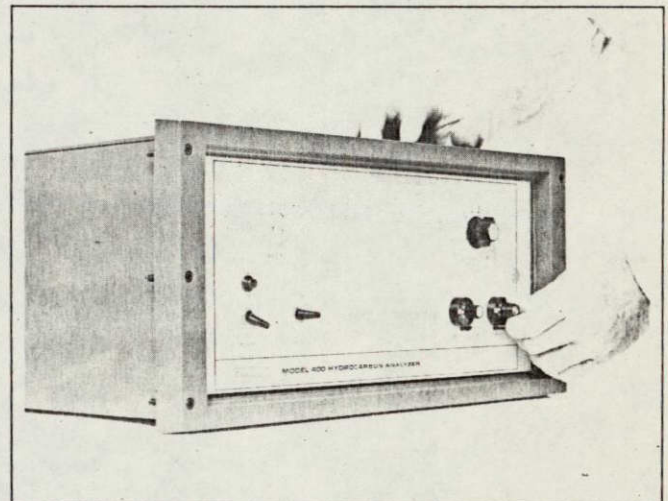
**Safety** — To provide maximum safety, the Model 400 is equipped with flame-out indicator, flame arrester and optional automatic fuel shut-off.

**Reliability** — Solid state construction with modular plug-in circuit boards provide reliability and ease of maintenance.

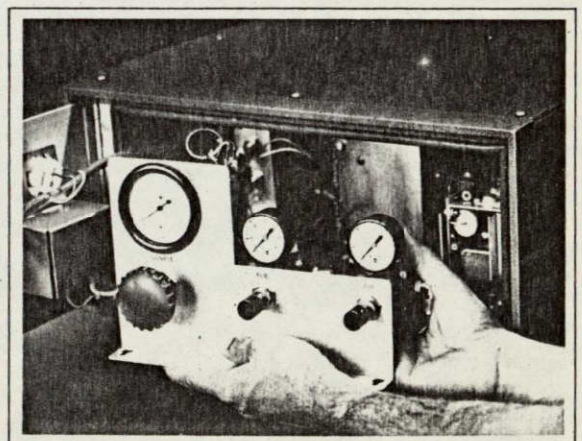
(D) **Operation** — Electronic span calibration, wide dynamic range, large indicating meter, and conveniently located controls provide ease of operation and maintain high accuracy.

(E) **Ease of Maintenance** — Front, top, and rear access provide maximum accessibility. All flow controls, related gauges, and the burner are mounted as a compact module which can easily be removed as a unit for maintenance or testing. All electronics are modularized with plug-in circuit boards and test jacks for easy troubleshooting and replacement.

(D)



(E)



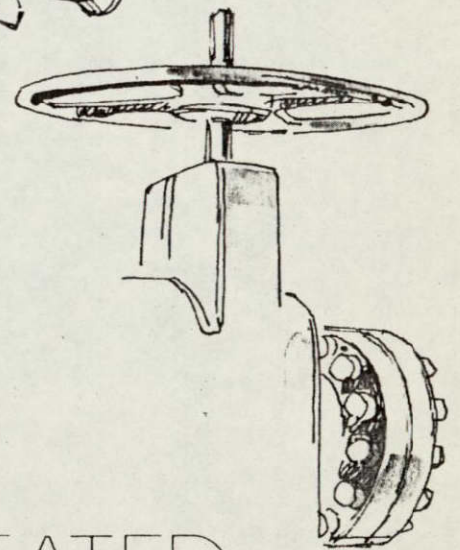
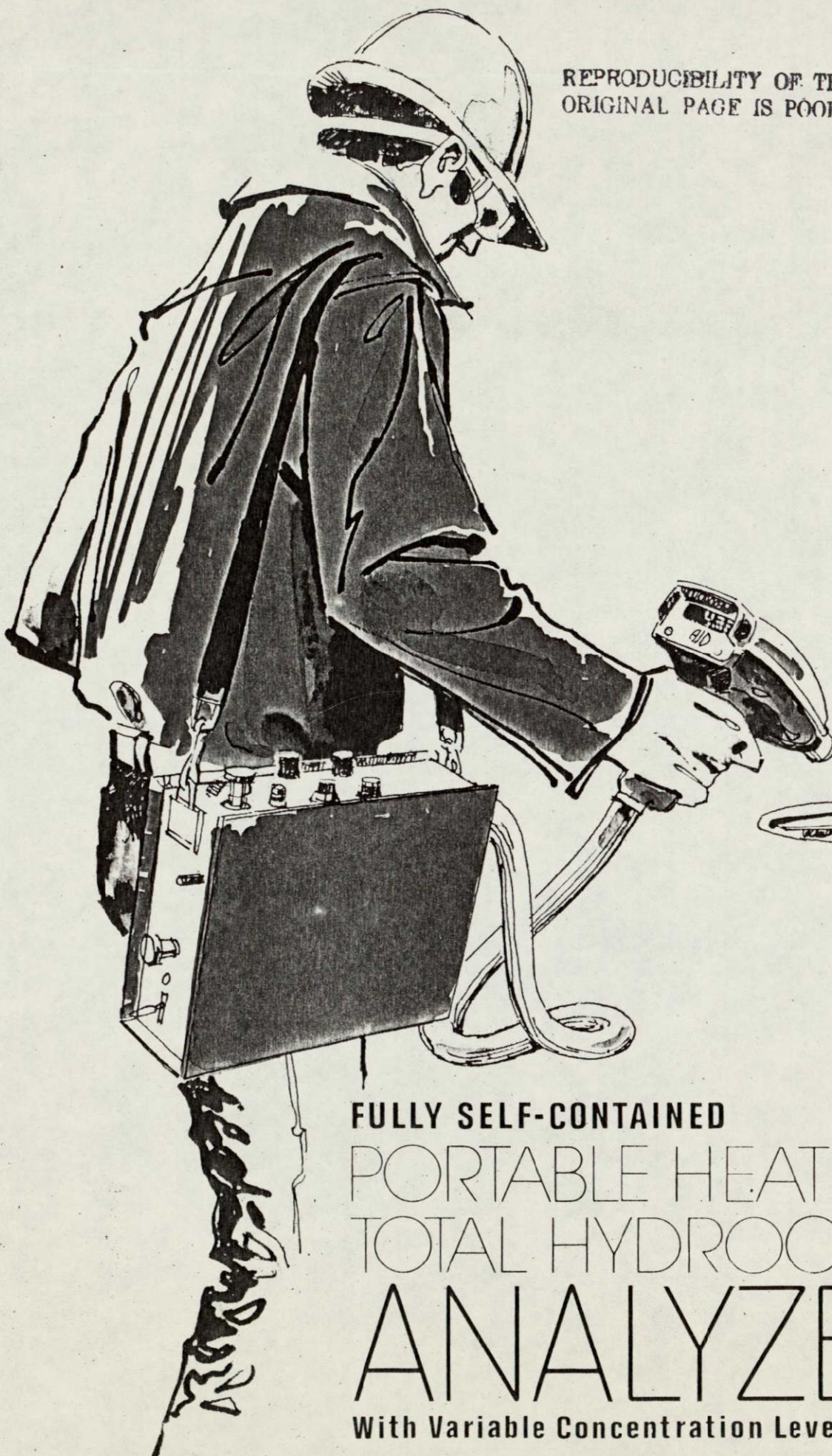
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**MODEL**

**5150**



**FULLY SELF-CONTAINED  
PORTABLE HEATED  
TOTAL HYDROCARBON  
ANALYZER**

**With Variable Concentration Level Alarm**



# SPECIFICATIONS

## MEASUREMENT

<b>Technique:</b>	Hydrogen Flame Ionization Detector for total organic carbon.
<b>Ranges:</b>	Digital Readout: 0-200ppm (Sensitivity to 0.1ppm) 0-2000ppm
	Recorder: 0-10ppm, 0-100ppm, 0-1000ppm Full Scale on 1 mv recorder.
<b>Minimum Detectable:</b>	0.1ppm as Methane
<b>Response Time:</b>	5 seconds
<b>Noise:</b>	Less than 0.1ppm
<b>Sampling Rate:</b>	Approximately 600ml/min

## OPERATION PERIOD

<b>Fully Portable:</b>	Minimum 8 hours
<b>With External Supplies:</b>	Indefinite

## POWER REQUIREMENTS

<b>Fully Portable:</b>	Self Contained Battery Pack and Hydrogen Supply
<b>External Supplies:</b>	105-130 v ac (220v. optional) at 25 watts maximum including battery recharging. Hydrogen Supply from 1800psi max to 30psi minimum at 20ml/min.

## PHYSICAL

<b>Case size:</b>	27.3cm (10 3/4 in) x 24.1cm (9 1/2 in) x 12.1cm (4 3/4 in)
<b>Gun size:</b>	25.4cm (10in) x 20.3cm (8in) x 10.1cm (4in)
<b>Total weight:</b>	7.5Kg (16.5 lbs.)

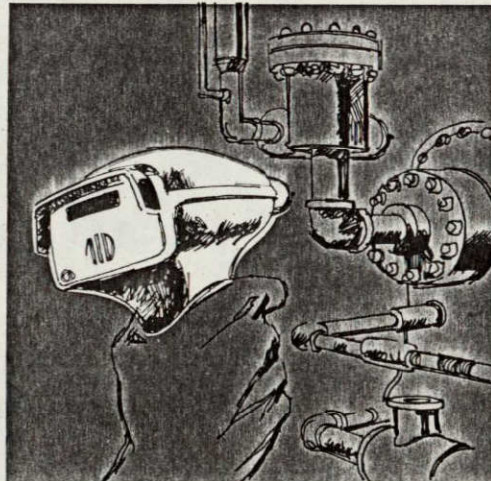
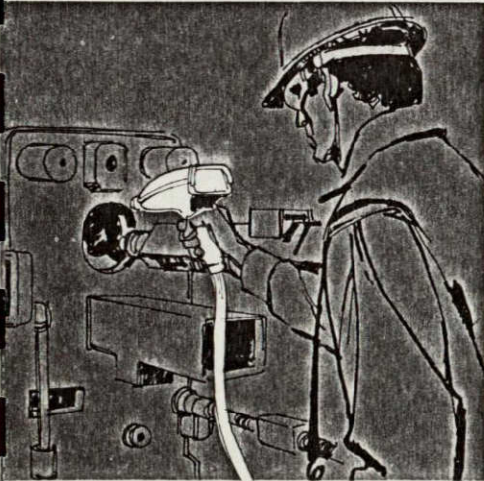
## ADDITIONAL FEATURES

<b>Flame Out Indication:</b>	Visual on Digital Readout plus Audible Alarm.
<b>Concentration Alarm:</b>	Audible Alarm adjustable from 0-1000ppm by direct reading dial.

# APPLICATIONS

The Model 550 Total Hydrocarbon Analyzer is an effective tool for the measurement of organic vapors in both environmental and industrial atmospheres. Several applications are illustrated below.

133 Model 550 Description, Operation and Performance. This Application Note, which is available from AID, describes in detail the operating parameters of the instrument as well as its calibration and use.



**ANALYTICAL INSTRUMENT  
DEVELOPMENT INC.**

ROUTE 41 & NEWARK ROAD  
AVONDALE, PENNSYLVANIA  
TELEPHONE: (215) 268-3181

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APPENDIX II  
CALCULATIONS

## APPENDIX IIa

Assuming a 1ml. sample was analyzed from the 8,000 p.s.i. tank and was found to contain 0.1 ppm. THC as methane.

The compressibility of  $N_2$  at 8,000 p.s.i. is 1.42.

Then

$$0.1 \times 10^{-6} \text{ ml THC/ml sample}$$

Assuming ideality and 1 atm pressure and 300°K

$$N = \frac{PV}{RT} = \frac{1 \text{ atm} \times 1 \times 10^{-6} \text{ l}}{0.082 \frac{\text{l} \cdot \text{atm}}{\text{mole} \cdot \text{K}} \times 300}$$

$$N = 4.1 \times 10^{-12} \text{ moles THC}$$

This  $4.1 \times 10^{-12}$  moles was in 1ml volume and

$\therefore$  the concentration was  $4.1 \times 10^{-9}$  moles/liter (container)

But the  $4.1 \times 10^{-12}$  moles came from the 8K tank where the

$N_2$  was compressed

$$P_1 V_1 = P_2 V_2 Z \quad \text{where } Z = \text{compressibility}$$

$$V_2 = \frac{1 \times 10^{-3} \text{ l}}{1.42 \times \frac{8000}{14.7}} = 1.3 \times 10^{-6} \text{ l}$$

Therefore the concentration of THC in the tank w.r.t. fixed volume is

$$\frac{4.1 \times 10^{-12}}{1.3 \times 10^{-6}} = 3.2 \times 10^{-6} \text{ moles/liter}$$

Appendix IIb Volume of  $\text{GN}_2$  at 8000 psi Required  
Gas Analysis

Assume the initial concentration of THC in the  $\text{LN}_2$  is 1 ppm, the hydrocarbon density is 0.62 and the vapor molecular weight is 26.

Then

$1 \times 10^{-6}$  l of THC in 1 l  $\text{LN}_2$

or

$$1 \times 10^{-6} \text{ l} \times \frac{620 \text{ g/l}}{26 \text{ g/mole}} = 2.4 \times 10^{-5} \text{ moles/l LN}_2$$

1 l of  $\text{LN}_2$  is isothermally expanded to 1.89 l at 8000 psi and 25°C

Then the molar concentration of the THC in the  $\text{GN}_2$  is  $\frac{2.4 \times 10^{-5}}{1.89} = 1.3 \times 10^{-5}$  moles/l at 8000 psi

For analysis, assuming that  $1 \times 10^{-9}$  moles THC is required

$$\frac{1 \times 10^{-9}}{1.3 \times 10^{-5}} = 8 \times 10^{-5} \text{ l of GN}_2 @ 8000 \text{ psi}$$

Expanding to FTP by

$$Z_1 P_1 V_1 = Z_2 P_2 V_2$$

$$V_2 = \frac{8 \times 10^{-5} \text{ l} \times \frac{8000}{14.7} \text{ atm} \times 1.42}{1.0 \times 1 \text{ atm}} = 6 \times 10^{-2} \text{ l} = 60 \text{ ml}$$