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Analysis of C2 and C3 hydrocarbons in ambient air. Section I ; Identification and quantification of volatile organics emitted from a landfill. Section II

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ABSTRACT

Title of Thesis:

SECTION I: ANALYSIS OF C_2 AND C_3 HYDROCARBONS IN AMBIENT AIR

SECTION II: IDENTIFICATION AND QUANTIFICATION OF VOLATILE ORGANICS EMITTED FROM A LANDFILL

Tsong-Sheng Chang, Master of Science, 1988

Thesis directed by: Prof. Joseph W. Bozzelli

SECTION I

A method was developed to analyze Acetylene, Ethylene, Ethane, Propylene and Propane levels in the ambient air. Chlorinated compounds within the operation retention time, Methyl chloride, Methylene chloride and Vinyl chloride, were monitored also.

Four sampling sites are located at Carteret, Elizabeth, Newark and Montville in New Jersey. Samples were taken during the summer of 1988. Two sample duration periods utilizing 12 and 6 liter stainless steel canisters were set up to take 24 hour air samples and instantaneous air samples (5 minutes collection period).

The average levels of Acetylene, Ethylene, Ethane, Propylene and Propane at the four sampling sites in North East New Jersey are 7.1, 7.0, 9.1, 4.9 and 6.3 ppb. The Newark sampling site has lowest C_2 C_3 levels with averages for the above compounds observed as 6.4, 2.8, 4.9, 1.6 and 2.9 respectively.

Water and some other interference problems in the analytical scheme are described, with some modification is also suggested.

SECTION II

A sampling method is designed, constructed and tested to collect samples of volatile organic compounds (VOC's) effluent from ground sites for further analysis and quantitation. It is composed of a sample collection system (closed loop flow), a hemispherical container covering 850 cm^2 area over a ground site and a Tenax packed adsorbent cartridge. GC/MS and capillary column GC are utilized to quantitate and identify the specific VOC's in these samples. The results show that samples collected by this method have varied characteristics with respect to ambient air samples and have very strong location dependency. Some improvements maybe still needed to get more representative data. For example, the air retained in the container should be swept out before sampling.

Although the sampling system is not yet completely optimized, we demonstrate that the VOC's found in the ambient air above a closed sanitary land fill site, are not unique gases effluent from the ground surface, but are more representative of those from other sources of contamination of the ambient air, such as ambient air, active dump site emissions or vehicular exhausts (NJ Turnpike/Highway 17) . The advantages, disadvantages and some improvements of this sampling method are also discussed.

SECTION I

ANALYSIS OF C_2 AND C_3 HYDROCARBONS IN AMBIENT AIR

SECTION II

IDENTIFICATION AND QUANTIFICATION OF VOLATILE ORGANICS EMITTED FROM A LANDFILL

by

Tsong-Sheng Chang

Thesis submitted to the Faculty of the Graduate School of
the New Jersey Institute of Technology in partial fulfillment of
the requirements for the degree of
Master of Science in Enviromental Science

1988

APPROVAL SHEET

Title of Thesis:

SECTION I:

ANALYSIS OF C_2 AND C_3 HYDROCARBONS IN AMBIENT AIR

SECTION II:

IDENTIFICATION AND QUANTIFICATION OF VOLATILE ORGANICS EMITTED FROM A LANDFILL

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TABLE OF CONTENTS

SECTION I

SECTION II

LIST OF TABLES

LIST OF FIGURES

Figure Page

SECTION I

SECTION II

SECTION I

ANALYSIS OF C_2 AND C_3 HYDROCARBONS IN AMBIENT AIR

CHAPTER I INTRODUCTION

The ambient air analysis for volatile organic compounds has been ongoing in the NJIT Air Pollution Research Lab for more than ten years by Tenax polymer adsorbent collection[1,2,3]. We have recently started to analyze the air samples by a second method, utilizing 6 or 12 liter polished stainless steel canisters.

Tenax is a polymer packing material. It has good trap and release characteristics for volatile organic compounds. But lighter VOC's, like C_2 - C_5 hydrocarbons are not trapped on the Tenax efficiently. So it is not suitable to measure these light hydrocarbon concentrations in the ambient air.

Canister method collects the whole air sample in the canister, including the light hydrocarbons, but it also collects water, CO_2, N_2 and O_2 that Tenax does not. The capillary column usually used to analyze the volatile air sample cannot separate the C_2 - C_5 hydrocarbons well. So the canister collection method with the normal capillary column is not suitable to separate C_2 C_3 and therefore quantitate these compounds.

In order to analyze C_2 C_3, a micro packed Carbosieve G column (1.6 mm OD, 1.0 mm ID, 1 meter length) was used to separate and quantitate C_2 C_3 in this work.

CHAPTER II EXPERIMENT

A. SAMPLE COLLECTION

1. SAMPLING SITES

We took samples from 4 sites labelled on Figure 1.

- Site 1 : On the roof of a police station in a industrial area, Carteret, New Jersey. The site is on the west side of the Arthur Kill River across from Staten Island.
- Site 2 : In the Mattano Park of Elizabeth, New Jersey. The site is half mile west from New Jersey Turnpike and 1 mile north of Turnpike exit toll area #13 .
- Site 3 : On the roof of Faculty Hall at NJIT, Newark. The site is at 161 Warren St., the central ward of Newark 1 mile west of the Newark downtown area.
- Site 4 : In the basement of a house in Montville, NJ. It's a suburban residential area, 3 miles north from Interstate Route 80 and 280. This house uses natural gas as heat supply. We took samples 5 feet away from the natural gas boiler and storage water heater.

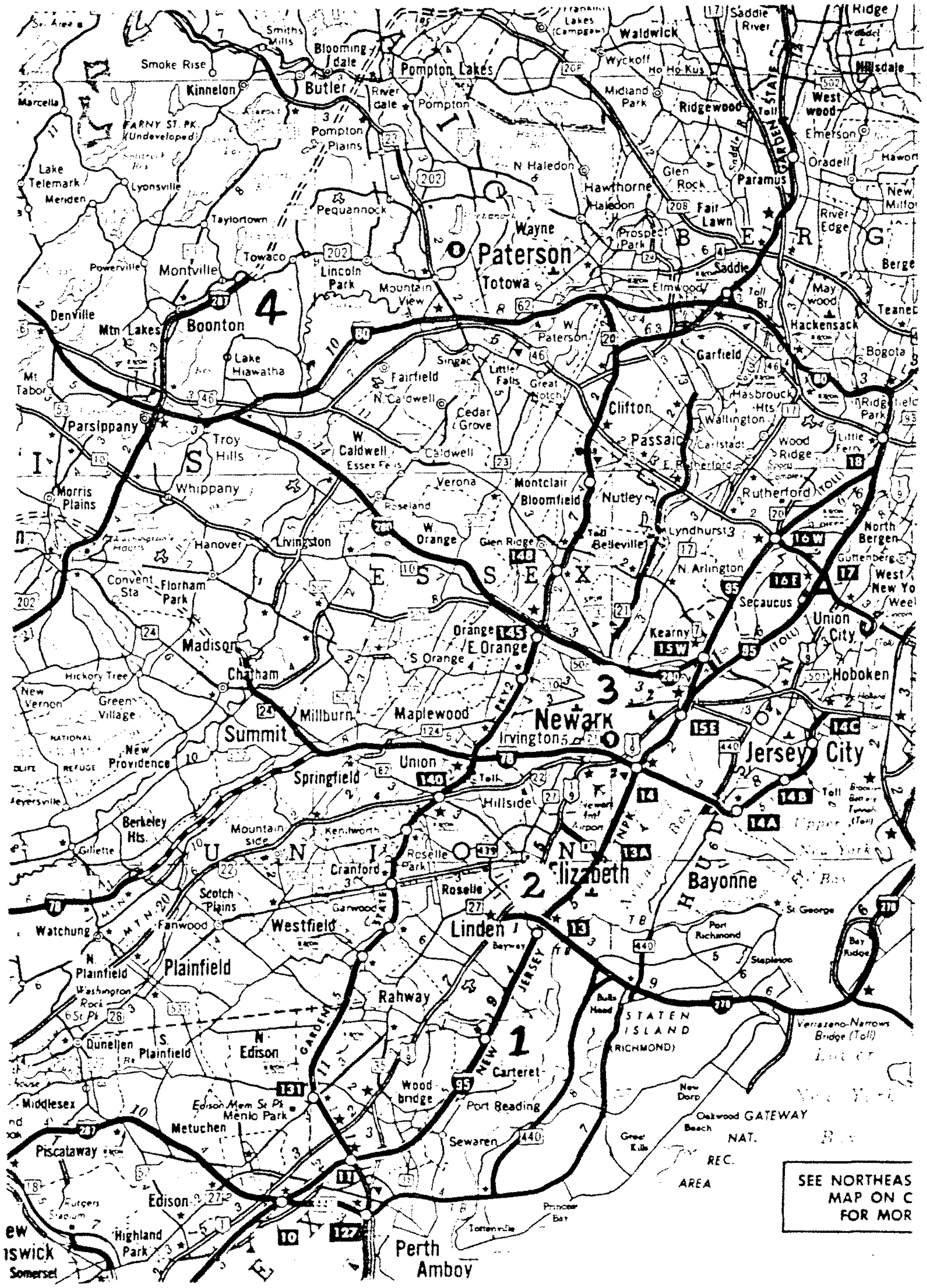


Figure 1. Location of the Sampling Sites

2. 24 HOUR SAMPLER

This method collects samples on an average flow for a 24 hour time period to get a measurement of VOC's for 24 hour average exposure.

The sample collectors used in site 1 and 2 were constructed by Y. J. Shen (M.S. thesis 1988) [4] for the Staten Island / New Jersey project of the Air Pollution Research Laboratory in New Jersey Institute of Technology. [5] This method was developed by the Environmental Monitoring System Laboratory (EMSL) of US EPA [6] as a possible alternative to collection of air samples on solid sorbents.

The sampler is shown in Figure 2. A glass fiber filter is put on the inlet of the air sampler. A stainless steel, metal Bellows pump, from Metal Bellows Company, Sharon, MA, Model no. MB-151, pumps air into a 6-liter canister. The canisters, internally polished stainless steel canister, were manufactured by Demaray Scientific Instruments Ltd. Pullman, WA. A pressure gauge installed between canister and pump allows reading of the pressure in the canister.

A critical orifice is installed between pump and the inlet filter opening to control the flowrate at about 500 ml/min over the 24 hour period. When absolute pressure difference of the downstream and upstream sides of the orifice is greater than a certain value, critical pressure, the mass flow rate through the orifice depends on only pressure, temperature and density of upstream side. [7] After starting the pump, downstream side of the orifice (inlet side of the pump)

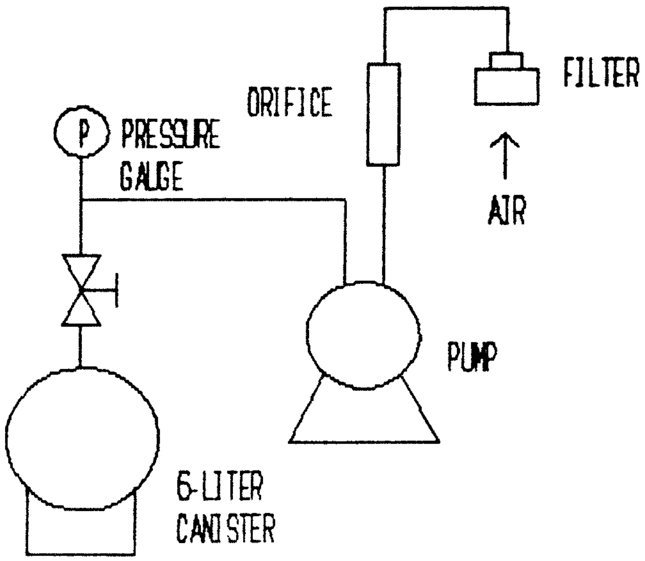


Figure 2. 24 Hour Air Sampler

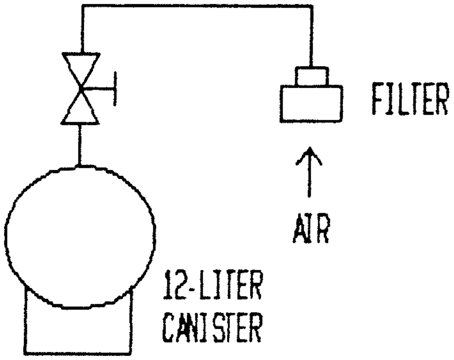


Figure 3. Air Sampler for Instantaneous Sample

is evacuated, pressure is kept low (vacuum, about 20 Torr) here. The upstream pressure is 1.0 Atmosphere and remains constant. (Ambient atmospheric pressure usually varies, by only a few mm of Hg.) This constant pressure across the orifice causes a constant mass flowrate through the orifice. The outlet side of pump is connected to the polished canister. The orifice is a 2.54 cm length of 34 gauge stainless steel hypodermic needle.

3. INSTANTANEOUS SAMPLER

The sample collector used in site 3 and 4 is shown as Figure 3. It is composed of a 12-liter canister with a stainless steel Bellow valve (to limit contamination from valve), necessary compression fittings and a glass fiber inlet filter. The internally polished stainless steel canister was manufactured by Scientific Instrumentation Specialists, P.O. Box 8941, Moscow, Idaho. The filter is installed to prevent particulates from being drawn into the sampling line and canister.

4. PREPARATION OF CANISTERS AND SAMPLING

Before sampling, all the canisters have to be cleaned and evacuated. We evacuate the canisters for about 40-60 minutes (evacuated to 1 mm Hg), filled with zero air (from Spectra Gases, Kearny NJ) to 30 psig, then vented to ambient. We repeat this procedure 5-6 times. And finally, evacuate the canister for sampling use.

To take a 24 hour sample, we turn on the pump and check whether the pressure reading on pressure side of the pump goes up to make sure the connection has no leaks. Then the valve on the canister is opened to let air into the canister. We allow the pump to operate for 24 hours. Next day, the valve is closed, the pump is turned off and the canister is returned to the lab for analysis.

To take an instantaneous sample, we just open the valve on the canister to let air into the canister till it is filled up. It takes about 5 minutes. The final pressure in the canister after sampling is then 1 atmosphere.

B. EQUIPMENT AND ANALYSIS

1. THE GAS CHROMATOGRAPH SET UP

An analysis system was set up as shown in Figure 4. A Tracor 550 gas chromatograph with flame ionization and electron capture detectors was utilized. Column was made of a 1.6 mm OD, 1.0 mm ID and 1 meter length Nickel tube and packed with Supelco Carbosieve G, 60-80 mesh. A make up gas, N_2 (50 ml/min), was introduced after the column. Then the eluent was split to a FID and an ECD. Before the ECD, we used a second Nitrogen gas make up to boost ECD flow (total 48.8 ml including make up and purge).

A tubing tee with a concentric inlet line from the GC column

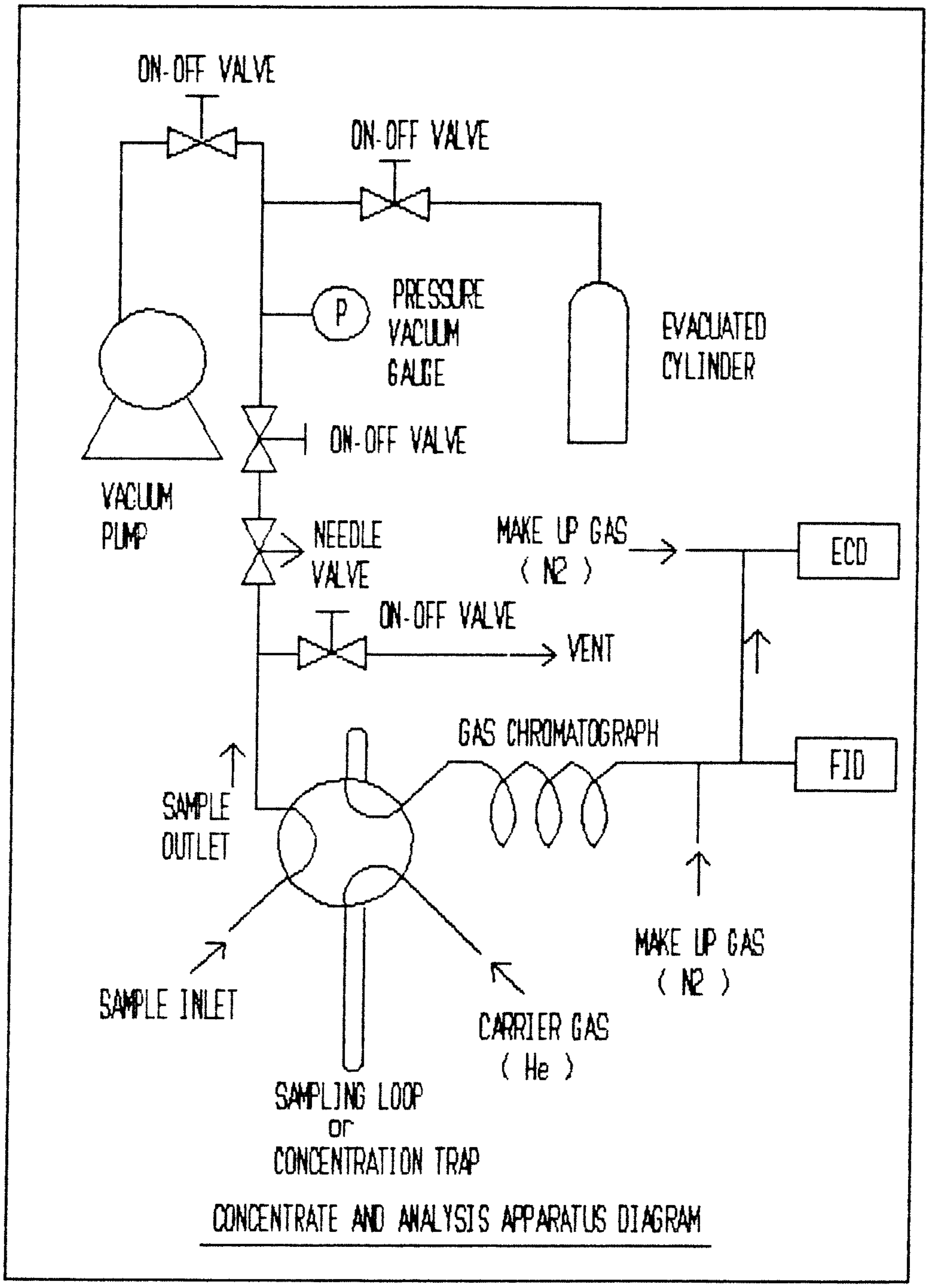


Figure 4. Schematic Diagram of Trap/Analysis System

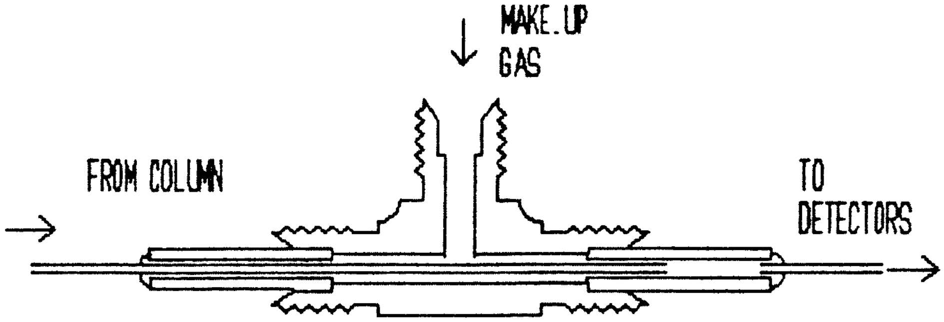


Figure 5. A Fitting Configuration to Eliminate Dead Volumn

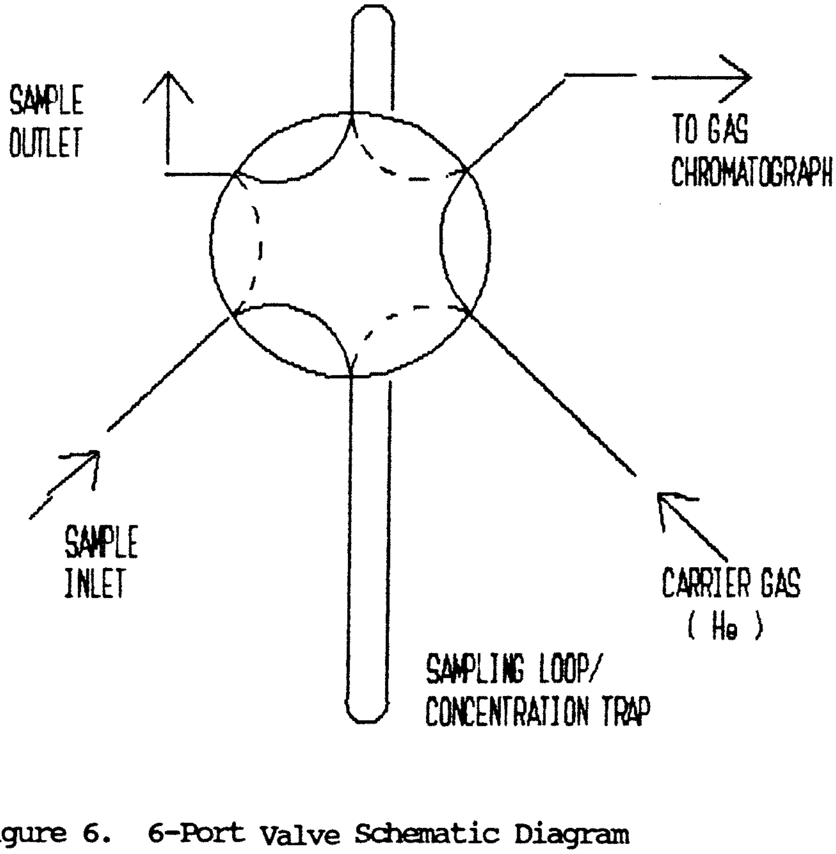


Figure 6. 6-Port Valve Schematic Diagram

which passed beyond the inlet of make up gas shown in Figure 5, eliminated eddy current and dead volume in the elution stream to the detector. The end of GC column is inserted through a short (2 cm length) piece of 1/8" stainless tube and welded in order to connect this column end to the inlet of an 1/8" tee. The outlet end of the tee was also connected to a piece of 1/8" stainless tube welded over 1/16" stainless tube. The end of GC column is inserted through the tee into the 1/8" tube on the opposite end. Make-up gas is introduced on the side end of tee with 1/8" tube.

Followings are a list of control parameters of the GC :

— Carrier gas : 14.4 ml He, 12.6 ml to the FID and 1.8 ml to the ECD. Split ratio is 1.8/12.6 = 0.14.
— Column temperature : stays at 135 °C for 2 min and raises at a rate of 10 °C/min to final temperature 195 °C
— Make up gas : 50 ml/min N_2 before the splitter; and 47 ml N_2 before the ECD for both make up and purge
— FID gas : 40 ml/min H_2 and 400 ml/min air
— FID temperature : 250 °C
— Elcetrometer : input range 10, attenuation 2 and attenuation 16 on integrator
— ECD saturation current: 6 nano Amp
— ECD temperature : 350 °C

2. LOADING AND INJECTION APPARATUS

A six port valve, Model No. 5618 from Carle, Anaheim, CA , with a sampling loop was used to concentrate and inject sample. It is shown in Figure 4 and a more detailed diagram is shown in Figure 6.

Sampling loop (cryo trap) is made of a piece of Nickel tube, 1.6 mm OD, 1.0 mm ID and 32 cm length, representing a volume of 0.26 ml. It is connected to two ports of the 6-port valve. Carrier gas of the GC is connected to the 6-port before entering the GC to carry the sample into the column when injection.

The sample inlet port of the valve is connected to sampling canister to load air sample. The other port is connected to an evacuated cylinder (a 2 liter known volume former standard gas cylinder from Scott Specialty Gases). The 2 liter known volume cylinder connecting lines can be opened to a vacuum pump, to evacuate the known volume cylinder to 1 torr pressure. The evacuated known volume cylinder is used to draw air through the cryo trap and measure the volume of air drawn through the loop by monitoring the increase in pressure.

The 6-port valve is wrapped with heating tape as well as heat insulation material and kept at 110 ^{o}C. All the transfer lines, the line from sampling canister to cryo trap and the line from cryo trap to GC, are also wrapped with heating tape and kept at about 105 ^{o}C to eliminate VOC's from condensing in the tube and valve and to keep the valve and transfer lines clean.

3. LOADING AND ANALYSIS OF SAMPLE

Before loading air sample, the 2 liter cylinder is evacuated to 29 inch Hg or higher vacuum. When the 6-port valve is on load position (counter clock wise, solid line), shown in Figure 6. The sampling loop/cryo trap is immersed in liquid Nitrogen. The valve of the sampling canister is then opened. Air sample is drawn by the vacuum in the 2 liter cylinder, going through the cryogenic trap. Volatile organic cmopounds in the air sample are trapped cryogenically in the trap. The amount of the air sample (volume, ml) going through the trap is determined from the pressure increase of the known volume cylinder. One inch Hg pressure is equlvalent to 73 ml. The 6-port valve is then turned clock wise to the inject position (dash line) and liquid Nitrogen replaced with 90 ^{o}C hot water. VOC's trapped in the loop vaporize and flow into the GC column with carrier gas.

4. LOADING AND ANALYSIS OF STANDARD GAS

Inorder to analyze standard gas, the standard gas cylinder is connected to the port of sample inlet on 6-port valve instead of the sampling canister. Standard gas is purged through the sample loop, which is immersed in a hot water bath about 90 ^{o}C, to keep the loop at constant temperature, and then vented to atmosphere from the valve between the 2 liter cylinder and the sample outlet port of 6-port valve (shown in Figure 4). When the 6-port valve is switched from load to injection positon, a known volume (volume of cryo loop at 90 ^{o}C) certain amount of standard gas is injected into the column.

C. SPIKE TEST

Comparison of retention time on standard and sample chromatograms can help in verifying the peak identities on the chromatograms. Some interferences in the sample, however, cause the retention times to shift from those in the standard. A certain amount of standard gas spiked into the air sample allows us to verify peak identities in the chromatograms.

A tee with septum on the side port is installed on the sample inlet of 6-port valve. When starting to load an air sample, a certain amount of standard gas was injected into the tee. The standard gas is carried with the air sample to the trap and cyrogenically trapped. All other procedures are identical to the sample analysis. Figure 7 & 8 show two GC chromatograms. One is sample chromatogram and the other one is spiked chromatogram. Peaks of sample and standard gas have identical retention time, verifying the peak identities.

D. IDENTIFY CHROMATOGRAM INTERFERENCES

Several peaks eluting between the C_2 and the C_3 known hydrocarbon groupings were observed in both FID and ECD. These were initially unidentified peaks. They displayed poor chromatographic peak shapes and eluted at slightly varying retention times. We thought they might

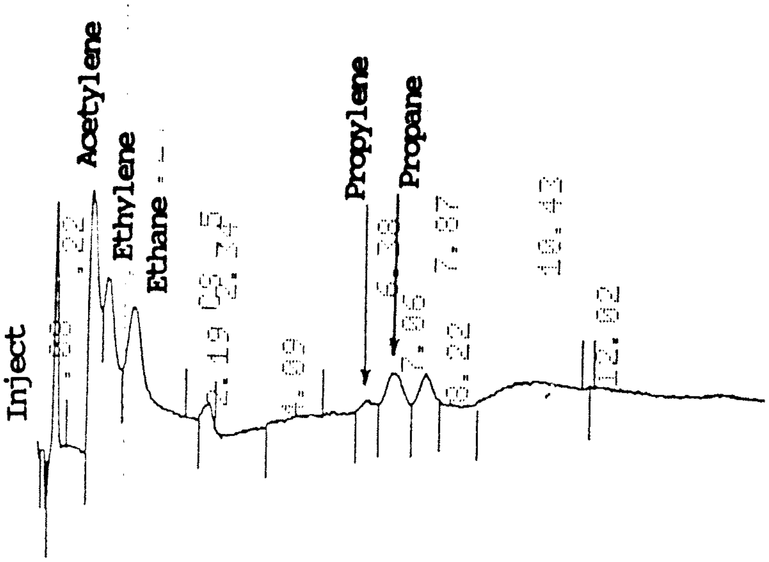


Figure 7. Air Sample Chromatogram

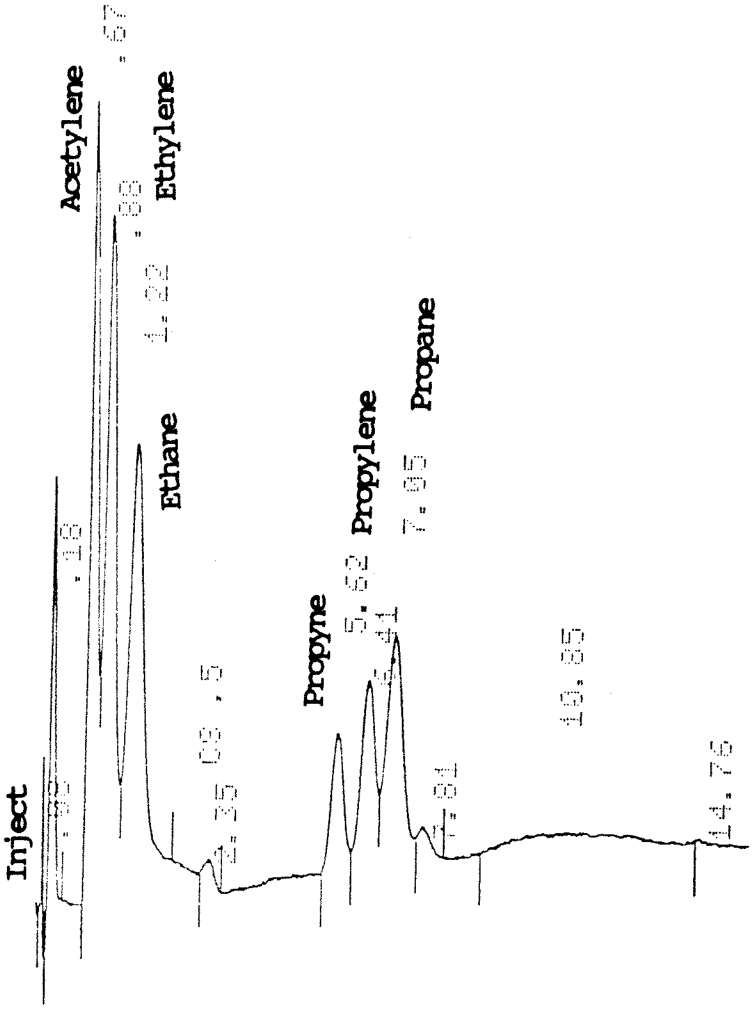


Figure 8. Chromatogram of Sample Spiked with Standard

be some contamination in the column, so we injected about 0.25 ml Acetone liquid, to try and eliminate the contaminants. A large amount solvent flushed through a column may remove contaminations in the column but it may also change the surface characteristics of the packing material or coat a thin layer of stationary phase on the packing material.

After a flush of Acetone, the unidentified peaks disappeared; but the C_2 peak shape changed. The C_2 peaks looked like shoulders on other peaks, shown in Figure 7. Same plateau shape peak was also observed in ECD chromatogram.

We obtained identical chromatograms from many samples and the plateau peak did not show up in the temperature program blank test. This means that the interference is not in the column but in the air sample we inject.

In order to discover what was causing the interference, a 1/16" tee was installed between the 6-port valve and the column. A septum was put on the side port of the tee to allow direct injection into column. We injected 1 ml and 2 ml of laboratory air, air over a water surface at room temperature, carbon dioxide, Oxygen, Nitrogen and 0.5 ul of water respectively.

The chromatograms obtained when injecting CO_2, O_2, N_2, air and water are shown in Figure 9. N_2 does not cause any peak on the chromatogram. Injecting CO_2, showed a small base line shift on ECD,

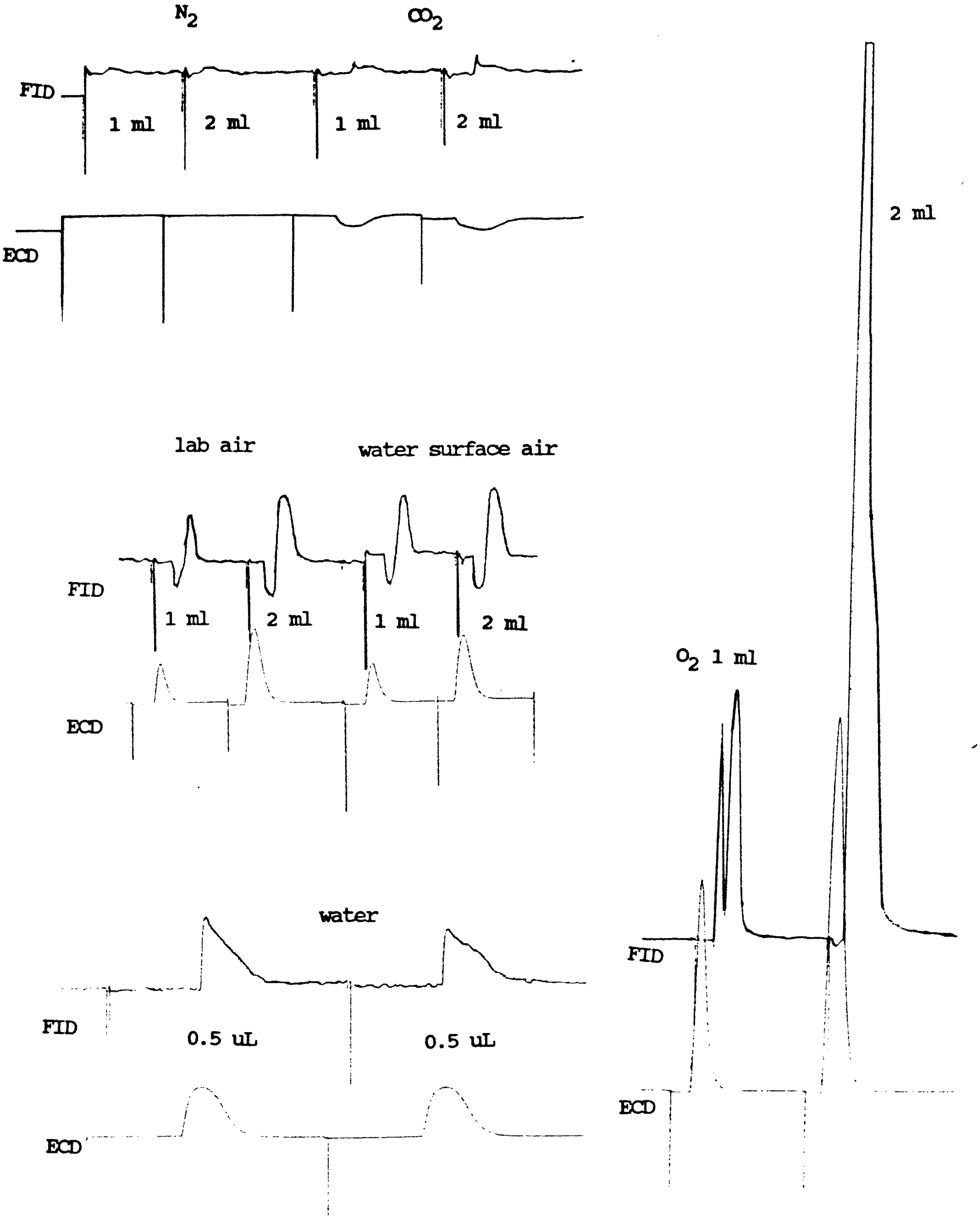


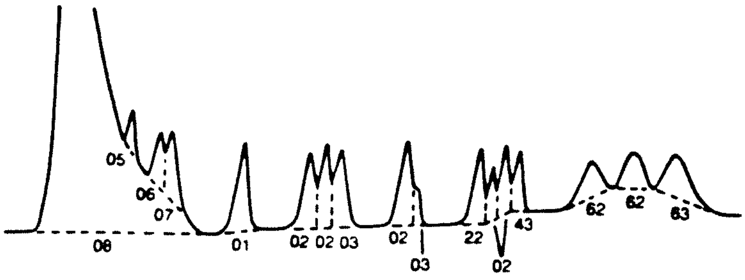
Figure 9. Chromatogram of Some Species to Look for Interference

but no noticable interference on FID. When we injected O_2, we observed peak at about 0.2 min. Injecting both lab air and air on water surface (1 ml and 2 ml) gave peaks at 0.2 min also and the peak size about 1/5 of that of O_2 peak, further verifying that O_2 causes the peak at 0.2 min.

When we injected 0.5 uL water, we found water caused a large peak at about 0.7 min. Its shape looks like a "saturate peak", going up quickly and coming down slowly. Comparison to the sample chromatograms, demonstrated that water caused the poor C_2 peaks.

Because of the water interference on C_2 peaks, the integration peak area does not represent the actual peak area of each C_2 peak. The principle of integration in the Varian 4270 integrator, is that it draws the baseline from the beginning of the first peak (of the fused peaks) to the end of the last peak, as shown in Figure 10, the integrator then defines the individual peak areas at the peak valleys. This yields higher concentrations of C_2 is because it includes a broad H_2O peak. The peak area contributed by water needs to be subtracted from the peak area got from integrator.

In actual calculation, it's difficult to get the exact peak area contributed by the water from the integrator, which can be subtracted for each peak, so we used a corrected peak height to do the calculation for C_2 peaks. We simulate the water peak and treated it as the baseline of C_2 peaks. We then measure the C_2 peak heights.



01	BASELINE RESOLVED
02	FUSED
03	LAST OF FUSED GROUP
05	RESOLVED RIDER PEAK
06	FUSED RIDER
07	LAST OF FUSED RIDER
08	TAILING (SKEWED) PEAK
20	FORWARD HORIZONTAL (FH)
40	BACKWARD HORIZONTAL (BH)
60	BASELINE FORCED AT VALLEY POINT (BL)

Figure 10. Integration principle of Integrator

CHAPTER III RESULT AND DISCUSSION

A. SAMPLING VALVE AND LOOP DEAD VOLUME ESTIMATION

We initially used a 1.0 ml sample loop, which came with the 6-port valve from Carle, to inject standard gas and a 1/16" loop to load and inject air sample respectively. We had to change the loop every time we changed analysis. This was inconvenient and hard on the fittings. So determined the volume of the 1/16" sample loop. If we know its volume then we can inject standard gas by using this loop and don't need to change loop, i.e. use only one loop for both sample and standard.

We compare peak areas of standard gas by using each loop. Table 1 is the results of injections of standard gas for each loop. Figure 11 displays the results as line chart. The average peak area ratio is 0.297.

By calculation, the 1/16" loop is 0.26 ml (32 cm, 0.04" ID). Assume the dead volume of the valve and fittings is X. We can resolve the X by

$$\frac{0.26 + X}{1.0 + X} = \frac{0.297}{1}$$

$$X = 0.05 \text{ ml}$$

A comparison of peak areas for two sampling loop to get vol of the unknown vol loop
inject standard gas of C1 to C4
the first sampling loop : 1 ml , 1/8 " Sainless steel
the second sampling loop : ? ml , 1/16 " Nickel

Loop 1 (1 ml)

	run 1		run 2		run 3		average
	P A	deviation	P A	deviation	P A	deviation	
Methane	6676	1.59	6515	-0.86	6523	-0.74	6571
Acetylene	10133	-2.72	10406	-0.10	10710	2.82	10416
Ethylene	13180	0.51	13127	0.11	13031	-0.62	13113
Ethane	13339	-0.08	13386	0.27	13324	-0.19	13350
Propyne	16573	0.96	16085	-2.02	16590	1.06	16416
Propylene	17829	0.75	17443	-1.44	17819	0.69	17697
Propane	20994	0.59	20545	-1.57	21076	0.98	20872

Loop 2 (unknown volume)

	run 1		run 2		run 3		average	ratio of
	P A	deviation	P A	deviation	P A	deviation	P A	2 loops
Methane	1910	-1.51	1950	0.55	1958	0.96	1939	0.295
Acetylene	3099	-1.62	3173	0.73	3178	0.89	3150	0.302
Ethylene	3908	-0.51	3965	0.94	3911	-0.43	3928	0.300
Ethane	3947	-2.39	4081	0.92	4103	1.47	4044	0.303
Propyne	4684	-2.91	4830	0.12	4959	2.79	4824	0.294
Propylene	5038	-0.68	4856	-4.27	5324	4.95	5073	0.287
Propane	5962	-5.21	6160	-2.06	6747	7.27	6290	0.301
					average ratio			0.297

Table 1. Results of Injecting Standard Gas with Different Sampling Loops

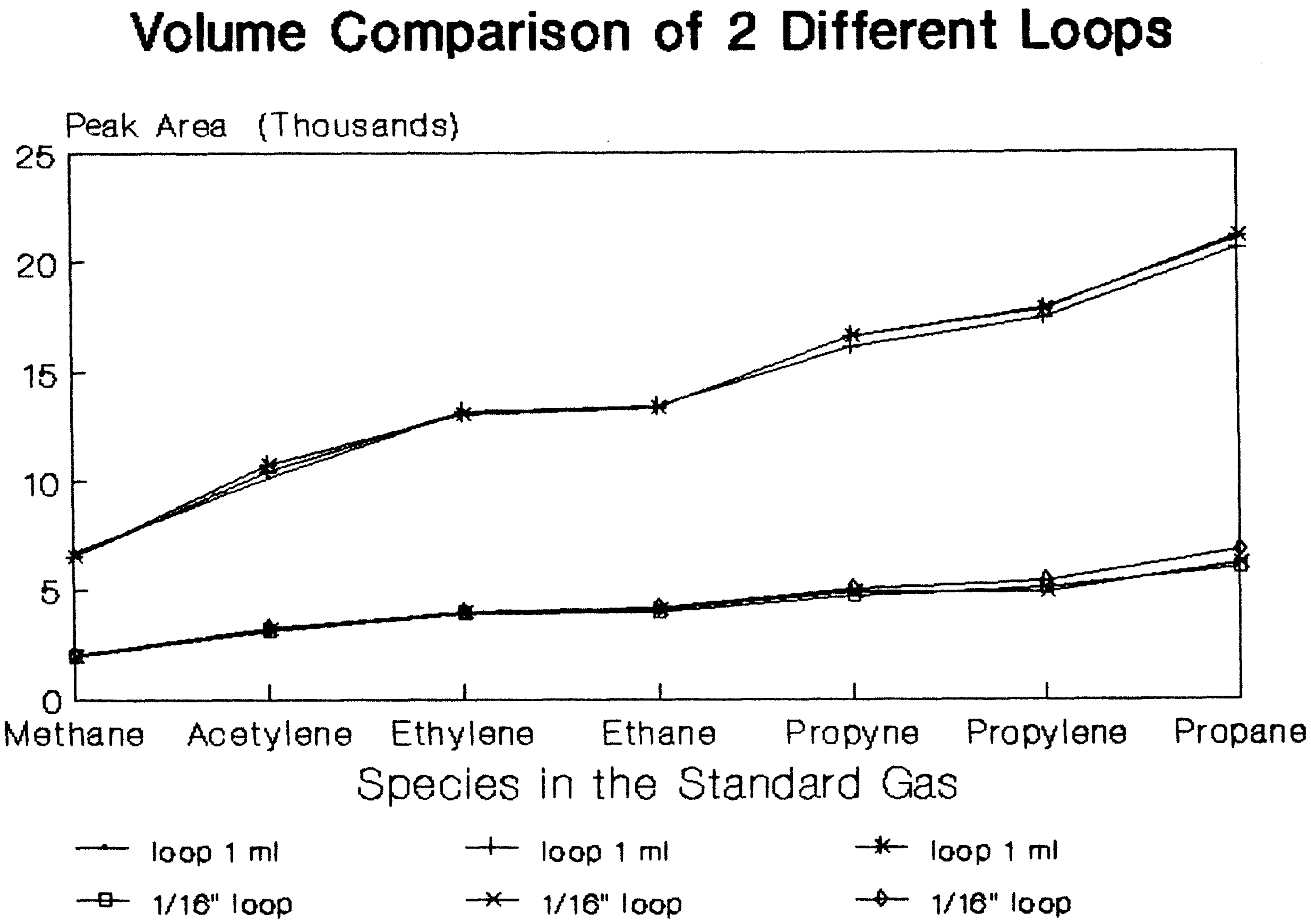


Figure 11. Comparison of Peak Areras of Standard Gas Injected with Two Different Sampling Loop

So, we use 0.31 ml (0.26 + 0.05) as the volume of the 1/16" loop in our calculation for standard gas.

B. SPIKE TEST

Figure 7 and 8 show a sample chromatogram and a chromatogram of sample spiked with standard gas. Acetylene, Ethylene and Ethane come out earlier in the spike test than they do in the standard gas analysis. Propyne, Propylene and Propane have similar retentention times in both sample and standard gas analysis. Because methane can not be trapped with liquid nitrogen, we did not obtain an increased peak area for Methane in the spike test. We do not quantitate Methane.

C. PLUGGING IN THE CRYO TRAP AND SAMPLE VOLUME LIMITATION

The cryo trap usually becomes blocked when we load air sample through the trap. This limits our loading volume and decreases the detection sensitivity.

The pressure in the trap is between the pressure of the evacuated cylinder and the pressure in the sampling canister. Because we use a needle valve to control the flow rate, most of the pressure resistance is across the needle valve before the trap becomes blocked. The pressure in the trap is therefore closer to the pressure of the sampling canister. But when the trap is blocked, flow stops completely and the pressure drop is across this blockage point.

Substances in the air sample obviously condense or become solid in the trap at liquid nitrogen temperature and vaporize to the gas phase when we immerse the trap in hot water. The quantity of these solid becomes very important in the concentration mechanism, so the trap is not plugged.

At certain pressure and temperature, when the vapor pressure of a substance is higher than its saturate pressure, it condenses or becomes solid if the temperature is lower than its melting point at that pressure. Figure 12 shows the relationship between temperature and saturate vapor pressure of Acetylene, Ethylene, Ethane, Propylene, Propane, CO_2, O_2 and N_2.[8]

Nitrogen, Oxygen, Argon, Carbon dioxide and water are the main components in the air.[8] Figure 13 is their temperature vs. vapor pressure diagram.

Nitrogen would not trapped in the liquid Nitrogen bath. Because the pressure in the trap is lower than 1 atmosphere, it requires a lower temperature to condense than it would at 1 atmosphere. So Nitrogen would not block the trap.

Oxygen would also not block the trap. In our interference experiment discussed in section B, 1 ml or 2 ml of Oxygen caused a peak on the chromatogram. Oxygen composition in the ambient air is 20%. If

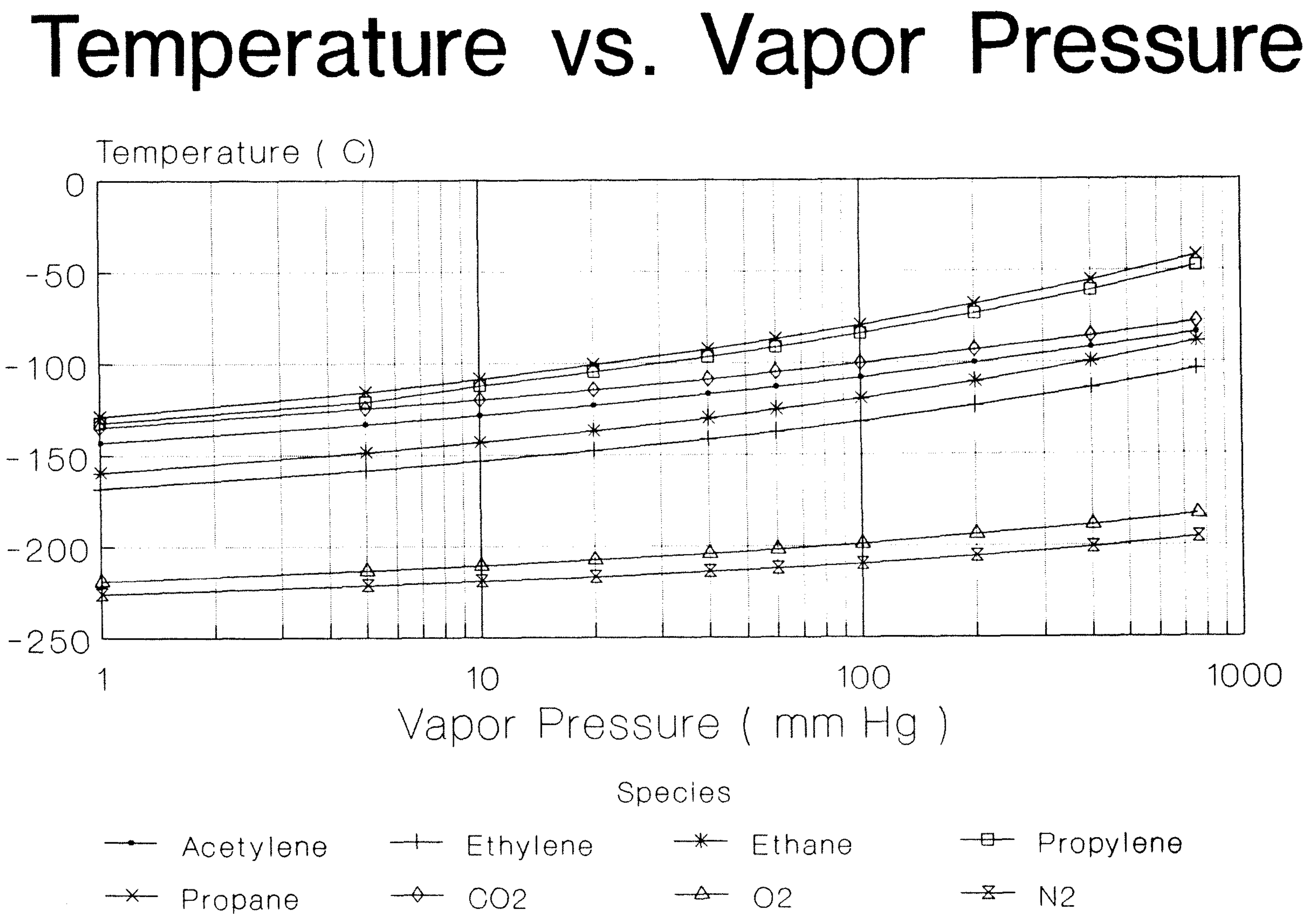


Figure 12. Temperature vs. Vapor Pressure of C_2 C_3

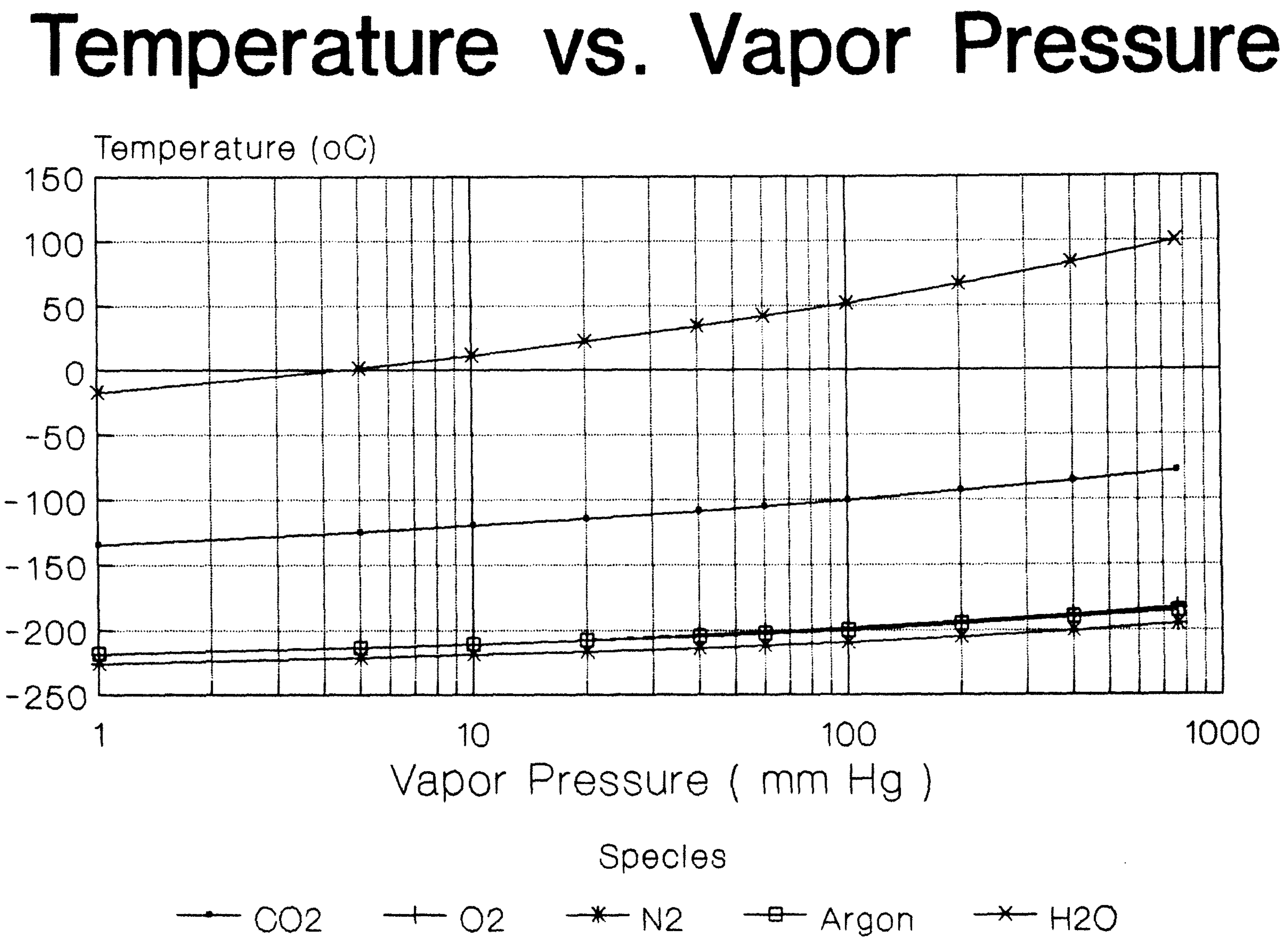


Figure 13. Temperature vs. Vapor Pressure of Major Components of Air

Oxygen is trapped in the liquid nitrogen bath, we would have 76 ml of Oxygen in 380 ml sample. It would cause a huge peak, but in our sample analysis the Oxygen peak is samll. Oxygen is not trapped and does not cause this problem. The melting point of Oxygen is -218.4 ^{o}C lower than -195.8 ^{o}C (boiling point of N_2) and it still has a significant vapor pressure at liquid Nitrogen temperature, so it is not trapped.

H_2O has highest boiling point in the major components of air. The temperature of liquid Nitrogen is -195.8 ^{o}C (boiling point at 1 atm). No doubt, at that temperature H_2O becomes solid.

Assume an air sample at 25 ^{o}C and 60% humidity. Saturate vapor pressure at 25 ^{o}C is 23.756 mm Hg. [Chemical Engineers' Handbook, page 3-45] So, the vapor pressure of water is 23.756 x 0.60 = 14.254 mm Hg at 60% humidity. Assume we load 380 ml of air sample through cryo trap. The volume of H_2O is 14.254 / 760 x 380 = 7.13 ml in gas phase. Molar volume is 24.5 liter at 25 ^{o}C. It becomes 7.13 / 24500 x 18 = 5.24 x 10^{-3} cm^3 = 5.24 ul in liquid phase (density 1.0) and 5.82 ul in solid phase (assume density 0.9). The ID of cryo trap is 0.04", so its cross sectional area is $(0.04 \times 2.54)^2 / 4 = 0.0081$ cm^2. If this amount of H_2O becomes solid in the trap, it will occupy a length of 0.00524 cm^3 / 0.0081 cm^2 = 0.719 cm. From the above calculation, H_2O could easily cause the trap blockage.

We perform the same calculation for CO_2 and Argon and compare them with H_2O.

Species	composition in air* (fraction)	gas phase volume loaded (cm^3)	liquid phase volume** (10^{-3} cm^3)	solid phase volume# (10^{-3} cm^3)	occupied length in trap (cm)
CO_2	0.000314	0.12	0.20	0.14	0.017(s)
Argon	0.00934	3.55	4.13	—	0.51 (l)
H_2O	—	7.13	5.24	5.82	0.72 (s)

* Air composition is adopted from Himmelblau; "Basic Principles and Calculations in Chemical Engineering"; 3rd ed.; Prentice-Hall Inc., New Jersey ; 1974.

** From Chemical Engineers' Handbook, page 3-8 and 3-11.

liquid CO_2 density : 1.101 at -37 °C

liquid Argon density : 1.402 at -185.7 °C

Same source as **.

solid CO_2 density : 1.56 at -79 °C

From the above calculation, Argon could also causes the trap blockage. Melting point of Argon is -189.2 °C and boiling point is -185.7 °C. They are very close. Argon has a higher melting point than Oxygen's (-218.4°C) although they have similar boiling point (boiling point of Oxygen is -183°C). So Argon is trapped easier at liquid nitrogen temperature than Oxygen.

CO_2 would be trapped in the liquid Nitrogen and cause the trap blockage also, but the amount of CO_2 in the air is low relative to H_2O and Argon. The trap blockage could also be a combination effect of 2 or all 3 species.

D. CAUSE OF C_2 PEAK SHIFT TO EARLIER TIME IN AIR SAMPLES

The air samples showed C_2 peaks which eluted earlier than in the standard. It could be H_2O, Argon or CO_2, which can be trapped in the liquid nitrogen. When we replace liquid Nitrogen with hot water, these species evaporate to gas phase. They expand quickly and essentially increase (temporarily) the volume flow through the column to make the C_2 peaks elute earlier.

The volume of CO_2 in a sample injection is 0.12 cm^3 (according to the calculation in previous section). The flow rate of carrier gas is 14.4 ml and the retention time shift ahead for C_2 peaks is 0.2 to 0.37 min. Comparing the volume of CO_2 to the carrier gas flow rate, it is very small. The retention time variation is not caused only by the CO_2. Water and Argon must, therefore, also contribute to the retention time shift.

These species when released also tend to overload the GC column, occupy some of the active sites, causing the column to retain the analytes less strongly. Because of strong adsorption between water and the packing of our column, it seems that the occupancy of the active sites is also an important cause to the retention shift.

E. CALCULATION OF HYDROCARBON CONCENTRATION IN CANISTER SAMPLE

Assumptions include: A 100% cryo trap and thermal release efficiency as well as that the sample gas obeys the ideal gas law.

For each species, the ratio of the peak area of sample and the peak area of standard gas on the chromatograms equals the ratio of the numbers of moles injected. The number of moles of each species equals to total moles of the injected air or gas times its mole fraction concentration. We can use ppb by volume because moles are directly proportional to volume.

$$\frac{\text{peak area of specific species in air sample}}{\text{peak area of specific species in standard}}$$

$$= \frac{\text{moles of specific species in air sample}}{\text{moles of specific species in standard}}$$

$$= \frac{\text{total moles of air sample} * \text{mole fraction of specific species in air}}{\text{total moles of standard} * \text{mole fraction of specific species in std}}$$

according to ideal gas law,

$$\text{moles} = \frac{\text{Pressure} * \text{volume}}{\text{R} * \text{Temperature}}$$

where, R is ideal gas law constant.

So, for each species, we have

$$\frac{\text{peak area of specific species in air sample}}{\text{peak area of specific species in standard}} = \frac{(P_{air}*V_{air}/(R*T_{air})) * X_{air}}{(P_{std}*V_{std}/(R*T_{std})) * X_{std}} \quad \text{eq<a>}$$

where, P_{air}, V_{air}, T_{air} and X_{air} are pressure, volume, temperature and mole fraction of the air sample analyzed. They are the same for standard gas.

In this analysis, an evacuated cylinder is used to draw air through cryo trap. The pressure in this cylinder rises from P_1 to P_2. The moles of loaded sample gas are equal to the moles of compounds condensed on the trap plus the moles of gas going through the trap into the cylinder.

$$\text{total moles of the loaded gas} = \text{total moles of compounds condense on the trap} + \text{total moles of the gas drawn into the cylinder}$$

Because the concentration levels of the organic compounds in the analyzed air are very low, around several ppb, we can neglect the moles of compounds condense on the trap. So,

$$\text{total moles of the loaded gas} = \text{increase total moles of gas in the cylinder} \qquad \text{eq <b>}$$

Then, according to the ideal gas law again,

$$\text{increase total moles of gas in the cylinder} = \frac{P_2 * V_{cyl}}{R * T_{cyl}} - \frac{P_1 * V_{cyl}}{R * T_{cyl}}$$

$$= (P_2 - P_1) * V_{cyl} \; / \; (R * T_{cyl})$$

where, V_{cyl} and T_{cyl} are volume and temperature of the evacuated cylinder.

Substitute this into equation <a> and <b>, we have

$$\frac{\text{peak area of specific species in sample}}{\text{peak area of specific species in standard}} = \frac{(P_2-P_1)*V_{cyl}/(R*T_{cyl}) * X_{air}}{(P_{std}*V_{std}/(R*T_{std})) * X_{std}}$$

So, the concentration of specific compounds in the air sample, C_{air}, are equal to

$$C_{air} = \frac{PA_{sample}}{PA_{standard}} * \frac{(P_{std}*V_{std}/(R*T_{std})) * C_{std}}{(P_2-P_1)*V_{cyl}/(R*T_{cyl})}$$

Cancelling the ideal gas law constant, R, we get

$$C_{air} = \frac{PA_{sample}}{PA_{standard}} * \frac{(P_{std}*V_{std}/T_{std}) * C_{std}}{(P_2-P_1)*V_{cyl}/T_{cyl}}$$

In this work, we used a standard gas mixture from Scott Specialty Gases, containing C_1 to C_4 with their concentrations all 20 ppm ±2 ppb. Standard gas mixture was purged through a 0.31 ml sampling loop to atmosphere, 14.7 psi. The sampling loop was maintained at 90 °C. A Scotty number IV cylinder was used as the evacuated known volume cylinder. Its volume and dead volume of tubing and fitting is 2200 ml. In actual operation and calculation, units and values of the parameters are

PA : peak area, mv sec, from chromatograms

P_{std} : 14.7 psi, atmosphere pressure

V_{std} : 0.31 ml

T_{std} : 95 ^{o}C, sampling loop is kept in hot water

X_{std} : ppm, from manufcacturor, Scott Specialty Gases

V_{cyl} : 2200ml

T_{cyl} : room temperature, ^{o}C

P_2-P_1 : reading from vacuum gauge, inch Hg

In order to match units, we convert the above equation to

$$C_{air}(ppb) = \frac{PA_{sample}}{PA_{standard}} * \frac{\frac{P_{std}}{14.7*T_{std}} * V_{std} \quad * C_{std}}{\frac{(P_2-P_1)}{29.92*T_{cyl}} * V_{cyl}} * 1000$$

F. ANALYSIS RESULT

1. C_2 C_3 CONCENTRATIONS

Table 2 is an example of the calculation sheet used to calculate the concentrations of each C_2 and C_3. Table 3 lists the analysis results of Acetylene, Ethylene, Ethane, Propylene and Propane for the four sampling sites. Figure 14 is a bar chart of average concentrations for four sampling sites. Propyne was not observed in most of the samples with our detection limit of 0.5 ppb. Therefore, only list data for other five C_2 C_3 hydrocarbons, Acetylene, Ethylene, Ethane, Propylene and Propane.

```
          Calculation sheet of canister air samples
    ========================================================= Standard         GC paramet
          Sample pick up date :          6/26/88           ------------------- ----------
          Site, Canister no.       :     Elizabeth, #E       Std ID   C1-C4     Range 10
          Analysis date  :               7/12/88             vol (ml)      0.31  FID 250 C
          Evacuated chamber vol (ml) :      2200             temp(C)      95.00  ECD 300 C
          Laboratory temperature (C) :        25             P (psia)     14.70  Att 16 -

                                            Run 1              Run 2              Run 3
    LHCE0626.WK1                      ------------------ ------------------ -------------------
    standard : 7/12/88                 /\P(inHg)    3.60  /\P(inHg)    3.30  /\P(inHg)     2.50
 ---------------------------------------------------------------------------------------------
    Compound    Std ppm   PA or PH  PA or PH     ppb   PA or PH     ppb   PA or PH      ppb
 ---------------------------------------------------------------------------------------------
 1. Acetylene     18.55        43       11.0     5.56      11.0     6.06        11     8.00
 2. Ethylene         20      39.3       24.0    14.30      24.0    15.60        17    14.59
 3. Ethane        19.99      28.3       28.0    23.16      28.5    25.72        21    25.02
 4. Propyne       19.99     62029    ND        ND        ND        ND        ND        ND
 5. Propylene     20.07     70184      22354     7.49     19744     7.21     15956     7.69
 6. Propane       19.99     89639      29723     7.76     23227     6.62     17986     6.76
 =============================================================================================


        total run no. :         3
                         relative
              Avg ppb   std dev %
             -------------------          Remark :            Temp prog          Loop
                 6.54     16.11                               --------------     -------
                14.83      3.76                               135(2)-10-195      1/16"
                24.63      4.38           * I error : integration error of integrator
                 --        --             * a huge peak of Methylene chloride was observed
                 7.46      2.64           * ND : not detected
                 7.05      7.22
             ====================
```

Table 2. An Example of Calculation Sheet

Site 1 (Carteret) C2 C3 Concentrations (ppb)

Date	Acetylene	Ethylene	Ethane	Propylene	Propane
6/9/88	2.8	5.1	5.3	3.6	3.9
6/27/88	5.3	12.0	6.3	1.9	4.5
7/3/88	8.1	15.8	23.9	10.9	9.5
7/15/88	9.8	5.1	7.4	3.4	11.5
8/2/88	8.1	4.4	4.4	1.7	3.9
average	6.8	8.5	9.4	4.3	6.7

Site 2 (Elizabeth) C2 C3 Concentrations (ppb)

Date	Acetylene	Ethylene	Ethane	Propylene	Propane
6/21/88	1.9	6.6	13.1	6.6	7.1
6/27/88	6.5	14.8	24.6	7.5	7.1
7/3/88	4.0	3.0	3.0	1.1	1.4
7/9/88	12.2	8.8	5.4	4.5	8.5
7/15/88	8.2	10.7	17.5	43.7	22.4
8/2/88	5.8	4.3	7.4	1.3	2.3
average	6.4	8.0	11.8	10.8	8.1

Site 3 (Newark) C2 C3 Concentrations (ppb)

Date	Acetylene	Ethylene	Ethane	Propylene	Propane
7/25/88	3.4	1.6	2.4	ND *	trace #
7/28/88	8.9	4.6	6.1	1.5	3.1
8/5/88	6.8	2.3	6.1	1.6	2.8
average	6.4	2.8	4.9	1.6	2.9

Site 4 (Basement) C2 C3 Concentrations (ppb)

Date	Acetylene	Ethylene	Ethane	Propylene	Propane
7/8/88	14.4	15.1	14.3	4.7	7.4
7/11/88	3.9	3.8	8.3	0.5	4.5
7/20/88	12.0	14.3	11.7	5.0	12.2
7/25/88	4.8	1.7	6.2	1.5	5.7
average	8.8	8.7	10.1	2.9	7.4

* ND: not detected
\# trace: observed but not integrated

Table 3. Analysis Results of C_2 C_3 for Four Sampling Sties

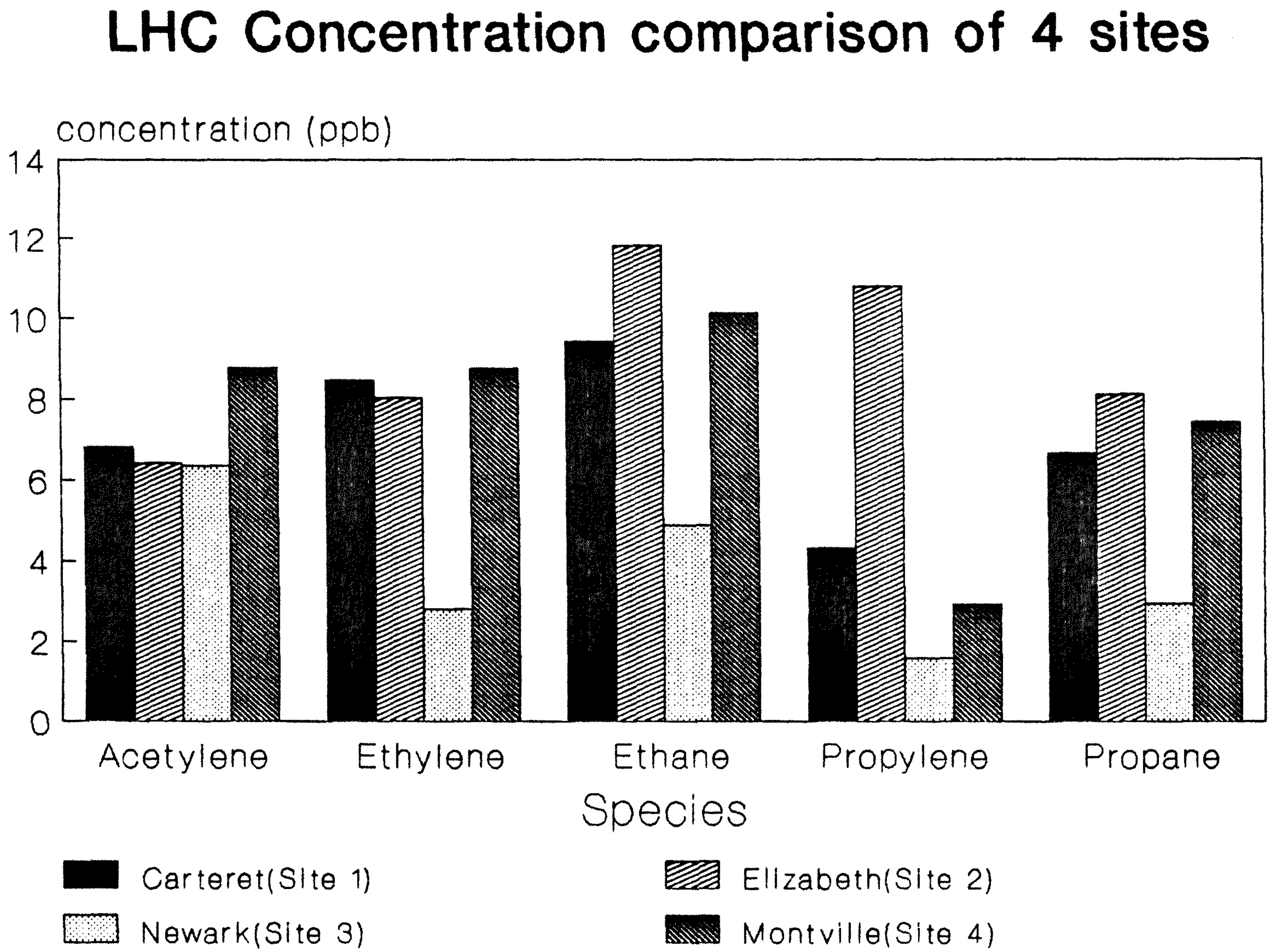


Figure 14. Average C_2 C_3 Concentrations on Four Sampling Sites

The average C_2 C_3 concentrations of Site 1 (Carteret) are 6.8, 8.5, 9.4, 4.3 and 6.7 ppb (Acetylene, Ethylene, Ethane, Porpylene, Propane), shown in Table 3. The concentrations varied with date from 2 ppb to 24 ppb.

The average C_2 C_3 concentrations of Site 2 (Elizabeth) are 6.4, 8.0, 11.8, 10.8 and 8.1 ppb, shown in Table 3. The concentrations also varied with date and didn't show any consistent tends.

The average C_2 C_3 concentrations of Site 3 (Newark) are 6.4, 2.8, 4.9, 1.6 and 2.9 ppb, shown in Table 3. Samples of this site had consistent lower C_2 C_3 levels than other 3 sites, except Acetylene.

The average C_2 C_3 concentrations of Site 4 (Basement) are 8.8, 8.7, 10.1, 2.9 and 7.4 ppb, shown in Table 3. It had higher C_2 C_3 levels than the Newark samples.

Site 1 and 2 are beside the industrial areas. They were expected to have higher C_2 C_3 levels. Some high levels of C_2 C_3 were observed in these two sites. For example, 24 ppb of Ethane on 7/3/88 at Site 1 and 44 ppb of Propylene on 7/15/88 at Site 2. But sometimes low levels were observed.

Site 3 is on the roof of a 4 floor building. Limited industrial area in its residential neighboring area probably cause its consistent lower C_2 C_3 levels. Site 4 had relatively high C_2 C_3 levels due to the use of natural gas and the levels changed as the use condition of the heater and boiler.

2. ANALYSIS ACCURACY

In our calculation sheet, shown in Table 2, relative standard deviation for each sample was calculated also. The relative standard deviations of Acetylene, Ethylene and Ethane are 12.8%, 8.8% and 6.2% respectively. Figure 15 is a distribution of the relative standard deviations for all the samples of these 3 compounds on four sites.

Due to the integration accuracy, the relative standard deviations of Propylene and Propane are higher. It's about 25%.

G. FURTHER MODIFICATION

Water interference is a severe problem. We tried putting a 16 cm, 1/4" OD stainless tube packed with desiccant like Calcium sulfate on the outlet of the sampling canister and before cryo trap and hoped it could absorb moisture of air sample. The result did not display any improvement, instead some extra peaks but not the target hydrocarbons appeared. These peaks were not needed and we discontinued the Calcium sulfate test.

A dual cryogenic trap loading system could be a good method to resolve water problem. Load air sample through two trap in series, the first trap kept at -50 ^{o}C and the second cooled with liquid nitrogen. Because the interested species, C_2 and C_3 compounds, have much higher vapor pressure relative to H_2O, referring Figure 12 & 13, they will not condense in the first trap, but most of H_2O is trapped in the first trap. After loading sample, heat up the second trap and inject into GC. A schematic diagram of dual-trap loading system is shown in Figure 16.

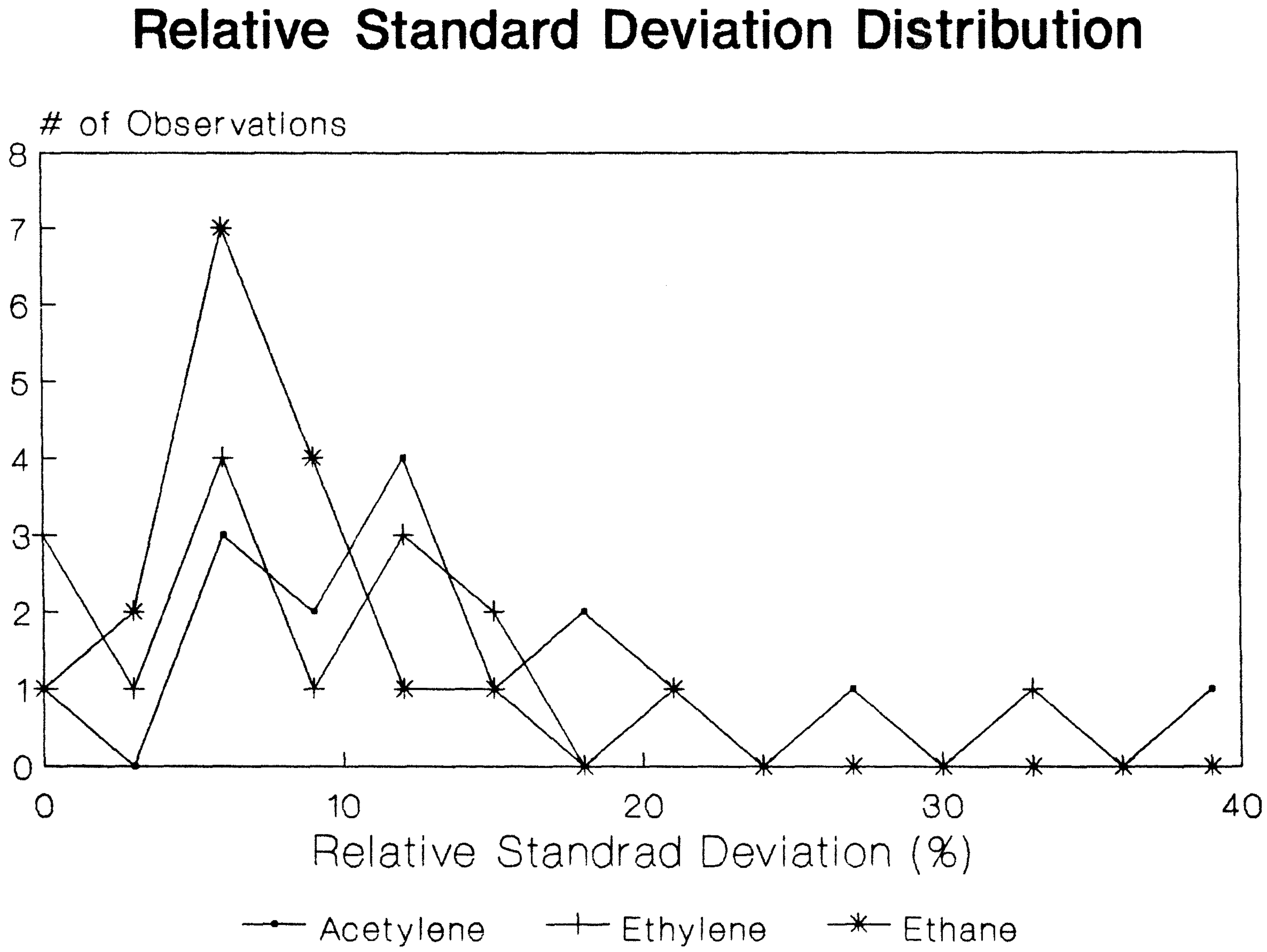


Figure15. Distribution of Relative Standard Deviation for Acetylene, Ethylene and Ethane

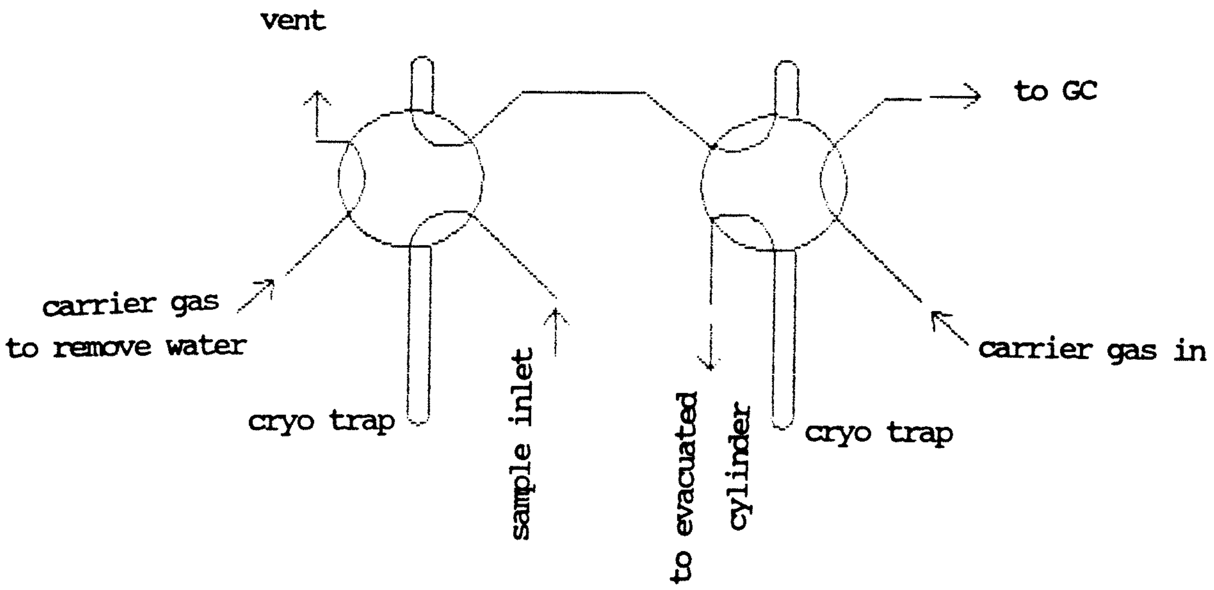


Figure 16. A dual-trap sample loading system

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SECTION II

IDENTIFICATION AND QUANTIFICATION OF VOLATILE ORGANICS EMITTED FROM A LANDFILL

CHAPTER I INTRODUCATION

The air quality in Hackensack Meadowland land fill has been analyzed for a period of time.[9,10] More than ten VOC's were determined to monitor the air quality.

In order to measure the VOC emissions on the ground surface in the land fill, a method was developed to take the air sample near the ground surface containing the VOC's being emitted from the ground surface.

This work describes our initial experimental set up in addition to our initial experimental results on this project.

CHAPTER II EXPERIMENT

A. SAMPLE COLLECTION

In this work, we collected two different kinds of samples, ambient air samples (ambient sample) and samples representing effluent from the soil or ground (ground sample).

1. AMBIENT AIR SAMPLE COLLECTOR

Ambient air samples are collected using the apparatus diagramed in Figure 17. The sampler includes a particulate and ozone filter, a Tenax adsorbant trap, clean Tygon plastic tubing downstream of the trap, a rotameter, needle valve and pump assembly in order of air flow path. Organic volatile compounds (VOC's) in the air are adsorbed on Tenax polymer (60-80 mesh) in the trap. The Tenax trap is mounted in a metal box and a particulate filter is connected to it under the metal cover to protect them from rain. The metal housing is supported on a metal rod. The height of the inlet is 5.5 feet which is about adult breathing level. Rotameters, needle valves and the pump assembly are contained in a wood box which is at the base of the sampler and supports the metal trap housing.

A glass fiber filter is used to prevent particulate matter from being drawn into the trap. It is impregnated with sodium thiosulfate to decrease ozone which is present; thus avoiding the oxidation of the

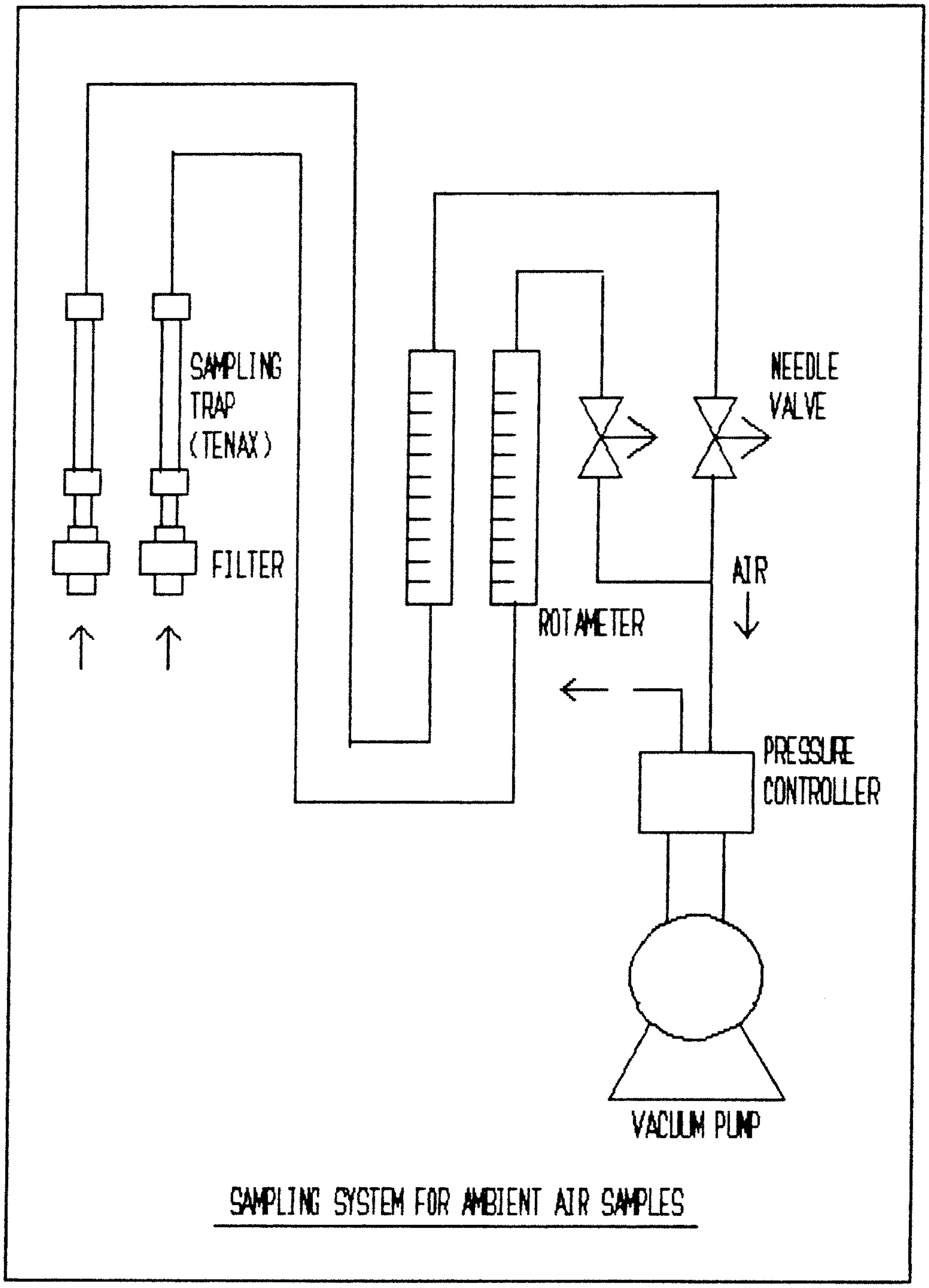

Figure 17. Schematic diagram of Ambient Air Sampler

Tenax, and minimizing the formation of artifacts. Thiosulfate coated filters have been tested for this purpose and have proven to reduce the ozone interference without removing organic vapors.[11]

Flow is controlled by varying the needle valve setting on the inlet of the pumps and monitored by calibrated rotameters (flow range 0-50 ml/min). Before use, each rotameter was checked against a soap film flow meter to get a calibration curve, which is required for each rotameter. A typical calibration curve plot is shown in Figure 18. X axis shows the reading on the rotameters and Y axis shows actual flowrates (ml/min). Donna and Carol are the identification names of the samplers. Each channel needs a rotameter, so each sampler has two rotameters called Left and Right. The rotameters are Porter model A-125-3 (Porter Instrument Co., PA) and measure air flow rates between 0 and 50 cm^3/min. Figure 19 is the schematic diagram of the apparatus used to do the calibration. The soap film flow meter is put on the air inlet to the trap to measure ambient air flow at atmospheric temperature and pressure (ATP). A pressure gauge is mounted just after the trap (before the pump) on the calibration apparatus to insure the trap used for flow calibration has the normal correct flow resistance.

The vacuum pumps, manufactured by Gillian instruments (Wayne, NJ) are powered by reachargable 6V batteries (9 amp-hour). The sampling pump assemblies contain an integrated pressure/vacuum controller which is set well below the pressure (or vacuum) capacity of the pump. This pressure control maintains a very constant pressure drop across the needle valve, if the regulated pressure is kept well below the

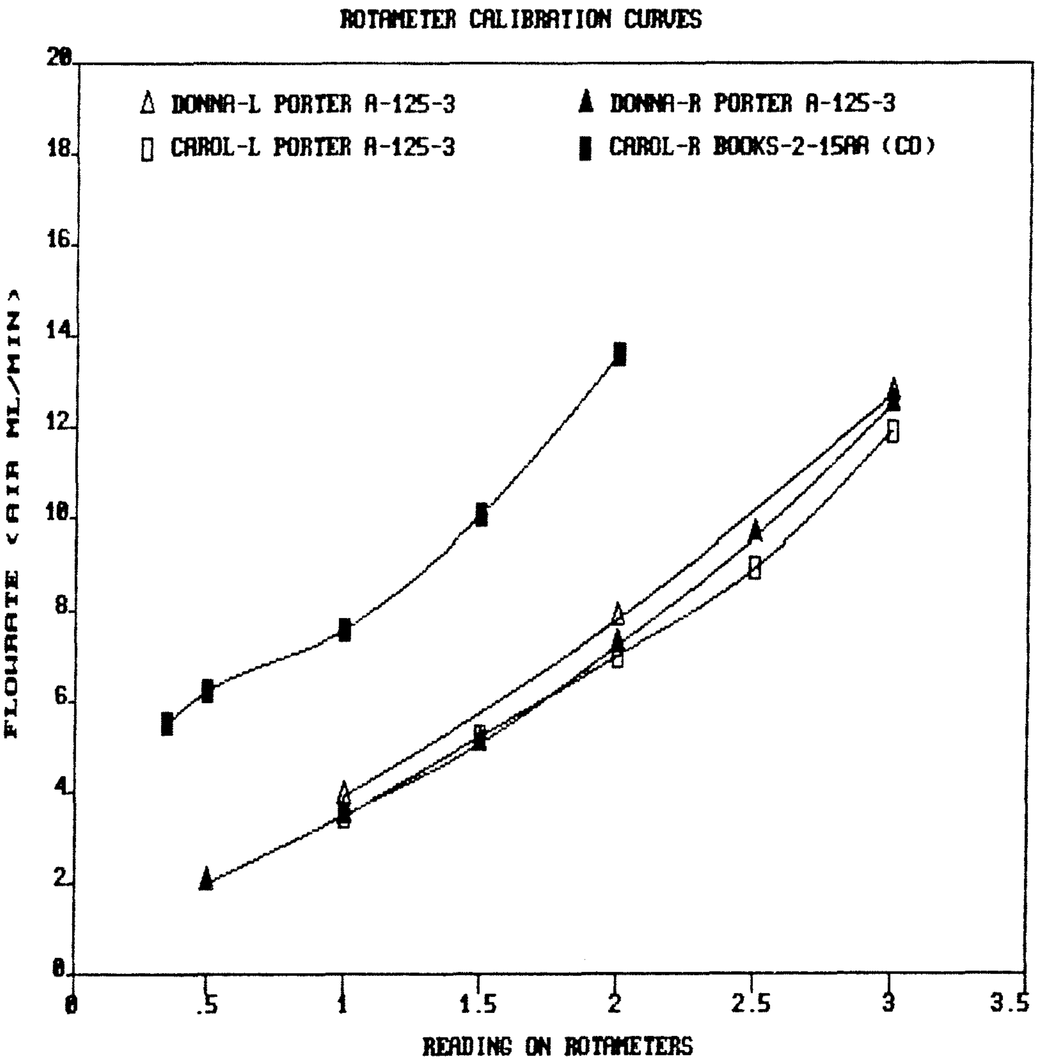

Figure 18. Calibration Curves of Rotameters on Sampler

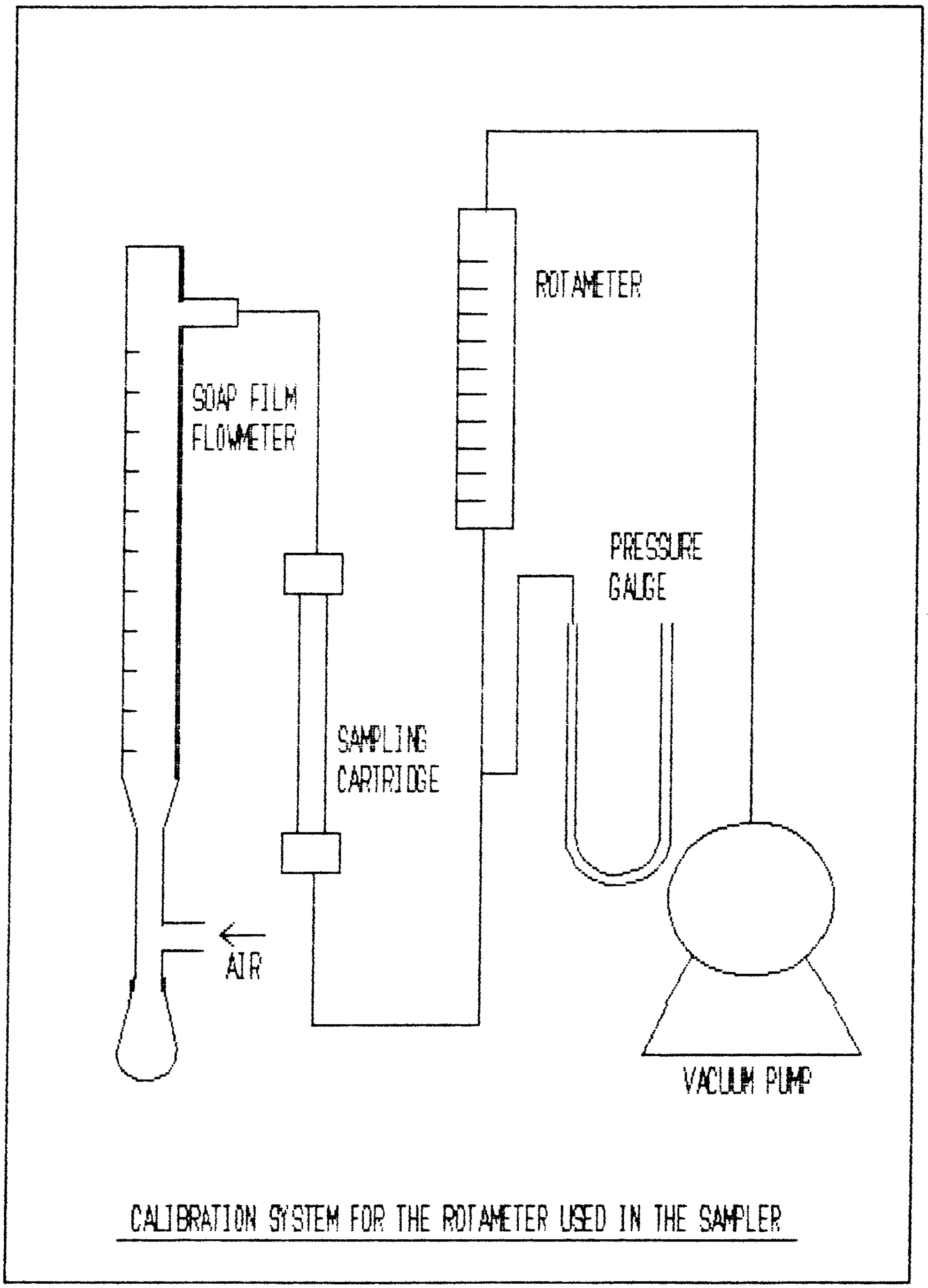

Figure 19. Calibration System for the Rotameters Used in the Samplers

capacity of the pump, then the pump can easily maintain this constant pressure differential for significant changes in line or battery supply voltages as well as changes in sampling conditions. Constant flows, within ±3 percent are easily obtained for long uninterrupted periods of sample collection under condition of rain/snow, widely changing temperature, etc..

2. GROUND SAMPLE COLLECTOR

Ground samples were collected by using similar Tenax traps and sampling pump assemblies as those used in the ambient air sample collection but a different collector configuration and a special container used to cover and isolate the sampled ground area.

The apparatus used in the ground sample collection included pumps, needle valves, rotameters, and traps which are the same as that used in the air sample collection. A special hemispherical container, as shown in Figure 20, was used to isolate an area of 850 cm^2 on the ground surface and approximately 4 liters in volume. The air containing volatile organic compounds emitted from the ground surface was drawn in through a glass fiber filter. The VOC's were then trapped on the Tenax sampling trap with remaining air drawn through the Tygon tubing, rotameter, needle valve, pump assembly and then returned to the isolated container. An activated charcoal trap was put in the return line (in series) before the container and after the pump, to remove contaminants from the transfer line and the vacuum pump. It also ensured that no compounds entered into the system from outside of

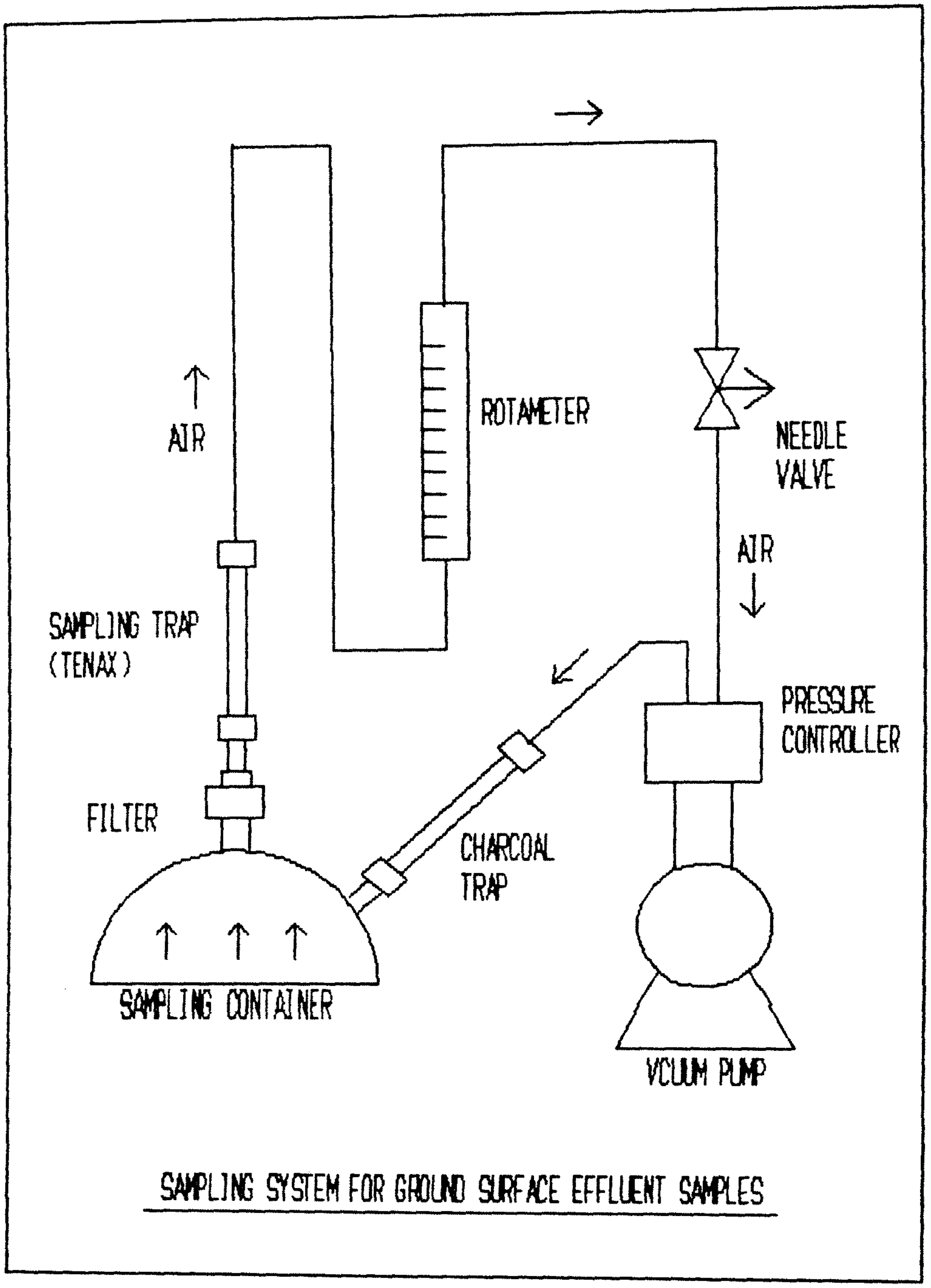

Figure 20. Sampling System for Ground Surface Effluent Samples

the ground air sample volume by keeping the pressure constant in the vessel.

3. PREPARATION OF TENAX TRAPS

Tenax polymer adsorbent is chosen for trapping the sample compounds, as it has been shown to readily adsorb and release these materials.[12,13,14] The efficiency of Tenax porous polymer for collection of trace organic vapors, the subsequent recovery of these vapors and the breakthrough characteristics of the vapor have been investigated in the air research laboratory of NJIT. [15]

The 60/80 mesh Tenax used in the sample collection traps is exhaustively extracted in order to remove any volatile fractions remaining in the polymer. Sixteen hour Soxhlet extractions with acetone, cyclohexane and methanol, consecutively, are followed by vacuum drying at 120°C. This treatment removes noticeable quantities of viscous liquid material from the Tenax. The sorbent is packed into traps fabricated of 1/4 inch OD(0.64 cm), 0.53 cm ID and 15 cm length stainless steel tubing. The packing is retained in the traps with plugs of silanized glass wool, and each contains 0.4 to 0.6 grams Tenax. The traps are fitted with compression connectors at each end for attachment to the sampling and desorption equipment. Removable connectors and ferrules are required for the traps desorbed on the Tekmar 5000 automatic desorber.

After packing, the traps are attached to a manifold and heated to 300 ^{o}C, with a purge of nitrogen flow at about 10 ml/min through each trap. This initial conditioning requires approximately 3 days to remove the extraction solvents completely, but subsequent reconditioning after field use is generally completed in 12 hours or over night. Completeness of conditioning is assured by desorbing one or several traps from each manifold batch and analyzing the effluent in the same manner as a sample. After conditioning, the traps are sealed with caps attached to the compression fittings and stored in individual glass culture tubes with Teflon lined screw caps. Glass wool packing is used to cushion each trap.

4. TARGET COMPOUNDS

Utilizing the known limitations of Tenax for collection of volatile organics and from previous work in our laboratory [16], plus the view point of species which cause or are suspected of causing harmful health effects to humans, we have determined a list of target compounds. It is shown on Table 4.

5. SAMPLING AND COLLECTION SITE LOCATION

Samples were collected over 24 hours by drawing air through the traps at a flow of 5 to 10 ml/min, so total volume collected is approximately 10 liters. Normally, one channel is set at 5 ml/min and

Table 4 Target Compound List

	Compound	Mol Wt.	* Response Multiplicity Factor	ppm in Standard
1.	Dichloromethane	85	7.0186	10.45
2.	1,2-dichloroethane	97	4.1572	16.70
3.	2-Butanone	74	2.6771	2.81
4.	Tetrahydrofuran	72	2.0218	2.17
5.	1,1,1-Trichloroethane	133.5	3.1226	12.97
6.	Benzene	78	1.0000	13.27
7.	Trichloroethylene	131.5	3.1300	20.34
8.	Methylcyclohexane	98	0.9349	10.81
9.	Toluene	92	0.7716	9.68
10.	Tetrachloroethylene	166	2.7800	18.69
11.	Ethylbenzene	106	0.7183	4.01
12.	p & m-Xylene	106	0.7054	8.12
13.	o-Xylene	106	0.7171	2.77
14.	Trimethylbenzene	120	0.6591	1.51
15.	Naphthalene	128	0.5562	3.47

* Required multiplicity factor to normalize molar response of these compounds relative to a Benzene factor of 1.

one at 10 ml/min. Ambient air samples were also taken at the same site to compare with ground samples. Start time and stop time were recorded to calculate actual sampling time. Weather and special conditions of the surroundings were also recorded.

Samples were taken in the Hackensack Meadowlands landfill, from January 1987 to July 1987. A map of the landfill is shown in Figure 21. A asterisk ( ) marks the location of our sampling site.

B. INSTRUMENTS AND ANALYSIS

A desorption/concentration system on line with gas chromatograph was utilized to do the quantitative analysis and some idetification work. Samples were desorbed, concentrated in the desorption/ concentration system and then injected into the GC column to be analyzed. Most of the qualitative work was done by GC/MS. The samples analyzed on GC/MS were desorbed into a 10 cm^3 evacuated stainless steel cylinder before analysis.

1. DESORPTION AND CONCENTRATE SYSTEM

A Tekmar model 5000 automatic desorber, manufactured by Tekmar Company, was used to desorb and concentrate the sample. It contains mainly a desorber, two cryogenic traps and a control panel. The desorber with adsorbent trap inside can be uniformly heated to a desired temperature. A carrier gas stream was flushed through the

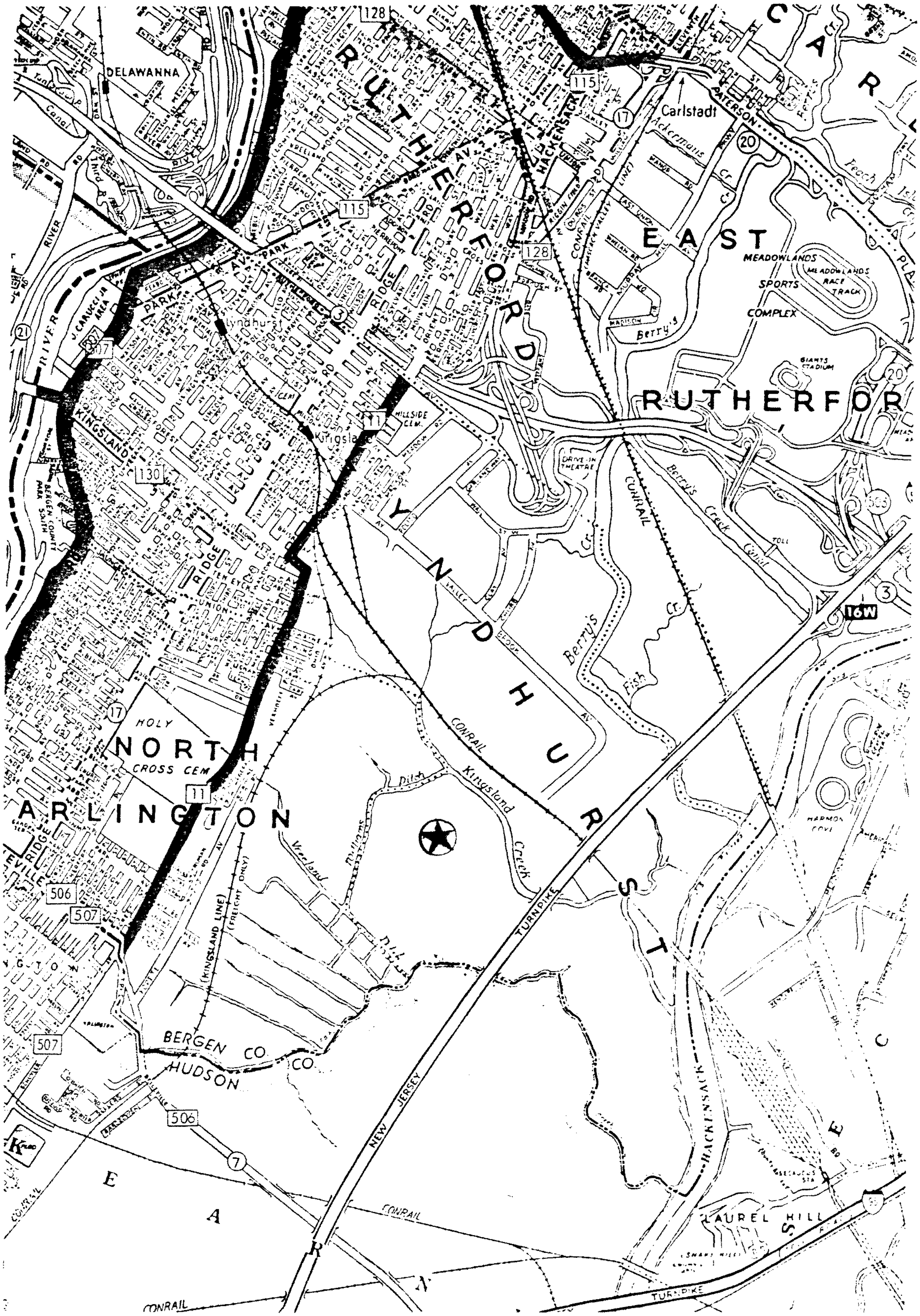

Figure 21. Location of the Sampling Site

trap to the first cryogenic trap, cryo-1. Sample compounds desorbed from the sampling trap are first cryogenically retrapped in the cryo-1 trap. After a certain desorption time, cryo-1 is heated. The compounds trapped inside cryo-1 evaporate and transfer to cryo-2 which is a smaller size trap for improved focusing . The transfer line is a piece of uncoated heated fused silica tubing. Cryo-2 is actually a precolumn section of the GC column. The sample is cryogenically trapped in the precolumn for 5 minutes and then heated at a rate better than 50 ^{o}C/sec to 200 ^{o}C to vaporize and inject the sample. The whole system is controlled by the Tekmar micro-processor. The operation procedure can be programmed and stored in the continuous memory. One can change the settings of desorption temperature, transfer line temperature, desorption time, transfer time, etc. The operation procedure used in this work on the Tekmar 5000 is shown in Table 5.

2. GAS CHROMATOGRAPH

A Varian 3700 gas chromatograph with dual detector, FID and ECD, and a capillary column were used to analyze the samples.

The column is Hewlett-Packard PONA capillary column (crosslinked Methyl silicone gum), 0.2 mm ID, 50 m length and 0.5 um film thickness. Carrier gas flow rate is 1 ml/min. The oven temperature was first held at 35 ^{o}C for 5 minutes and then programed at a rate of 10 ^{o}C/min to 190 ^{o}C.

To inject a standard gas mixture, a 6-port valve with 2 ml sam-

Table 5 Operation program of Tekmar 5000 Automatic Desorber/Injector

STEP	SETTING	REMARK
LINE HEATER	250°C	temperature of transfer tubing in the Tekmar 5000
VALVE HEATER	270°C	valve temperature
INJECTOR HEATER	210°C	injector temperature (cryo-2)
FURNANCE READY	40°C	desorption furnance before start
START INPUT	USER	manual control to start
PURGE 1 TIME	1.00 Min	purge time before desorption
CRYO-1	-150°C	cryogenic temperature of cryo-1
PURGE 2 TIME	0.00 Min	
FURNANCE DESORB	240°C	temperature of desorption
DESORB TIME	8.00 Min	desorption time
CONTINUE INPUT	USER	a pause untill GC is ready and manual continue
CRYO-2	-150°C	temperature of cryo-2
CRYO-1 TRANS	250°C	desorption temperature of cryo-1
TRANS TIME	5 Min	transfer time from cryo-1 to cryo-2
CRYO-2 INJECT	200°C	injection temperature of cryo-2
INJECT TIME	1.00 Min	injection time of cryo-2
FURNANCE BAKE	240°C	bake temperature after desorption step at desorption furnance
BAKE TIME	10.00 Min	bake time

pling loop is installed on the GC and connected to the second cryogenic trap of the Tekmar 5000 system.

3. GAS CHROMATOGRAPH / MASS SPECTROMETER

Analysis to confirm the identities of the peaks as assigned from the GC system are performed on a Kratos MS 25 magnetic sector mass spectrometer. A quarter of the total number of samples are analyzed by GC/MS. This analysis provides positive quanlitative verification of the target compounds.

4. ANALYSIS PROCEDURES

The Tenax trap, after sample collection, was put in the Tekmar 5000 desorber unit after the ready light was on, at which time the desorption oven temperature was 40 ^{o}C. Pressing the START button allows an initial flow of Helium carrier gas to purge air and water vapor from the sampling trap. This purge is held for 1 minute. The flow is then directed to cryo-1 and the desorbing temperature increases to 240 ^{o}C and held for 8 minutes to desorb the adsorbed VOC's. The VOC's species were carried by carrier gas to and then trapped in cryo trap 1 which was cooled by liquid nitrogen to -150 ^{o}C. A second desorption (heating cryo-1) is then carried out to transfer the VOC species to cryo trap 2 which is also cooled by liquid nitrogen at -150 ^{o}C and located above the injection port, just before the capillary column. Cryo trap 2 is then heated to 200 ^{o}C and the VOC's are injected into the column. The Tekmar 5000 sends a signal to the recorder to make an injection mark and a signal to the integrator system to initiate the integration.

The samples analyzed on the GC/MS were prepared by using thermal desorption system into a container including a 10 ml internally polished stainless steel cylinder and a stainless steel Bellows valve. Tenax trap was connected in series to a line of Helium and, on the down stream side to the precleaned and evacuated cylinder which was immersed in a cryo trap (- 60°C). The VOC'S were vacuum distillated into the cold cylinder from the Tenax held at 240°C for 30 minutes, then futher flushed with Helium into the cylinder, and pressurized to 45 psig with Helium. This cylinder was then connected up to the GC/MS and analyzed by injecting about 3 cm^3 STP of cylinder gas onto a cryo trap at the head of a fused silica capillary column (OV 101 10%, 30 m length).

CHAPTER III RESULT AND DISCUSSION

A. ANALYSIS RESULT

We collected 35 samples including samples collected from ground surface (ground samples) and ambient air samples (ambient sample). Table 6 lists the samples. It shows sample identification number (G,A,B, stand for ground sample, ambient air sample and blank), pick up date, and analysis method. Some of the result of the analysis are shown on Table 7, 8, 9 and 10. The ambient sample data include both concentration of the VOC's in the air and peak areas per liter of air collected for comparison results of the ground samples. The ground sample data are shown as emission rate, nanogram per hour per square meter soil surface, and peaks areas per liter of air collected.

B. CALCULATION OF THE RESULTS OF AMBIENT SAMPLES

Sample collection and desorption efficiency of 100% and that the gases obey ideal gas law are assumed. Desorption efficiency is shown by Pellizzari [13,14]. This implies all the target VOC's in the air are absorbed and all VOC's on the Tenax cartridge were desorbed and injected into column of gas chromatograph.

For each VOC, the ratio of the peak area of air sample and the peak area of standard gas on the chromatograms is equal to the ratio

Sample ID #	pick up date	Analysis Method	Sample ID #	pick up date	Analysis Method
401G	4/10/87	GC	413G	5/1/87	GC
402G	"	GC/MS	414G	"	GC
403G	"	GC	415G	"	GC/MS
404G	"	GC/MS	416A	"	GC/MS
405A	"	GC	417B	"	GC
406B	"	GC	418B	"	GC/MS
407G	4/21/87	GC	419G	6/12/87	GC
408G	"	GC/MS	420G	"	GC
409G	"	GC	421G	6/16/87	GC
410G	"	GC	422G	"	GC
411B	"	GC/MS	423B	6/17/87	GC
412G	5/1/87	GC	424G	"	GC
			425G	"	GC

* G: ground surface air samples
A: ambient air samples
B: blank samples

Table 6. Sample List

```
                         AIR SAMPLE ANALYSIS REPORT
-------------------------------------------------------------------------------
   Trap #                |      15                      |      17
   Sample ID #           |     410A                     |     409G
   Run Date              |   4/25/87                    |   4/25/87
   Picked Dt             |   4/21/87                    |   4/21/87
   Bz std A              |   179224                     |  179224
   V of smpl             |     17.6                     |    11.8
   samp time             |    24.45                     |   24.45
===============================================================================
    Compound             | Pk area  P A/liter    ppb    | Pk area P A/liter ng/hrM2
-------------------------------------------------------------------------------
 1. Methylene chloride*  |  4.12E+05  2.34E+04 1.64E+01  | 9.09E+04 7.71E+03 1.06E+02
 2. Ethylene dichloride* |  1.02E+04  5.78E+02 2.40E-01  | 1.28E+04 1.09E+03 1.01E+01
 3. 2-Butanone           |  5.99E+04  3.40E+03 9.10E-01  | 0.00E+00 0.00E+00 0.00E+00
 4. Tetrahydrofuran      |  6.05E+04  3.44E+03 6.94E-01  | 1.35E+05 1.14E+04 3.84E+01
 5. 111-Trichloroethane* |  1.81E+04  1.03E+03 3.20E-01  | 1.21E+03 1.03E+02 9.89E-01
 6. Benzene              |  1.63E+05  9.24E+03 9.22E-01  | 4.22E+04 3.58E+03 6.45E+00
 7. Trichloroethylene*   |  2.37E+04  1.35E+03 4.21E-01  | 2.57E+04 2.18E+03 2.07E+01
 8. Methylcyclohexane    |  2.78E+04  1.58E+03 1.47E-01  | 1.49E+04 1.26E+03 2.67E+00
 9. Toluene              |  1.11E+04  6.32E+02 4.87E-02  | 4.19E+05 3.55E+04 5.83E+01
10.Perchloroethylene*    |  1.09E+03  6.22E+01 1.73E-02  | 7.35E+03 6.23E+02 6.65E+00
11 Ethylbenzene          |  2.11E+03  1.20E+02 8.60E-03  | 1.24E+04 1.05E+03 1.86E+00
12 Xylene, p,m           |  2.46E+03  1.40E+02 9.85E-03  | 1.94E+04 1.64E+03 2.84E+00
13 Xylene, o             |  1.44E+03  8.19E+01 5.86E-03  | 1.33E+04 1.13E+03 1.98E+00
14 Trimethylbenzene      |  1.17E+03  6.67E+01 4.39E-03  | 0.00E+00 0.00E+00 0.00E+00
15 Naphthalene           |  0.00E+00  0.00E+00 0.00E+00  | 0.00E+00 0.00E+00 0.00E+00
===============================================================================
   * CHLORO-CONTAINING COMPOUNDS
```

Table 7. Analysis Results - 1

```
                         AIR SAMPLE ANALYSIS REPORT
-------------------------------------------------------------------------------------------------
    Trap #              |      10                  |      2                 |      9
    Sample ID #         |     412G                 |    413G                |     414G
    Run Date            |    5/1/87                |   5/1/87               |    5/1/87
    Picked Dt           |    5/1/87                |   5/1/87               |    5/1/87
    Bz std A            |    173272                |  173272                |   173272
    V of smpl           |      6.7                 |    6.6                 |      12
    samp time           |     22.13                |   22.13                |    22.13
=================================================================================================
     Compound           | Pk area  P A/liter ng/hrM2 | Pk area P A/liter ng/hrM2 | Pk area P A/liter ng/hrM2
-------------------------------------------------------------------------------------------------
 1. Methylene chloride* |  0.00E+00 0.00E+00  0.00E+00 | 2.18E+04 3.30E+03 2.91E+01 | 1.52E+04 1.27E+03 2.03E+01
 2. Ethylene dichloride* | 0.00E+00 0.00E+00  0.00E+00 | 1.45E+04 2.19E+03 1.31E+01 | 0.00E+00 0.00E+00 0.00E+00
 3. 2-Butanone          |  0.00E+00 0.00E+00  0.00E+00 | 2.19E+04 3.32E+03 9.72E+00 | 1.26E+04 1.05E+03 5.58E+00
 4. Tetrahydrofuran     |  0.00E+00 0.00E+00  0.00E+00 | 7.00E+03 1.06E+03 2.28E+00 | 8.34E+03 6.95E+02 2.72E+00
 5. 111-Trichloroethane* | 0.00E+00 0.00E+00  0.00E+00 | 2.40E+04 3.64E+03 2.24E+01 | 1.39E+04 1.15E+03 1.29E+01
 6. Bezene              |  8.77E+03 1.31E+03  1.53E+00 | 3.82E+04 5.78E+03 6.67E+00 | 2.95E+04 2.46E+03 5.16E+00
 7. Trichloroethylene*  |  1.05E+04 1.57E+03  9.69E+00 | 1.91E+04 2.89E+03 1.76E+01 | 8.47E+04 7.06E+03 7.81E+01
 8. Methylcyclohexane   |  0.00E+00 0.00E+00  0.00E+00 | 9.75E+03 1.48E+03 2.00E+00 | 9.85E+03 8.20E+02 2.02E+00
 9. Toluene             |  1.45E+04 2.16E+03  2.30E+00 | 7.85E+03 1.19E+03 1.25E+00 | 8.16E+04 6.80E+03 1.30E+01
 10.Perchloroethylene*  |  1.46E+04 2.18E+03  1.51E+01 | 0.00E+00 0.00E+00 0.00E+00 | 0.00E+00 0.00E+00 0.00E+00
 11 Ethylbenzene        |  1.31E+04 1.95E+03  2.23E+00 | 0.00E+00 0.00E+00 0.00E+00 | 2.78E+03 2.31E+02 4.73E-01
 12 Xylene, p m         |  0.00E+00 0.00E+00  0.00E+00 | 0.00E+00 0.00E+00 0.00E+00 | 9.28E+03 7.74E+02 1.55E+00
 13 Xylene, o           |  2.01E+04 3.00E+03  3.42E+00 | 0.00E+00 0.00E+00 0.00E+00 | 1.74E+04 1.45E+03 2.96E+00
 14 Trimethylbenzene    |  0.00E+00 0.00E+00  0.00E+00 | 0.00E+00 0.00E+00 0.00E+00 | 0.00E+00 0.00E+00 0.00E+00
 15 Naphthalene         |  0.00E+00 0.00E+00  0.00E+00 | 0.00E+00 0.00E+00 0.00E+00 | 0.00E+00 0.00E+00 0.00E+00
=================================================================================================
   * CHLORO-CONTAINING COMPOUNDS
```

Table 8. Analysis Results - 2

```
                        AIR SAMPLE ANALYSIS REPORT
--------------------------------------------------------------------------------
    Trap #                |      1                       |      5
    Sample ID #           |    419G                      |    420G
    Run Date              |   6/12/87                    |   6/12/87
    Picked Dt             |   6/12/87                    |   6/12/87
    Bz std A              |   108195                     |  108195
    V of smpl             |     5.9                      |    5.62
    samp time             |     24                       |     24
================================================================================
     Compound             | Pk area  P A/liter ng/hrM2   | Pk area P A/liter ng/hrM2
--------------------------------------------------------------------------------
1. Methylene chloride*   | 1.72E+03 2.92E+02  3.40E+00  | 3.42E+04 6.09E+03 6.76E+01
2. Ethylene dichloride*  | 1.13E+03 1.92E+02  1.51E+00  | 0.00E+00 0.00E+00 0.00E+00
3. 2-Butanone            | 5.00E+02 8.47E+01  3.28E-01  | 1.46E+04 2.60E+03 9.56E+00
4. Tetrahydrofuran       | 1.00E+03 1.69E+02  4.81E-01  | 6.83E+04 1.21E+04 3.29E+01
5. 111-Trichloroethane*  | 3.95E+03 6.70E+02  5.45E+00  | 0.00E+00 0.00E+00 0.00E+00
6. Benzene               | 4.77E+03 8.08E+02  1.23E+00  | 0.00E+00 0.00E+00 0.00E+00
7. Trichloroethylene*    | 8.02E+04 1.36E+04  1.09E+02  | 0.00E+00 0.00E+00 0.00E+00
8. Methylcyclohexane     | 6.35E+04 1.08E+04  1.92E+01  | 2.90E+04 5.16E+03 8.79E+00
9. Toluene               | 1.61E+04 2.73E+03  3.78E+00  | 4.54E+03 8.07E+02 1.07E+00
10.Perchloroethylene*    | 0.00E+00 0.00E+00  0.00E+00  | 0.00E+00 0.00E+00 0.00E+00
11 Ethylbenzene          | 0.00E+00 0.00E+00  0.00E+00  | 0.00E+00 0.00E+00 0.00E+00
12 Xylene, p m           | 0.00E+00 0.00E+00  0.00E+00  | 0.00E+00 0.00E+00 0.00E+00
13 Xylene, o             | 3.65E+03 6.18E+02  9.17E-01  | 0.00E+00 0.00E+00 0.00E+00
14 Trimethylbenzene      | 9.25E+03 1.57E+03  2.14E+00  | 1.23E+04 2.20E+03 2.85E+00
15 Naphthalene           | 0.00E+00 0.00E+00  0.00E+00  | 0.00E+00 0.00E+00 0.00E+00
================================================================================
    * CHLORO-CONTAINING COMPOUNDS
```

Table 9. Analysis Results - 3

```
                        AIR SAMPLE ANALYSIS REPORT
-------------------------------------------------------------------------------
  Trap #               |        2                       |        6
  Sample ID #          |      421G                      |      422G
  Run Date             |    6/16/87                     |    6/16/87
  Picked Dt            |    6/16/87                     |    6/16/87
  Bz std A             |    108195                      |   108195
  V of smpl            |      6.03                      |     5.88
  samp time            |      24.5                      |     24.5
===============================================================================
   Compound            | Pk area  P A/liter ng/hrM2     | Pk area P A/liter ng/hrM2
-------------------------------------------------------------------------------

 1. Methylene chloride*  | 1.13E+03 1.88E+02  2.19E+00  | 8.38E+04 1.42E+04 1.62E+02
 2. Ethylene dichloride* | 0.00E+00 0.00E+00  0.00E+00  | 2.66E+04 4.53E+03 3.48E+01
 3. 2-Butanone           | 6.79E+03 1.13E+03  4.36E+00  | 3.50E+04 5.96E+03 2.25E+01
 4. Tetrahydrofuran      | 3.16E+03 5.24E+02  1.49E+00  | 3.64E+04 6.19E+03 1.72E+01
 5. 111-Trichloroethane* | 9.25E+04 1.53E+04  1.25E+02  | 1.53E+04 2.61E+03 2.07E+01
 6. Benzene              | 1.07E+04 1.78E+03  2.71E+00  | 2.96E+04 5.03E+03 7.48E+00
 7. Trichloroethylene*   | 6.92E+04 1.15E+04  9.22E+01  | 1.35E+05 2.29E+04 1.80E+02
 8. Methylcyclohexane    | 3.74E+05 6.20E+04  1.11E+02  | 8.16E+05 1.39E+05 2.42E+02
 9. Toluene              | 1.00E+05 1.67E+04  2.31E+01  | 3.41E+05 5.80E+04 7.84E+01
 10.Perchloroethylene*   | 1.74E+04 2.89E+03  2.60E+01  | 7.73E+04 1.32E+04 1.16E+02
 11 Ethylbenzene         | 6.99E+03 1.16E+03  1.72E+00  | 1.06E+05 1.81E+04 2.62E+01
 12 Xylene, p, m         | 7.18E+03 1.19E+03  1.74E+00  | 2.97E+04 5.05E+03 7.19E+00
 13 Xylene, o            | 4.40E+03 7.29E+02  1.08E+00  | 3.07E+04 5.22E+03 7.56E+00
 14 Trimethylbenzene     | 2.01E+04 3.34E+03  4.56E+00  | 3.25E+03 5.53E+02 7.36E-01
 15 Naphthalene          | 0.00E+00 0.00E+00  0.00E+00  | 0.00E+00 0.00E+00 0.00E+00
===============================================================================
    * CHLORO-CONTAINING COMPOUNDS
```

Table 10. Analysis Results - 4

of their relative number of moles injected. i.e.

$$\frac{\text{peak area of air sample}}{\text{peak area of standard}} = \frac{ppb_{air} * \dfrac{P_{air} * V_{air}}{T_{air}}}{ppb_{std} * \dfrac{P_{std} * V_{std}}{T_{std}}}$$

solving for concentrations of VOC's in the air (ppb_{air})

$$ppb_{air} = \frac{\text{peak area of sample}}{\text{peak area of standard}} * ppb_{std} * \frac{P_{std} * V_{std}}{T_{std}} * \frac{T_{air}}{P_{air} * V_{air}} \quad \text{<a>}$$

where:

air : the air sample collected through the trap

std : the standard gas injected

P_{air} = pressure of collected ambient air,
14.7 psia, estimated

V_{air} = total volume collected (liter)
calculated, flow rate times sampling time

T_{air} = temperature of collected ambient air,
25°C, estimated

P_{std} = 14.7 psia, sampling loop open to ambient

V_{std} = 2 ml, volume of sampling loop

T_{std} = 170°C, fixed

We used Benzene as standard in actual calculation. We defined ratio of molar response as response multiplicity factor, F. i.e.

$$F = \frac{\text{peak area of Benzene / concentration}}{\text{peak area of other species / concentration}}$$

so,

$$\frac{\text{peak area of other species}}{\text{concentration}} = F * \frac{\text{peak area of Benzene}}{\text{concentration}}$$

substituting into equation <a>, we obtain

$$ppb_{air} = \frac{\text{peak area of sample}}{F * \text{peak area of Benzene}} * ppb_{Bz} * \frac{P_{Bz} * V_{Bz}}{T_{Bz}} * \frac{T_{air}}{P_{air} * V_{air}}$$

The response multiplicity factor of target compounds are listed in Table 4.

C. CALCULATION OF RESULT OF GROUND SAMPLES

A sample collection and desorption efficiency of 100% for the target compounds and that the gases obey ideal gas law are also assumed.

let N = moles of standard injected to GC = $\frac{P_{std} * V_{std}}{R * T_{std}}$

emission rate of VOC (ng/m^2.hr)

$$= \frac{\text{peak area of VOC}}{\text{peak area of standard}} * N * Mw \ / \ \text{time} \ / \ \text{covered area}$$

where, Mw is the molecular weight of the specific VOC, time is the sampling time, covered area is the area covered by the hemispherical container (0.085 m^2) and R is ideal gas law constant.

Benzene was used as standard gas in our actual calculation also as previous section. The calculation formula becomes

emission rate of VOC ($ng/m^2.hr$)

$$= \frac{\text{peak area of VOC}}{F * \text{peak area of Beznene}} * N_{Bz} * Mw \ / \ \text{time} \ / \ \text{covered area}$$

Where, N_{Bz} is the moles of Benzene standard gas injected into GC.

D. COMPARISON OF AMBIENT AND GROUND SAMPLES

The initial results showed that the samples taken with the ground sampling method have different VOC concentrations than those taken via ambient sampling method. Figure 22 shows comparison of a ambient air sample, 410A, and some ground samples, 409G, 412G, 413G, 414G and 419G. 410A is shown as a bar and the air samples as lines. Because emission rate ($ng/m^2.hr$) and concentration (ppb) are not similar units, the data are shown as peak area of specific species per liter air collected in table 7, 8 and 9. 410A and 409G were taken at the same time and same location. 409G has higher concentration of Toluene and Tetrahydrofuran but 410A has higher concentration in

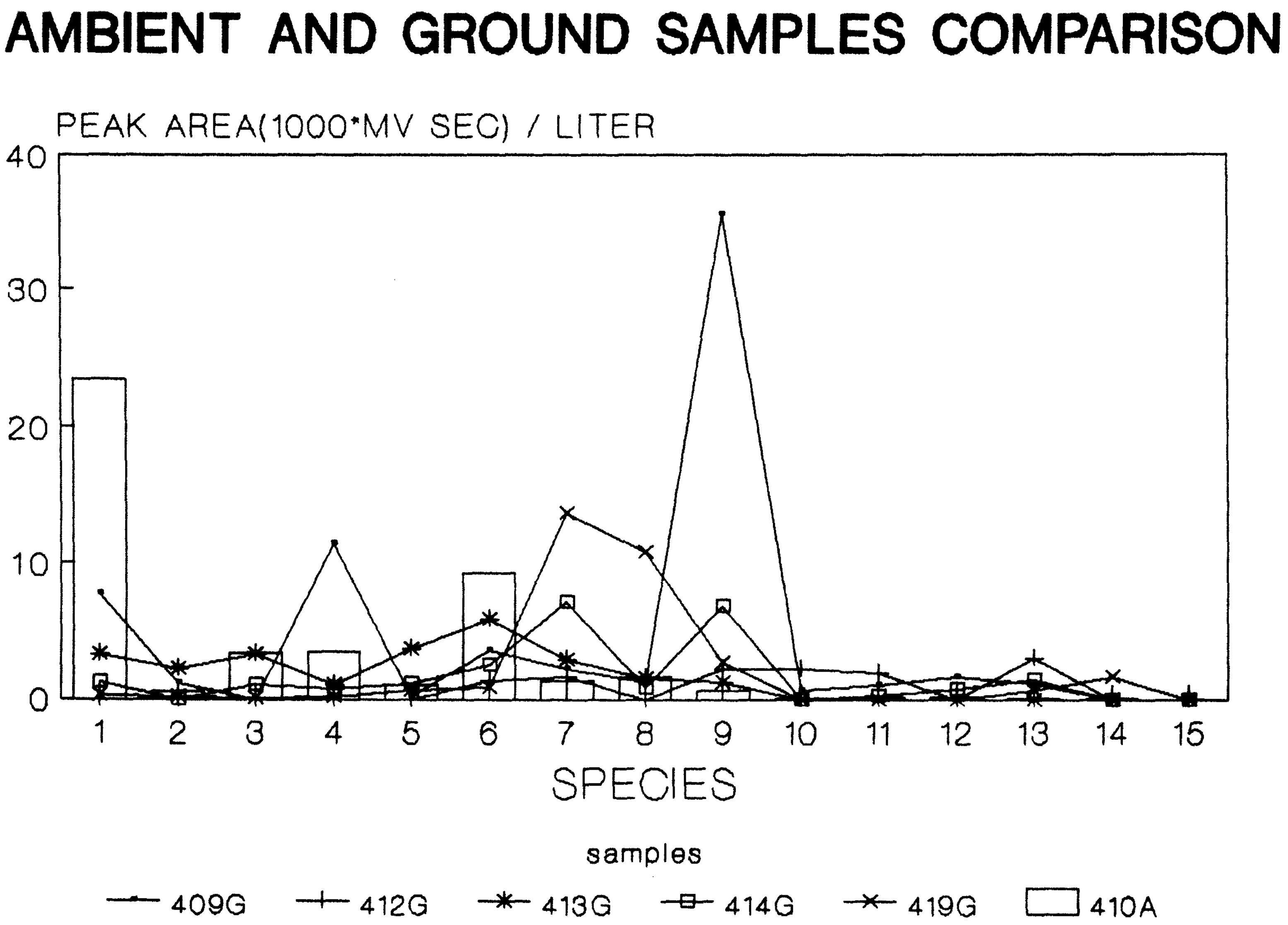

Figure 22. Comparison of Ambient and Ground Samples

Methylene chloride and Benzene. 412G, 413G, 414G were taken at the same site but different dates with 410A and 409G. The data does not show a clear relationship between the ambient and ground samples. They have quite different characteristics. This is not unexpected as there is no reason for the ground samples to exactly emulate the air characteristics.

E. COMPARISON OF GROUND SAMPLES

Three of the ground samples, as shown in Figure 22, 412G, 413G and 414G, were taken at the same date and same general location but seven meters from each other. 414G has higher concentrations in Trichloroethylene and Toluene. 413G has higher concentrations in Dichloromethane, 2-Butanone, 1,1,1-Trichloroethane, Benzene and Trichloroethylene. 412G has relatively higher concentrations of Perchloroethylene, Ethylbenzene and o-Xylene. They all show different characteristics. We conclude that the ground samples have a very strong location dependency.

F. REPRODUCIBILITY TEST OF GROUND SAMPLES

A sequential sampling of ground samples at the same location was done for a reproducibility test. In Figure 23, the first two samples, 419G and 420G, were taken on a cloudy rainy day (from 6/11/87 to 6/12/87). Data showed that concentrations of most VOC's were

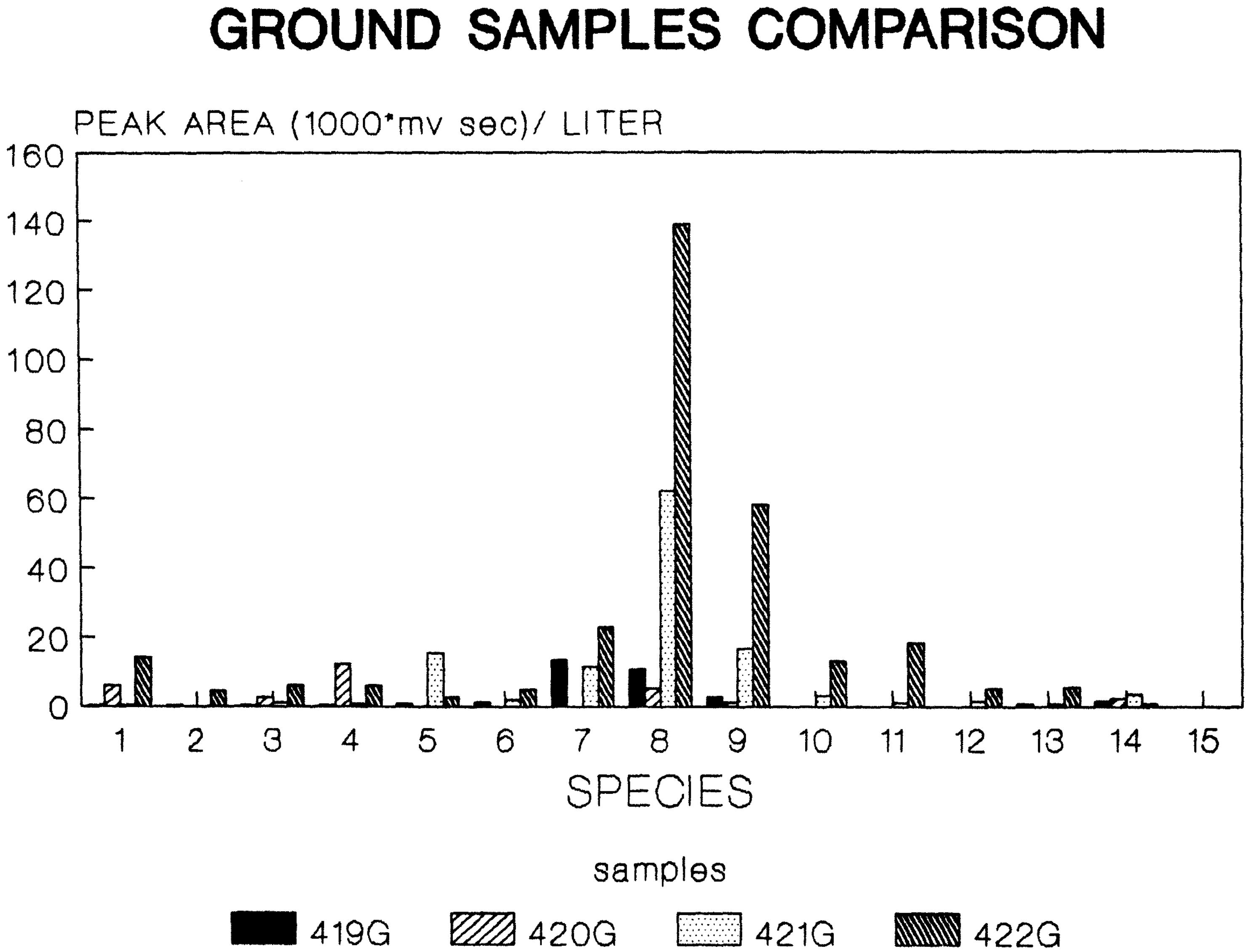

Figure 23. Comparison of Ground Samples

lower than on a dry day, except Trichloroethylene of 419G and Dichloromethane, Tetrahydrofuran of 420G. This may be explained by rain flushing the organic compounds out of the air and higher moisture content in the ground surface reducing or suppressing the emission rate of VOC's and also lower temperature would supress evaporation of compounds. Two other samples, 421G and 422G, were taken on a hot sunny day (6/15/87 to 6/16/87). Data shown in Table 10 and Figure 23, show that 422G has higher concentration of Dichloromethane, Trichloroethene, Methylcyclohexane and Perchloroethylene, and 421G showed higher concentration of 1,1,1-Trichloroethylene, Trichloroethylene and Methylcycolhexane. These drier ground samples show higher concentrations than the two samples taken at the same spots in a rainy day several days before. The third set, 424G and 425G, were taken consecutively after the second set also on a hot sunny day (6/16/87 to 6/17/87), where only sampling traps and batteries were changed and all other things were kept constant. The hemispherical sampling container was not moved or opened. The analysis of 424G and 425G show all the VOC's are trace or very low levels, lower than the earlier day. The largest peak height is about 1/15 of that on the earlier day.

The above analytical results, on the ground sample data in this work seems to show that actual VOC emissions from the ground surface, at the chosen land fill sites vary significantly. It appears that what might be occurring is that there is really little emission for any of our target VOC's from the sample collection sites. The first ground samples from a site (eg. 419G and 420G or 421G and 422G) showed target VOC concentrations which may result from ambient air. After VOC's were removed from the soil and air in the soil pores by our sample collection, the soil showed lower levels of the target VOC's. This may indicate little flux up through the ground and a sort of steady state condition for surface soils of adsorbed organics at concentration representative of ambient air.

The site where we took samples was a closed landfill site (not an active site) but near to an active dump site. This closed site was covered with several feet of clay. It maybe hard for VOC's to pass at significant rates through the layer of clay. There are many possible VOC's sources in and around this area, for air contamination, vehicle exhaust from the NJ Turnpike, Route 3 and Route 17, active land fill sites, background air levels, etc.

G. PRINCIPLE OF SAMPLER DESIGN AND VOC GROUND EFFLUENT ANALYSIS

Purpose of this sampler design is to obtain representative data to determine the emission rates of VOC's from ground surfaces. The air in the container covering the ground, containing the VOC's emitted from the ground, is drawn out at a specific flow rate over a specific period of time into the Tenax collection trap. We calculate the emission rate by dividing total sample mass collected by the sampling time period and the area covered by the container. To get proper data, we have to make some assumptions.

1. The concentrations of VOC's in the container are homogeneous.

The flowrate of our sampler to draw air out of the container is about 5 to 15 ml/min. The volume of the container is around 4 liter. It takes about 7 hours to sample one container volume. Homogeneity of VOC concentrations is accurate.

2. The input mass is equal to the output mass makes accumulation zero and the concentrations of VOC's in the container constant.

Apply the theory of mass balance and only consider the VOC's. Accumulation of VOC's in a system (the space covered by the container) is equal to the output flow rate of VOC's minus the input flow rate of VOC's. i.e.

Accumulation of VOC's = Output rate of VOC's - Input rate of Voc's

Consider the following three emission conditions and two sample flow relative rates.

Emission conditions:

a. input VOC flux << output flux
b. Input flux is aproximately equal to output flux
c. Input flux is >> output flux

where

input flux is the input flow of VOC's into the inverted sampling vessel from the ground emission process. Not controllable.

Output flux is the out flow to the sample cartridge.

Sample flow rates:

1. Low flow rate, a small number of air changes of sample vessel per sample collection time (less than 2).

2. High flow rate large number of air changes per sample collection time (greater than 10).

We now consider the plausible combinations of the above.

i, a + 1

Here we are mostly sampling air in the inverted wok volume, not ground emissions. One must subtract the mass of vapor VOC's from the total collected and then calculate the emission rates. the problem here is that the VOC's from the air are larger than from the ground and the errors are large. This is not recommended.

ii, a + 2

Here the initial air change is from ambient air (remember there will be dilution in the wok volume but mass is conserved) remainder of VOC will represent ground emissions. This system will give acceptable results and the initial mass of ambient air VOC's should be subtracted, even though it may represent a small correction.

iii, b + 1 or b + 2

Steady state is achieved and maintained, regardless of the air flow rate. Emission levels would be representative of ground emissions if the mass for one air volume of VOC is subtracted. The best situation would be if the initial VOC mass is small with respect to ground emissions, but this is difficult to control. High flow rates through the pump would help.

iv, c + 1

Levels will build up in the wok air chamber. Levels in the chamber will eventually reach stead state because as levels build up the output flux will by mass conservation increase. The initial VOC mass can be subtracted; but the problem is to determine whether equilibrium has been reached or not. If equilibrium is achieved early accuracy should be sufficient. If not low accuracy could result.

v, c + 2

This really can not occur at very high output flow rates. Not Applicable. The case reverts to Number ii above and is recommended.

This descriptive analysis is somewhat limited and is currently being applied in more mathematically quantitative manner. There is one limitation to the above and other than that it is representative. The limitation is that we have not considered equilibrium situations where we have a pool of liquids or adsorption into/onto soil surfaces. Here there is an exponentially decreasing term that needs be applied as the soil adsorbate is exhausted and a constant source term for a constant area liquid, but decreasing source as the liquid surface volume decreases.

In all case, homogeniety is assumed. At low flow rates, air above ground is mixed through diffusion. At high flow rates, volume under sampling vessel is mixed via turbulence.

H. ADVANTAGES AND DISADVANTAGES OF THE SAMPLER

A similar sampler based on these ideals has been used by Radian Corporation supported by Environmental Protection Agency. [17] They use nitrogen to purge through the sampling chamber, taking samples after the outlet concentrations reach a constant level (similar to case b + 2 in the previous E section).

This sampling method is good to quantitate emissions from landfill and land treatment facilities. But it still has some weak points. Since the enclosure is placed on a defined portion of an emission surface, it is difficult to evaluate how representive the observed emission rate is. Also placing an artificial object on an emitting source will disturb the turbulent velocity profile in the lower atmosphere, the concentration driving force for mass transfer, and vapor liquid equilibrium conditions, occuring under the natural wind conditions. Hwang [18] compared in more detail several volatile emission prediction methods.

This method is not very good, but it is still suggested to use in the case of that the mass transfer rate of gaseous species is less dependent upon natural wind conditions than that through the pores on soil.

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