ABSTRACT

Title of Thesis :

SECTION I: ANALYSIS OF C_2 AND C_3 HYDROCARBONS IN AMBIENT AIR
SECTION II: DEVELOPMENT OF SIMPLE ANALYSIS FOR POLYCYCLIC AROMATIC HYDROCARBONS
Li-Li Wu, M.S. Environmental Science, 1989
Thesis directed by: Dr. Joseph W. Bozzelli

SECTION I

A method was developed to analyze C_2 and C_3 light hydrocarbons: Acetylene, Ethylene, Ethane, Propyne, Propylene and Propane levels in the ambient air. Chlorinated compounds which eluted within the gas chromatograph operation conditions needed for the above hydrocarbons included Freon 12 and Methylene chloride, were also monitored.

Samples were collected from two sites, one located at Carteret and one at Elizabeth New Jersey. Samples were taken from September 1988 through July 1989. The sampling method used stainless steel canisters and was set up to collect 24 hour air samples at a constant flow rate of 30-35 cm^3/min.

The ambient air samples were preconcentrated by a

liquid nitrogen cryogenic trap on a gas sampling valve mounted outside the gas chromatograph and injected into the gas chromatograph by placing the cryoloop into an 100°C hot water bath to vaporize the compounds. The sample injected was equivalent to the concentration of 300 to 1000 ml of ambient air from the canister (volume depended on water vapor content of air).

Average levels of the specific compounds at the two sites are:

TABLE I ONE YEAR AVERAGE LEVELS OF DETECTED AMBIENT AIR COMPOUNDS

COMPOUND	YEAR AVERAGE LEVELS (PPBV) CARTERET(32)	ELIZABETH(38)[a]
ACETYLENE	6.61	6.34
ETHYLENE	8.12	6.81
EHTANE	8.89	7.69
PROPYLENE	4.53	9.42
PROPANE	6.67	16.84

a. number of samples from site

SECTION II

A simple analysis method was developed to determine the concentrations of total Polycyclic Aromatic Hydrocarbons in airborne particulates. The samples were collected over 24 hours on a glass fiber filter by a high volume air sampler at an industrial area, Carteret in New Jersey.

The samples were treated before analysis. An ultrasonic extraction, filter disc purification and thin layer plate isolation or filter cartridge (C18 and Fluorisil) isolation were used before analysis. Three analysis methods were used for analyzing the PAH (or Benzo(a)pyrene): Thin Layer Chromatography for Benzo(a)pyrene specific analysis and UV-Absorbance Spectrometer and UV-Fluorescence Spectrometry for total PAH analysis. 137 samples were extracted by three different solvents, ethanol, methylene chloride and cyclohexane, and analyzed by three instrumental techniques.

The results are presented as the ratio of the PAH concentration to Benzo(a)pyrene concentration. We have not been able to demonstrate that our method of total PAH analysis correlates linearly with specific Benzo(a)pyrene measurements. The results of analysis cannot distinguish between the following two conclusions :

a. That Benzo(a)pyrene dose not track total PAH and that the results of our analysis show the inequality of total PAH vs Benzo(a)pyrene that actually exists;
b. That Benzo(a)pyrene may track total PAH but our methods of analysis are not specific to PAH, i.e. we measure additional compounds which absorb and fluoresce in the regions of the uv where this analysis was performed.

I. ANALYSIS OF C_2 AND C_3 HYDROCARBONS IN AMBIENT AIR

II. DEVELOPMENT OF SIMPLE ANALYSIS FOR POLYCYCLIC AROMATIC HYDROCARBONS

by

Li-Li Wu

Thesis submitted to the Faculty of the Graduate School of
the New Jersey Institute of Technology in partial fulfillment of
the requirents for the degree of

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APPROVAL SHEET

Title of Thesis :

SECTION I :

ANALYSIS OF C_2 AND C_3 HYDROCARBONS IN AMBIENT AIR

SECTION II :

DEVELOPMENT OF SIMPLE ANALYSIS FOR POLYCYCLIC AROMATIC HYDROCARBONS

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SECTION I

ANALYSIS OF C_2 AND C_3 HYDROCARBONS IN AMBIENT AIR

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SECTION I ANALYSIS OF C_2 AND C_3 HYDROCARBONS IN AMBIENT AIR

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CHAPTER 1 INTRODUCTION

A number of methods for analyzing highly volatile C_2 to C_5 hydrocarbons (Acetylene through Pentane) in air have been developed over the past thirty years. These volatile organic compounds (VOCs) present in the atmosphere are of interest since some of these are known toxics or irritants. Certain classes of organic compounds such as C_2 compounds including, acetylene, ethylene, and ethane, and C_3 compounds including, propyne, propylene, and propane, are present in relatively high concentration and these participate in photochemical reactions resulting in the formation of irritating atmospheric oxidants (ozone, PAN) and smog. Our research deals with analyzing specific C2-C3 aliphatic (Acetylene and olefinic) hydrocarbons in ambient air.

The determination of hydrocarbon species in ambient air has routinely been accomplished by cryogenic concentration, followed by gas chromatography using flame ionization detection. The development of analysis methods began with the study of Eggertsen and Nelsen[1] in 1958. Hydrocarbons, in the atmosphere, from C2 to C5, were first trapped out in a short chromatographic column cooled in liquid oxygen. Altshuller and Bellar[2] designed the method of direct analysis (without a cold trap) using a 1 ml volume of air containing automative emissions including C_2 to C_4 hydrocarbons in relatively high concentrations of 0.01 to 1.0 ppm. Their analysis determinations were made by use of a 1/4 inch by 25 foot column operated at 25 ^{o}, and a flame ionization detector. The column was packed with one part by weight of dibutyl maleate to five parts by weight of C-22 firebrick. Feldstein and Balestrieri[3] analyzed C_2 to C_6 hydrocarbons by gas chromatograph with a freeze trap using a sample volume of 150 ml and their detection level was at ppb. Neligan[4] along with Stephens and Scott[5] have also investigated the hydrocarbons in the lower molecular weight range, C_2 to C_5 hydrocarbons. The most sensitive techniques of Stephens and Burleson in 1967[6] attained detection of VOCs in ambient air at the part per billion level using a volume of 0.1 L. They suggested that samples as large as 0.5 L and perhaps larger could be analyzed to increase senstivity.

Air samples were first collected in 1958[1] using evacuated glass containers having stopcocks lubricated with Dow-Corning high vacuum silicone grease. The air sample volume ranged from a few hundred milliliters to 5 or 10 liters. Other types of air collecting apparatus include: Scotchpack bag (heat-sealable plastic), which was reported in

1962[7]. Altshuller (1971)[8] and Lonneman (1974)[9] collected the air samples in 7-liter, 2-mil thick Tedlar bag (Du Pont Co.) by means of an automatic sequential air sampler.

Solid sorbents such as : charcoal, graphitized carbon black, and Tenax (1974) [10] were used to collect the air samples since 1971. This VOC collection was accomplished by trapping the vapors on the adsorbent. After the vapors are concentrated, they are recovered by thermal or solvent desorption, and analyzed by gas chromatography. The problem of using these sorbents are that they are not able to achieve precision for C2-C4 hydrocarbons, because those compounds tend to have low breakthrough volumes , irreversible adsorption, or decomposition on the solid sorbents. This analysis is therefore very difficult with sorbents for air sample collection.

The SUMMA polished stainless steel canister was designed in (1980)[11] to help solve the problem associated with C_2-C_5 VOC and from sample collection. Stainless steel canisters are not subject to sample permeation or photo-induced chemical effects, and they can be reused after a simple clean-up procedure. Various sample integrity studies of gases stored in SUMMA polished stainless steel canisters have been conducted in other laboratories. Harsch(1980)[11] reported stability of 10 halocarbons stored in canisters for month-long period at parts per trillion by volume levels. Cox (1983)[12] has discussed the storage stablilties of certain hydrocarbons in canisters at concentrations greater than 250 ppbv. McClenny (1984)[13], and Oliver (1985)[14] reported the storage stabilies of 15 VOCs (14 chlorinated, one brominated) at less than 2 ppbv. Concentrations of VOCs, chlorinated and aromatic (benzene, toluene, and o-xylene) hydrocarbons, in each canister were periodically determined during 7-day or 30 day storage periods. Their studies indicated the mean change in concentration per day was within +/- 3.2 %. The success of the SUMMA polished canister resulted in a new sampling and procedure for collection of VOCs[15].

Results of using the canister to collect the ambient air samples with quantitative analysis by cryo focusing under reduced pressure (10 mmHg) are reported in our study over a one year period. In the present study, we analyze the light hydrocarbons, C_2 to C_3, by a gas chromatograph and a column packed by carbosieve G, 60/80 mesh using parallel FID/ECD Detection. Our detection limit is at the 1 ppbv level.

For an accurate analysis of many VOCs in ambient air, preconcentration of air samples is required. Chromatograph supports are often used in a collection loop surrounded with cryogenic liquid to concentrate the VOCs in the cryotrap[1-6, 16]. Inert glass beads have more recently been used to pack the cryotrap instead of chromatographic supports[17]. Liquid oxygen and liquid nitrogen are a major cryogens used with glass beads. Cryogenic trapping has been shown to be a preferred preconcentration technique, particularly for the lighter VOCs, i.e., methanes, ethanes, and propanes. We utilized glass beads with liquid nitrogen for preconcentrating the ambient air samples, in a sampling loop under reduced pressure, in the present studies.

CHAPTER 2 EXPERIMENT

A. Sample Collection

1. Sampling Sites

There are two sampling sites (Figure 2-1) :

a. Carteret : On the roof of Carteret police department, NJ Turnpike exit #12, at the corner of Washington and Roosevelt avernue. About 12 meters above ground level.

b. Elizabeth : In Mattano park of Elizabeth which is in the NJ Turnpike near north and west of exit #13. The sampling equipment is 1.75 meters high from the ground.

2. Sampling Schedule :

Air sampling and analysis started in September, 1988 and ended in July, 1989. The air samples were collected every sixth day at each site. The total sampling time was 24 hours, from mid morning to mid morning of the following day.

3. Sample Collection Method

The air samples were collected at a constant flow

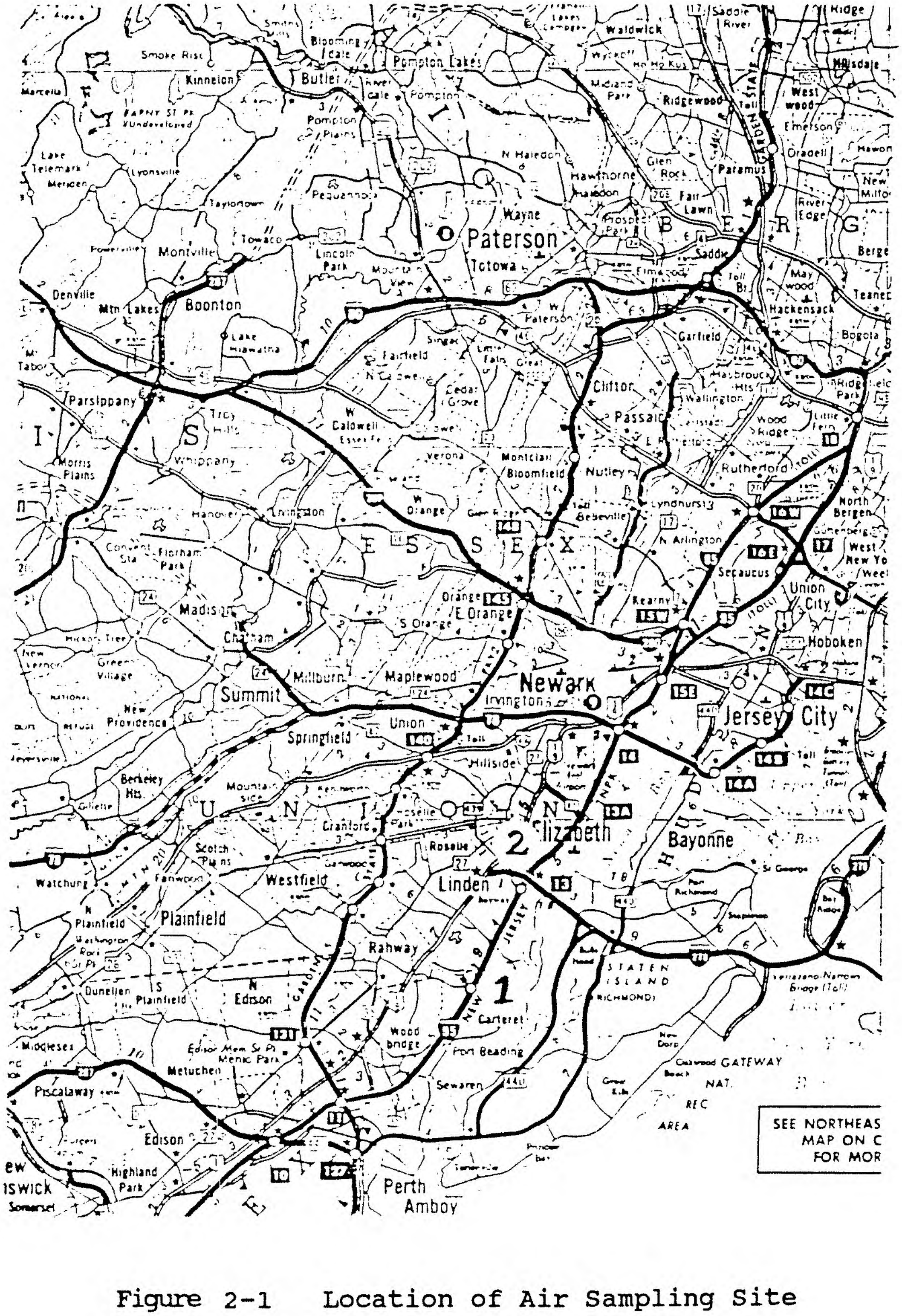


Figure 2-1 Location of Air Sampling Site

within a 24 hours time frame. All compounds were collected and volatile organic compounds were analyzed only.

A glass fiber filter is placed at the inlet of the air sampler to prevent particles from getting into the sampler. The sample was collected with a metal bellows pump (Metal bellows company, Sharon, MA, Model no. Mb-151, with capacity to maintain 2 atm pressure). The air is stored in a 5 liter evacuated canister (manufactured by Demaray Scientific Instrument Ltd. Pullman, WA). A pressure gauge installed between canister and pump showed the reading of pressure in the canister. (Figure 2-2)

The sampling flowrate was controlled by an orifice loaded between the filter and the pump inlet. The orifice, a 2.54 cm length of 34 gauge stainless steel hypodermic needle, was designed to control the flow, 30-35 ml/min, into the vacuum side of metal bellows pump which then pumped the sample into a 5-liter-canister. The pressure in the canister would increase from 0 psia to 30 psia (15 psig) within 24 hours. The pump's capacity significantly exceeded the flow through the orifice when there was one atmosphere of pressure across it. And thus the orifice always had vacuum on the pump inlet side and atmospheric pressure, from the ambient air, on the filter side. The

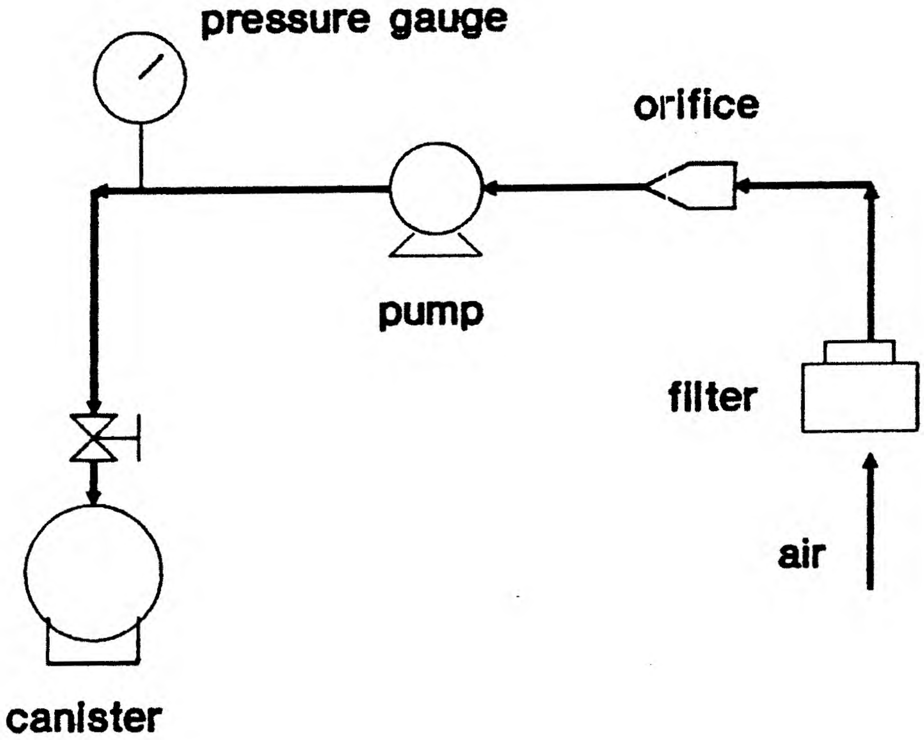


Figure 2-2 Air Sampler

orifice dimensions, therefore controlled the flow and the flow across the orifice was constant.

4. Preparation of Sampling Canisters

The canister must be cleaned and evacuated in the laboratory before being used to collect the air samples. It is cleaned by repeated pressurization and evacuation with zero air (Spectro-Gas, Kearny, NJ) for 6 cycles (Figure 2-3). A heating mantle was used for each canister to keep it warm during the whole cleaning procedure. We utilized 2 ways to clean the canister.

a. We evacuated the canister to 0.1 mm-Hg and held it under the vacuum for 40 to 60 minutes. After vacuum the canister, we filled it with zero air to 30 psig and vent the air to ambient. We then repeated this procedure 6 times. The canister was cleaned and evacuated on the last cycle. This procedure could clean canister completely but it was time consuming (It took 8 hours to finish the whole procedure).

b. We evacuated the canister to 0.1 mm-Hg for 5 minutes, filled with zero air to 30 psig, then vented to ambient. We repeated this procedure 10 times and it did clean the canister completely but took only two hours to finish the

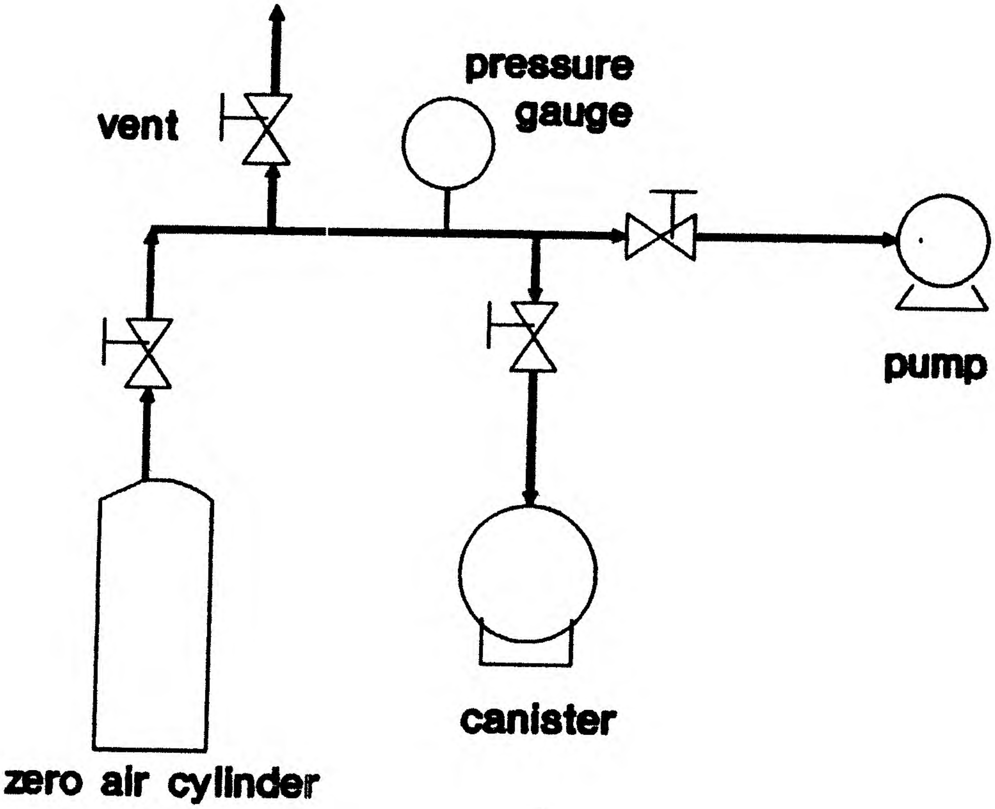


Figure 2-3 Cleaning Equipment

cleaning procedure.

B. Equipment and Analysis

1. System Construction

Figure 2-4 shows the construction for loading air sample from the sample canister through the Valco 6 port sample valve (Model No. FX0948, Vici Valco Instruments Co.,Inc. Houston, TX) to Gas Chromatographic analysis. The system lines tubeing are all warmed by heating tapes to 60 ^{o}C, from the inlet port to the tube of carrier gas before GC column. The valco 6 port valve is for controlling loading and injecting positions (Figure 2-5 and 2-6). The sample volume was measured by a evacuated cylinder and a pressure gauge. A vacuum pump was connected at the outlet of the evacuated cylinder.

2. Gas Chromatograph

A Gas Chromatograph (Tracor, model 550) was set up for analyzing the VOC. The column was packed with Carbosieve G (Supelco, Bellefonte, PA) and 1.6 mm OD, 1.0 mm ID, and 1 meter long nickle tube. The carrier was helium (Liquid Carbonic, Specialty Gas Corporation, Harrison, NJ) with 14.4

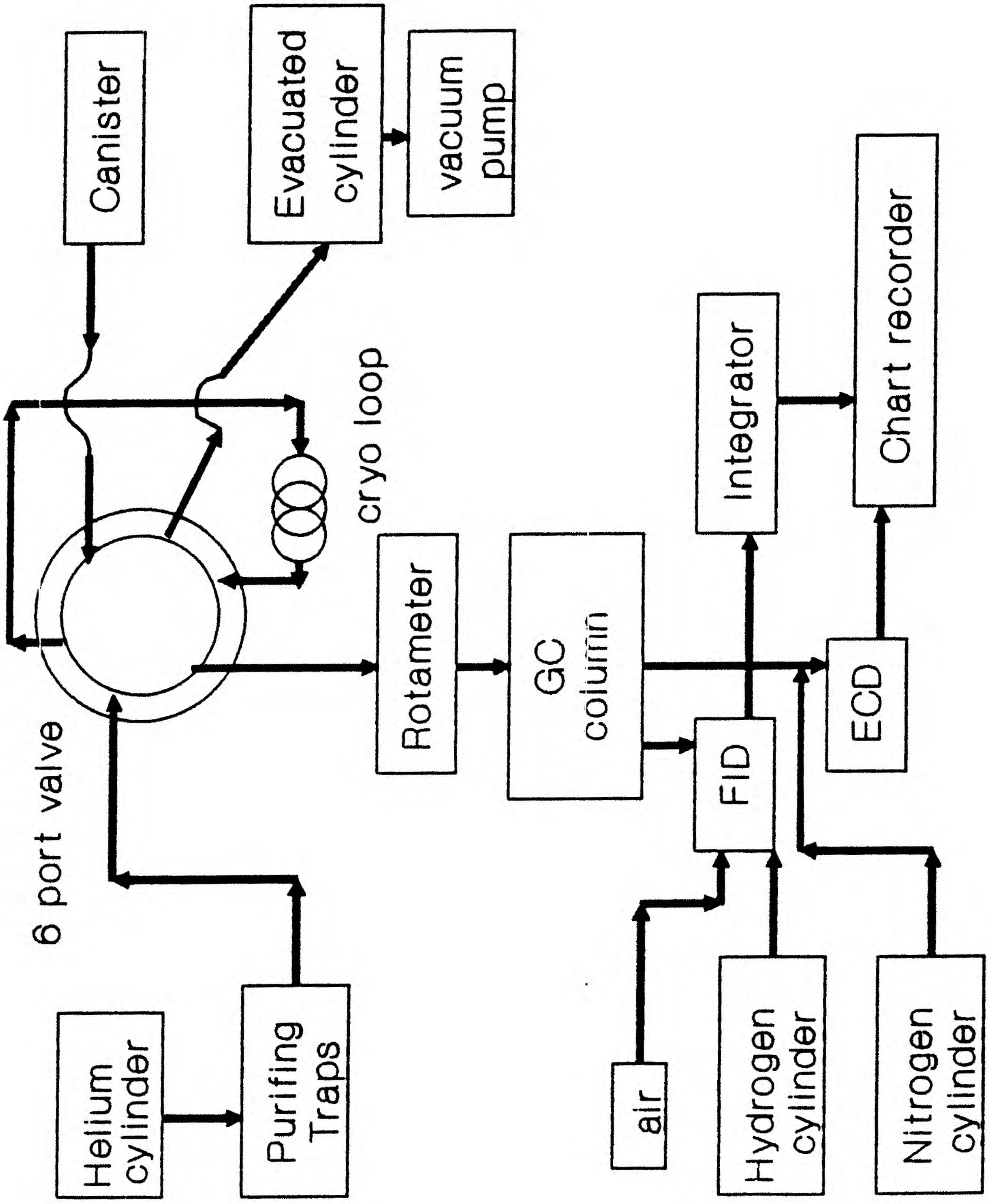


Figure 2-4 Illustraction of System Construction

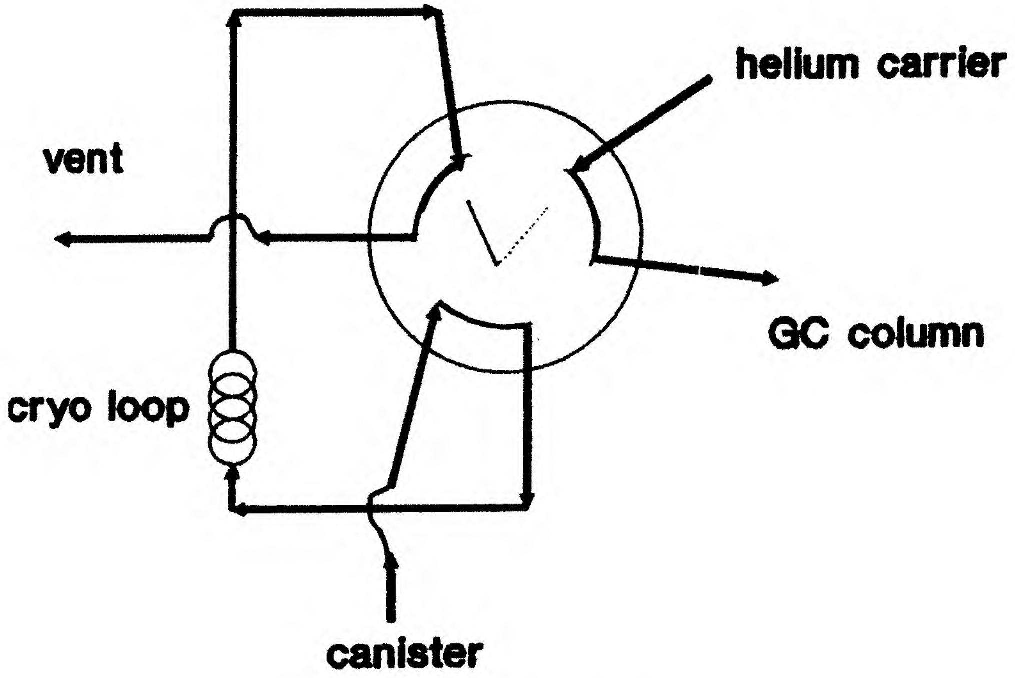


Figure 2-5 Loading Position

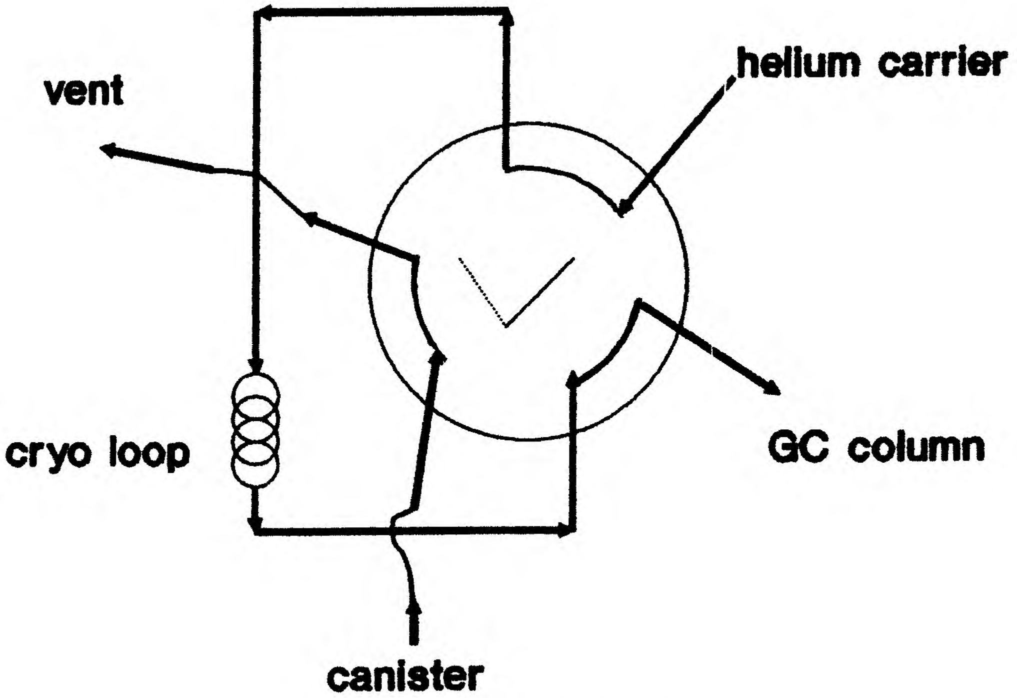


Figure 2-6 Injection Position

ml/min flowrate controlled by a rotameter.

The detectors included Flame Ionization Detector and Electron Capture Detector. A make up gas, nitrogen (50 ml/min), was introduced after the column. Then the eluent was split to the FID and ECD. Before the ECD, we used a second nitrogen make up gas to boost ECD flow (total 48.8 ml/min including make up and purge). The FID is used for quantifing the volatile organic hydrocarbons, (non oxygenated and non chlorinated) that we wanted to observe. The gases of the FID are hydrogen(46 ml/min) and air (450 ml/min) (Liquid Carbonic, Specialty Gas Corporation). The ECD is used for qualitating the chlorinated or oxygenated compounds, while the species can also be quantified by FID. The ECD peak identification verifies that no coelution of interfering hydrocarbons occurs.

The signals of the eluted compounds are collected on a chart recorder (Esterline Angus, model L1102s) and areas are calculated by an integrator (SP4290, Spectra-Physics, San Jose, CA).

The condition of the analyzing system is listed below:

GC Model : Tracor 550

Column : 1.6 mm OD, 1.0 mm ID, and 1 meter long nickle tube, Packed by 60/80 mesh carbosieve G (Supelco).

Detectors : ECD Tracor 560 and FID

Integrator : Spectra-Physics SP4290

Operating conditions :

a. GC condition

Time for a run : 30 minutes

Inject temperature : 100° C

Temperature programing : Isothermal 135 C for 3 min, temperature increase 6 c/min to 195°C final temperature.

Carrier gas : 14.4 ml/min He (12.6 ml/min to the FID and 1.8 ml/min to the ECD).

b. Detectors

FID : Temperature 260 °C

Hydrogen : 40 ml/min

Air : 400 ml/min

3. Analysis of Ambient Air Sample

a. Load air sample

The sample canister is connected at the inlet port and kept warm (30 °C, for mixing the air in the canister) with the 6 port valve is on the loading position, the sample is loaded into the sampling loop cooled with cryogenic liquid (liquid nitrogen), to condense and trap all the volatile organic compounds. The air is drawn through the loop by an evacuated 2200 ml cylinder. The cylinder is evacuated to 0.1 mm-Hg pressure absolute before loading sample. The loading flow is controlled by a needle valve on the inlet of the air sample at 75 ml/min. The total loading time for one sample run is 10 to 20 minutes and depends on the total inlet air volume.

The sampling loop is a 3.1 mm OD, 2.1 mm ID, and 21 cm long stainless steel tube packed with 200 micron glass beads. The glass beads are treated by rinsing in 6 M HCl solution, rinsing with a second distilled water, and then be dried in an oven at 250 C for two or three days. The glass beads serve to increase the surface in the sampling loop and help the compounds to condense in the loop more completely.

b. Inject air sample to the Gas Chromatograph

After loading enough sample volume into the loop, we close the valve on the canister and remove the cryogenic liquid, then place a 100° C hot water bath over the loop. All these actions should be as consistent in timing as possible for precision in injections. The hot water bath helps the VOC to vaporize in the loop and inject them with helium carrier into the GC smoothly.

The GC column is kept in 135° C isothermally for 3 minutes, then a temperature program of 6°C/min was used to raise the temperature to 195° C (it took 10 minutes to the final temperature). The column is held at 195°C isothermally for 10 minutes at the end of the temperature program. It takes 30 minutes to run a sample. Each sample run is duplicated two or three times.

4. Analysis of Standard Gas

a. Standard gas

A mixture of standard gas includes hydrocarbons from CH_4 to Butane supplied by Scott Specialty Gas (Scott Environmental Technology, Inc., Plumsteadville, PA). Scotty IV Analyzed gas is a mixed gas cylinder and it contains 8 compounds in nitrogen. Table 2-1 lists the compounds of the mixed standard gas and retention time of the different compound and indicates the target compounds that we routinely observed.

b. Loading and analysis of standard gas

(i) Loading the standard gas without cryogenic focusing

Table 2-1 List of target compounds

compound	concentration of standard gas (ppm)v	retention time (min)
Methane	19.6	0.63
* Acetylene	18.55	1.17
* Ethylene	20.00	1.45
* Ethane	19.99	1.88
* Propyne	19.99	6.65
* Propylene	20.07	7.43
* Propane	19.99	8.09
N-Butane	19.99	25.59

* target compound

Standard gas is loaded by a 1 ml loop at 1 atm, 25°C and injected to the GC at 100°C. The loop is 2.1 mm ID and 3.1 mm OD stainless steel tube (Type 304, 1/8" * 0.085", Alltech Associates, Inc. Deefield, IL) and it does not contain any glass beads. The standard gas is loaded by connecting the gas cylinder to the inlet port on 6-port valve where the sample canister is normally connected. The 6-port valve is on load position when the standard gas is inlet. The standard gas is loaded by purging the gas through the 1 ml loop and then vented to atmosphere. After two minutes of purging, we close the valve on the standard gas cylinder and inject the standard gas at 100 °C by immerging the loop in a hot water bath and Switching the 6-

port valve to the inject position. A known volume of standard gas is then injected by carrier gas into the GC.

(ii). Loading the standard gas with cryogenic focusing

For this process, a tee with septum is put right after the inlet port and connected the inlet port to a helium gas flow. The cryogenic loop is now the same as sample loop which is packed with glass beads. Before loading the standard gas the standard volume cylinder is evacuated to 0.1 mm-Hg. The gas is injected quantitatively by a syringe and be drawn through the tee to the cryogenic loop by the vacuum in the standard volume cylinder. To make sure that the standard gas is loaded into the cryo loop completely, the helium gas is purged through cryo loop 40 ml/mim for 2 minutes. The injecting procedure is then the same as air sample injection.

5. Identification of Target Compounds

a. Target compound

The target compounds are·identified by comparing the retention time of the compound in standard gas to that of the ambient air samples. Sometimes, we needed to spike the standard into the air sample gas to help the identification in ambient air samples. The samples contain some interferences, e.g. water and carbon dioxide , which result in deviation of retention time of a compound in the sample's chromatogram compared to the standard gas chromatogram.

The tee with septum in the inlet port is also used for spiking the standard gas. When starting to load an air sample, a certain (known) amount of standard gas is injected into the tee. Figure 2-7 gives the chromatogram of mixed standardd gas with the injection of 0.39 ml. Figure 2-8 (a) and (b) give the ambient air sample chromatograms. Figure 2-8 (a) is the chromatogram of air sample. Figure 2-8 (b) is the air sample chromatogram after spike with 0.5 ml of mixed standard gas.

b. Identification of chlorinated compound

Chlorinated hydrocarbons, methylene chloride and Freon 12 (Dichlorodifluoromethane), were also routinely detected in the ambient air. They were detected in both FID and ECD, both were identified by spiking the suspected compounds. The chromatogram of the spike test are illustrated by Figure 2-8 (c) for Freon 12 (spike 0.5 ul of pure gas) and Figure 2-9 (a) and (b) for methylene chloride.

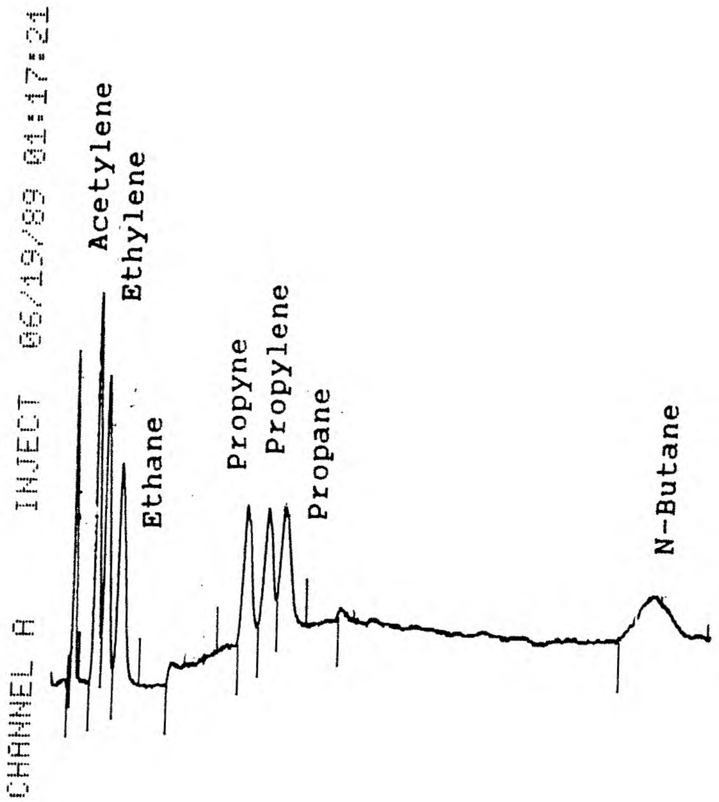


Figure 2-7 The chromatogram of mixed standard gas

inject volume : 0.39 ml
at 25 C , 1 atmosphere

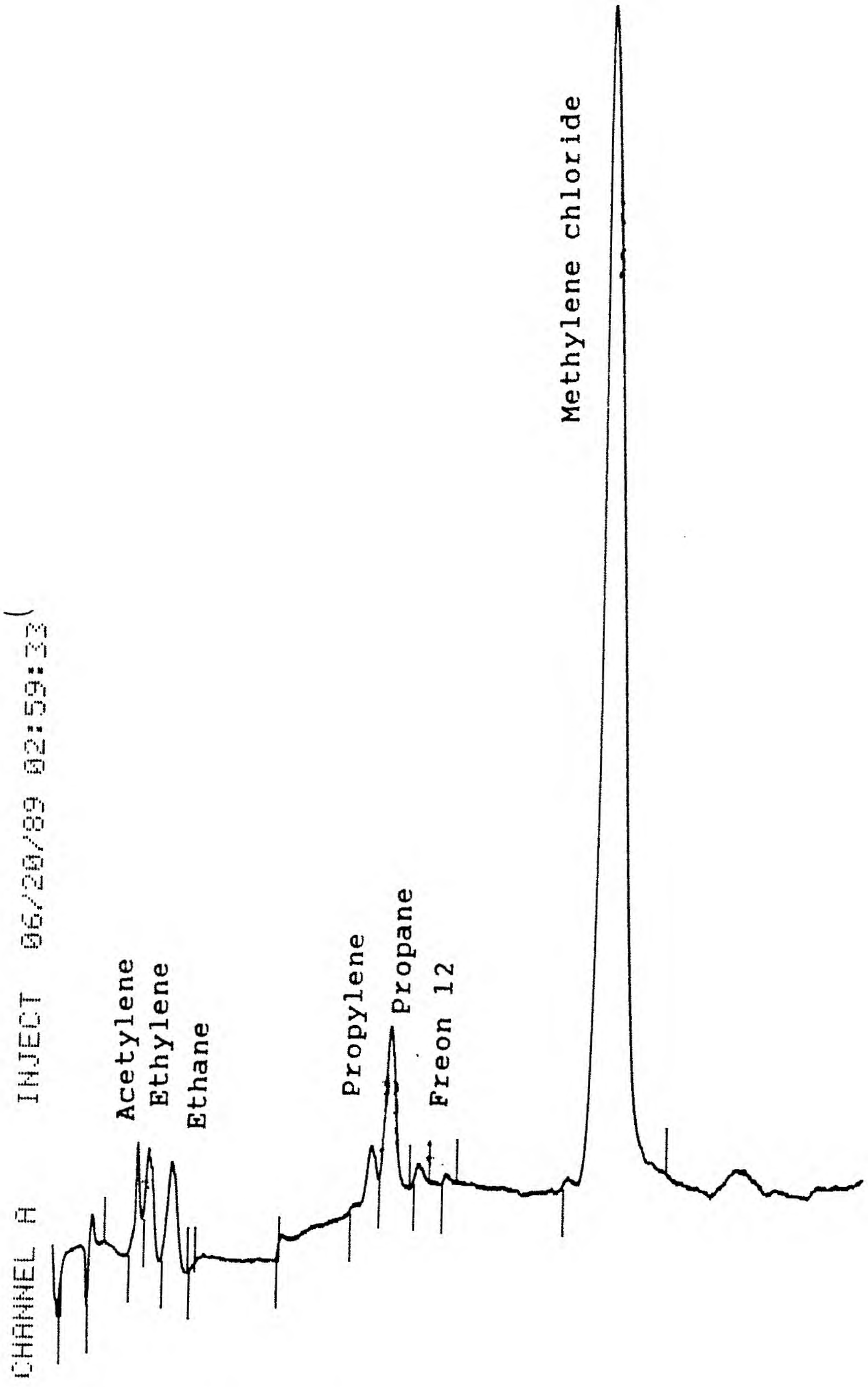


Figure 2-8 (a) The ambient air sample chromatogram

inject volume : 294 ml
sampling Date : 6/3/1989
sampling site : Elizabeth

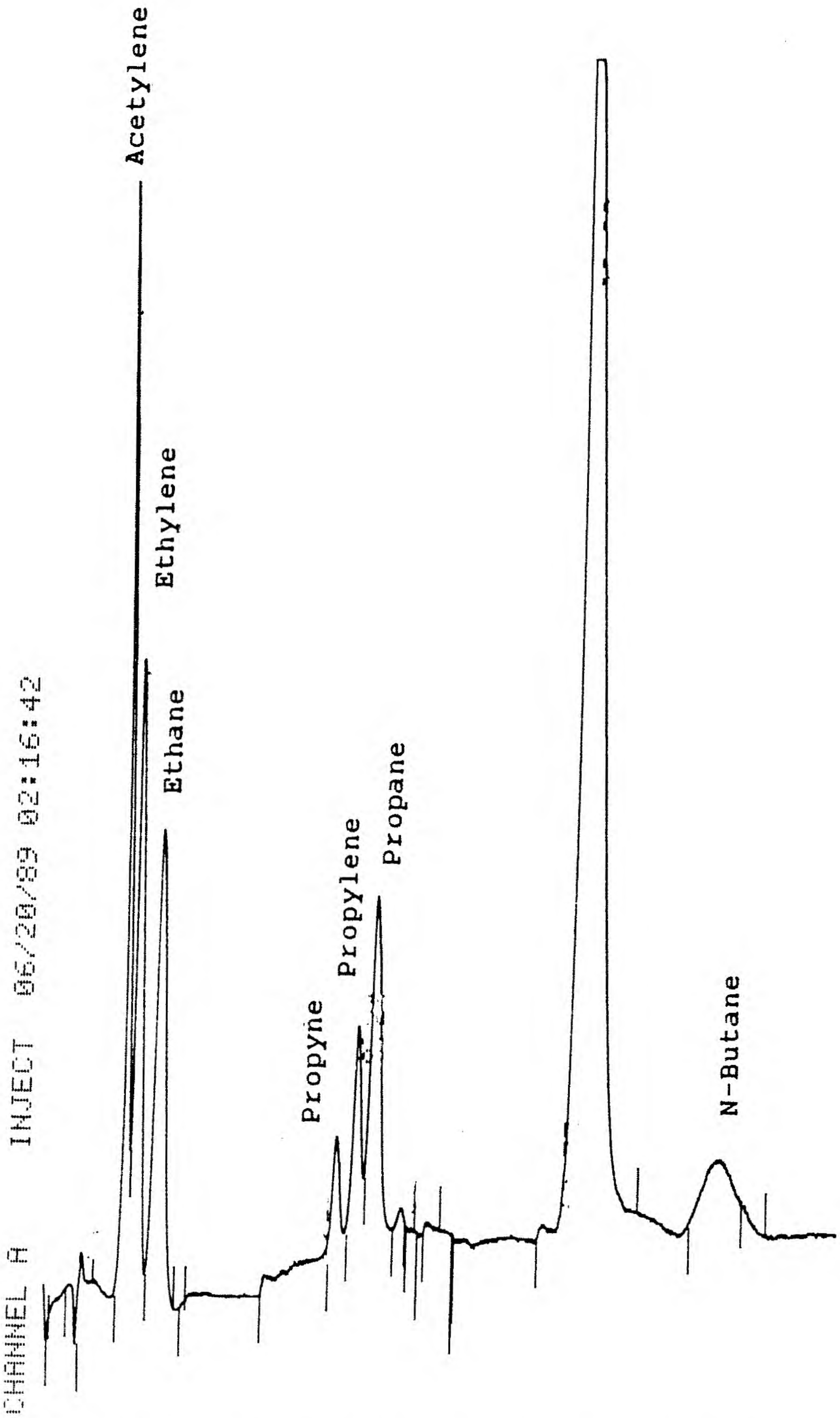


Figure 2-8 (b) The ambient air sample chromatogram spike with 0.5 ml standard gas

sample inject volume : 309 ml
sampling Date : 6/3/1989
sampling site : Elizabeth

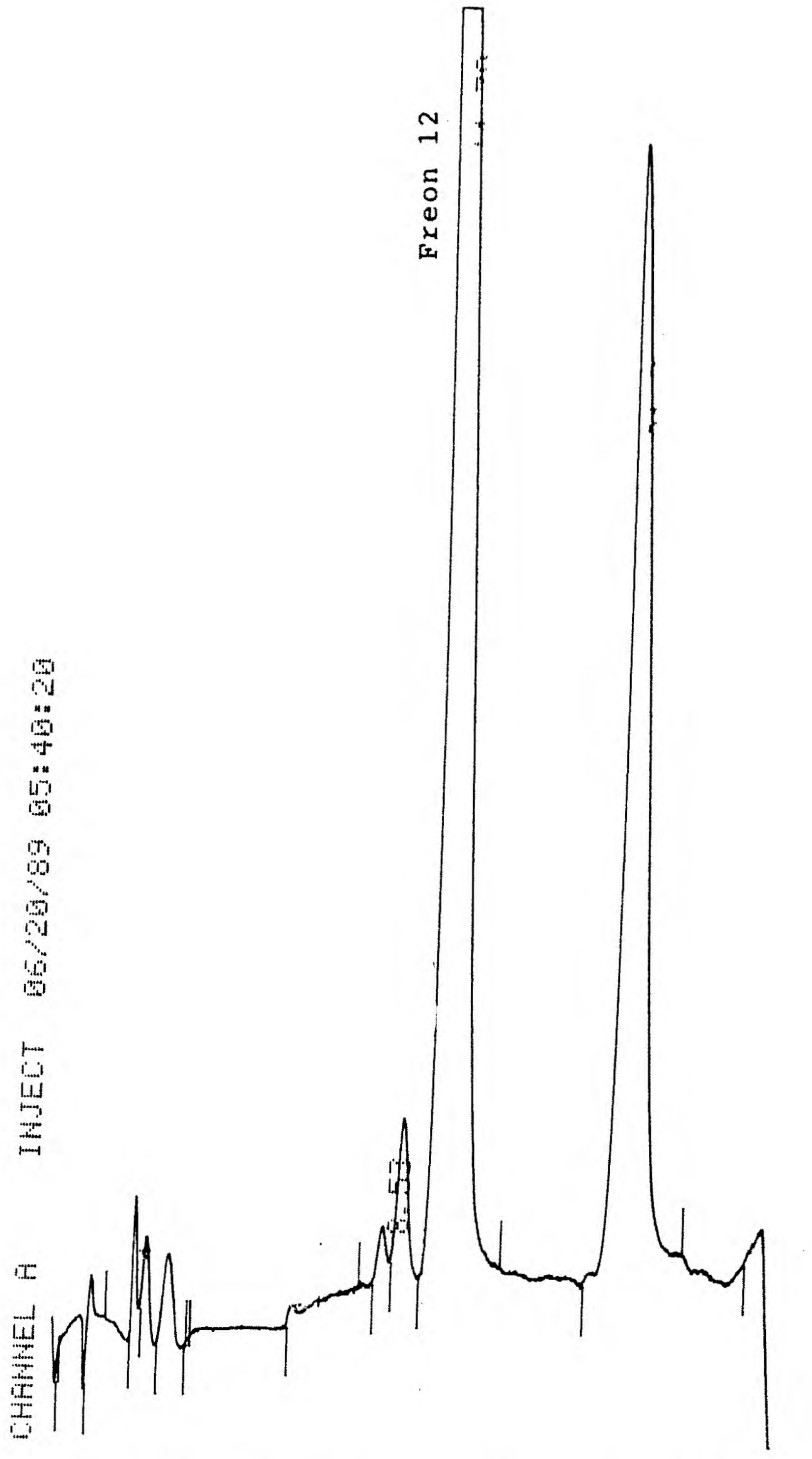


Figure 2-8 (c) The ambient air sample chromatogram spike with 0.5 ul Freon 12 pure gas

sample inject volume : 279 ml
sampling Date : 6/3/1989
sampling site : Elizabeth

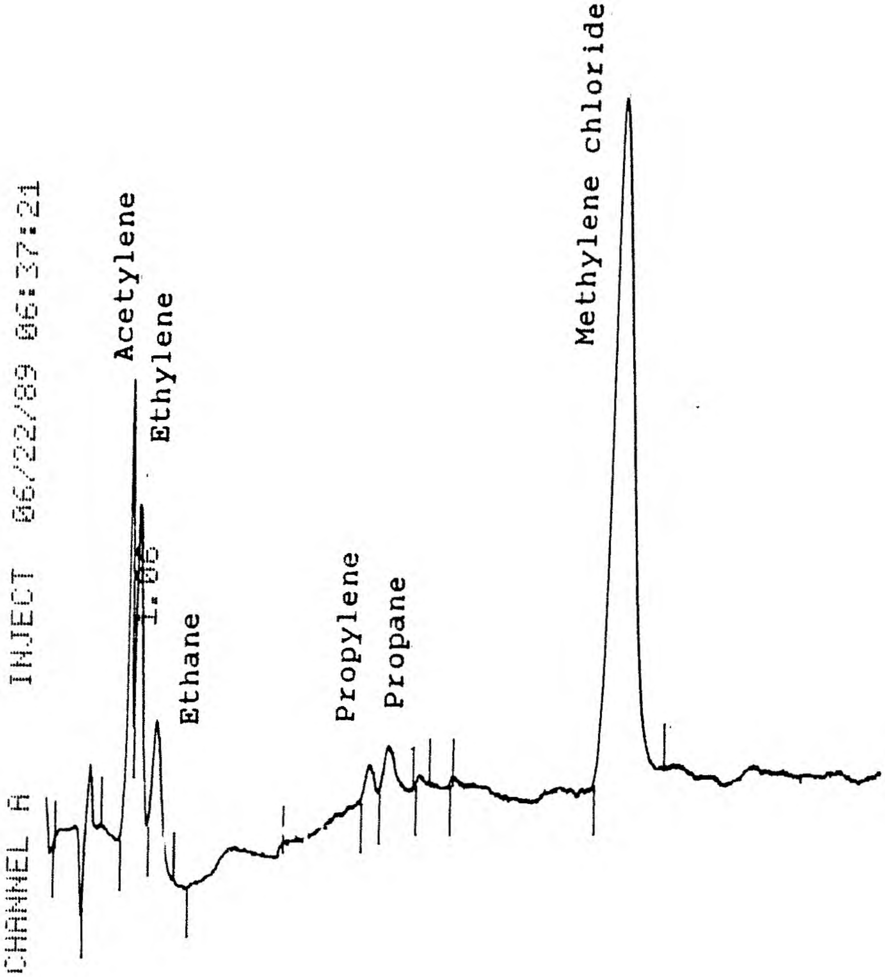


Figure 2-9 (a) The ambient air sample chromatogram

Inject volume : 294 ml
Sampling Date : 6/15/1989
Sampling site : Elizabeth

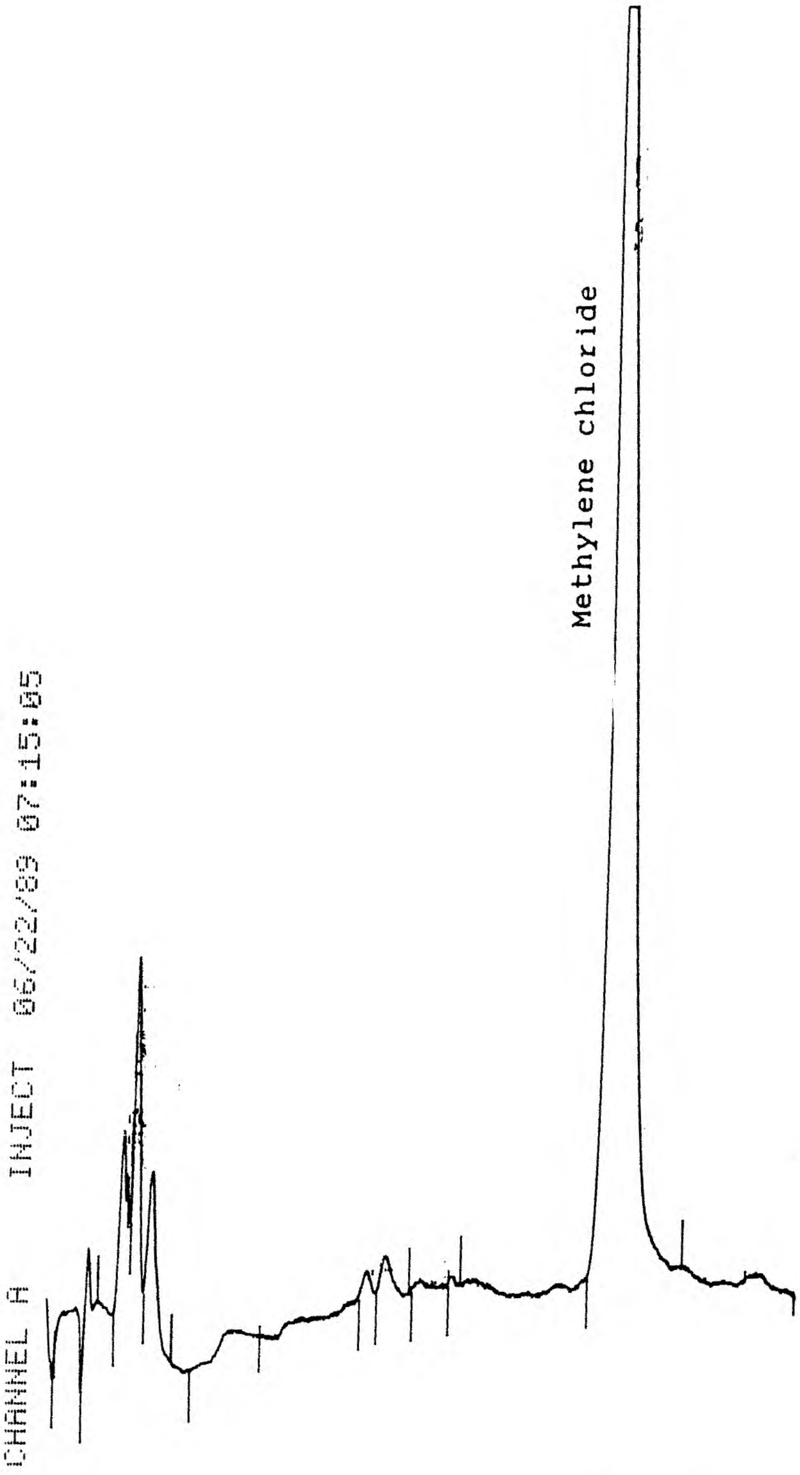


Figure 2-9 (b) The ambient air sample chromatogram
spike with 0.5 ul Methylene Chloride pure gas

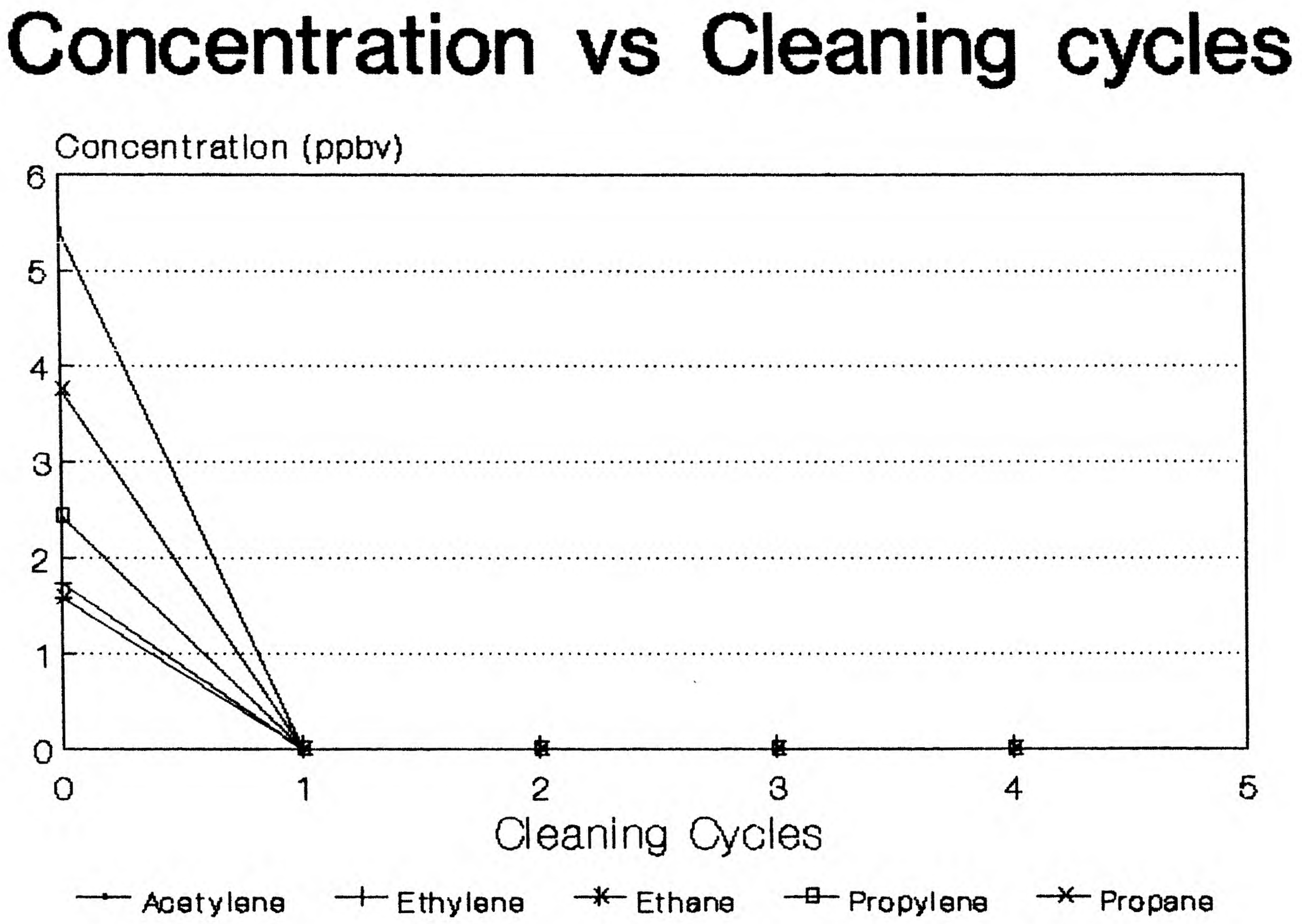
sample inject volume : 294 ml
sampling date : 6/15/1989
sampling site : Elizabeth

CHAPTER 3 QUALITY CONTROL

1. Blank Test

a. Cleaning procedure improvememt

Two different methods of cleaning the sample canister are investigated in this study. Our goal is to find a simple, but effective cleaning procedure and reduce the cleaning cycle time to an acceptable limit; but still retaining a through cleaning process. The first method is very time consuming. Six cycles of filling the canister with zero air and then evacuating for 45 minutes at 0.1 mm-Hg are found to be good for cleaning the canister effectively, but the step of keeping the canister in vacuumn for 45 minutes is deemed too time consuming. A faster (second) method, where we evacuate the canister only for 3 cycles and held it at vacuum for only 5 minutes is tried. A cleaning cycle curve (Figure 3-1) shows the condition of the zero air in the canister in each different cycle. The concentration of target compounds in the canister go to zero for only one cleaning cycle. After three cycles cleaning, all the compounds are undetectable. The chromatograms of three cleaning cycles are presented in figure 3-2, 3-3 and 3-4. We therefore concluded that the process of 3 cleaning cycles is



Sampling date 5/28/89, Elizabeth

Figure 3-1 Concentration of VOC in Canister vs Cleaning Cycles

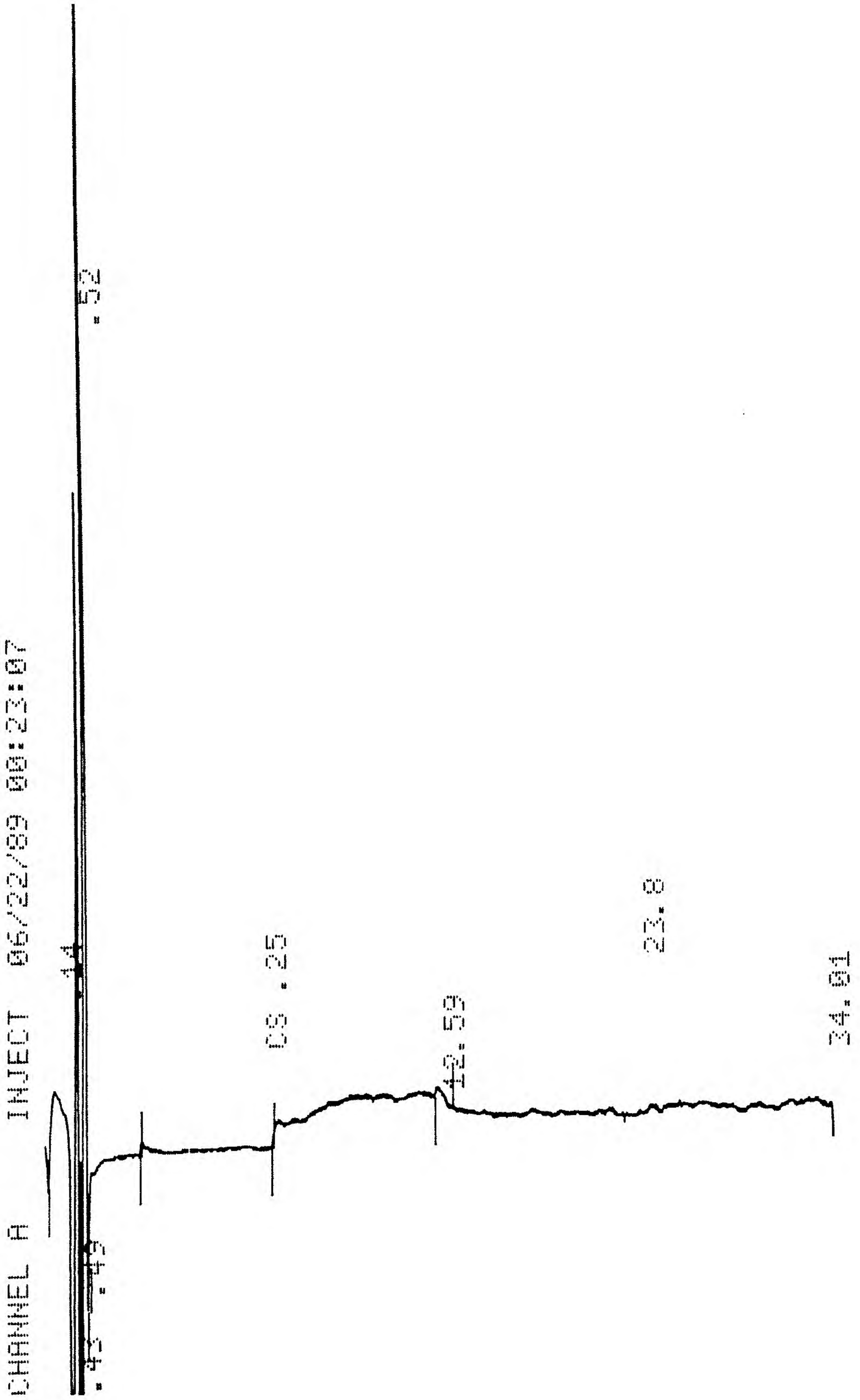


Figure 3-2 The GC Chromatogram of lank Test After One Cycle Cleaned

Inject Volume : 956 ml

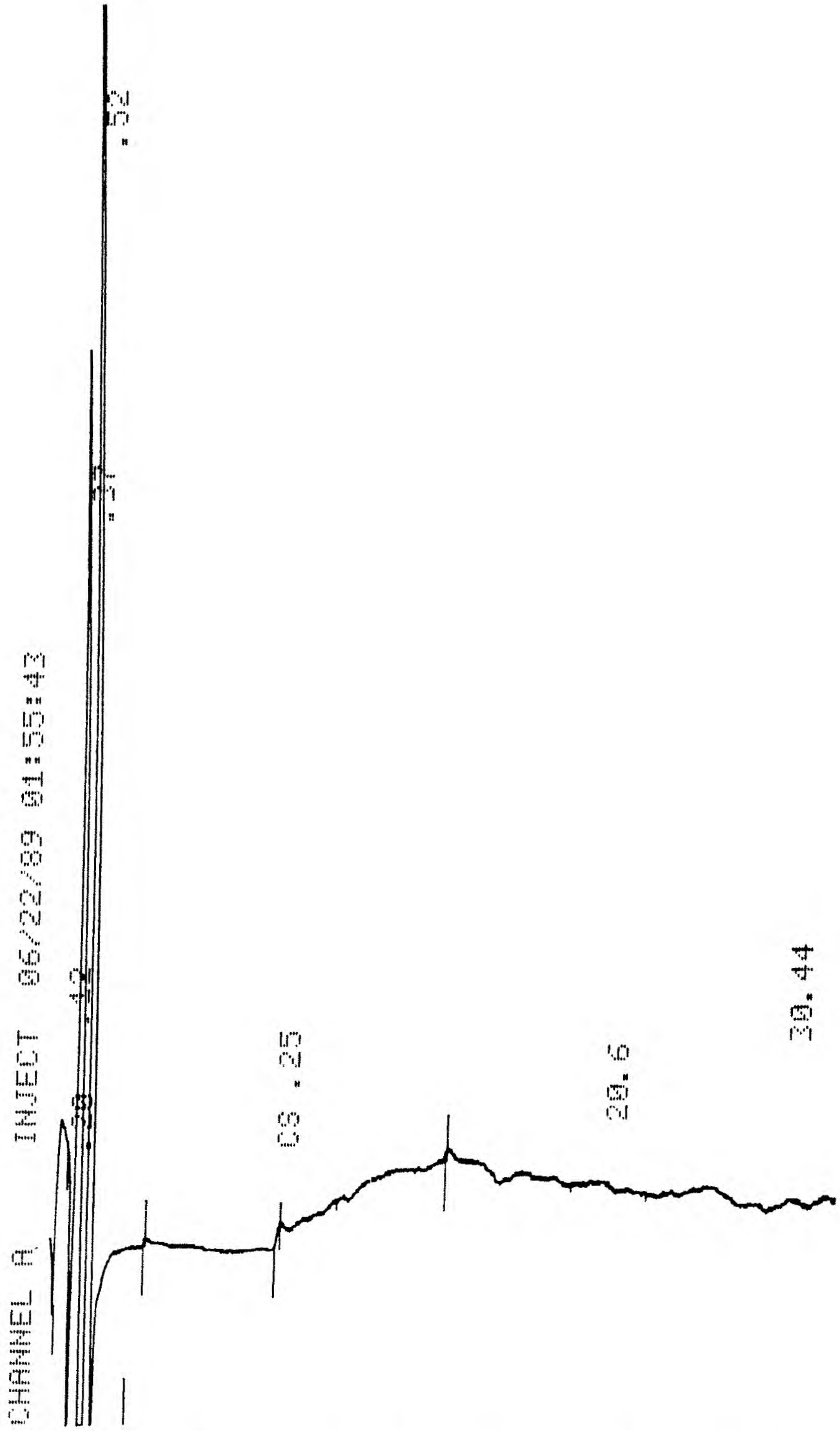


Figure 3-3 The GC Chromatogram of lank Test After Two Cycles Cleaned

Inject Volume : 1088 ml

considered sufficient for the sampling and analysis.

b. Blank tests of canisters

A sample from a "clean" canister is analyzed in the laboratory as blank. The sample canister is cleaned and evacuated as the routine procedure. Instead of collecting air sample, however the canister is filled with zero air to 30 psig (15 psia). Blanks are analyzed every two months through this procedure to insure the quality of sample collection. The chromatogram of the blank analysis is in figure 3-4. The tests of blank result non detected level of of all compounds.

B. Reproducibility of Analysis

1. Reproducibility of mixed standard analysis

The reproducibility of mixed standard analysis is determined by analyzing six runs of the standard gas, for both (separately) the cryo focusing and non-cryo focusing injection procedure. The results are listed in table 3-1 and 3-2. For cryo cooling analysis the relative standard deviation of acetylene is 3.7%, ethylene is 2.72%, ethane is 3.77%, propyne is 7.97%, propylene is 7.25%, and propane is

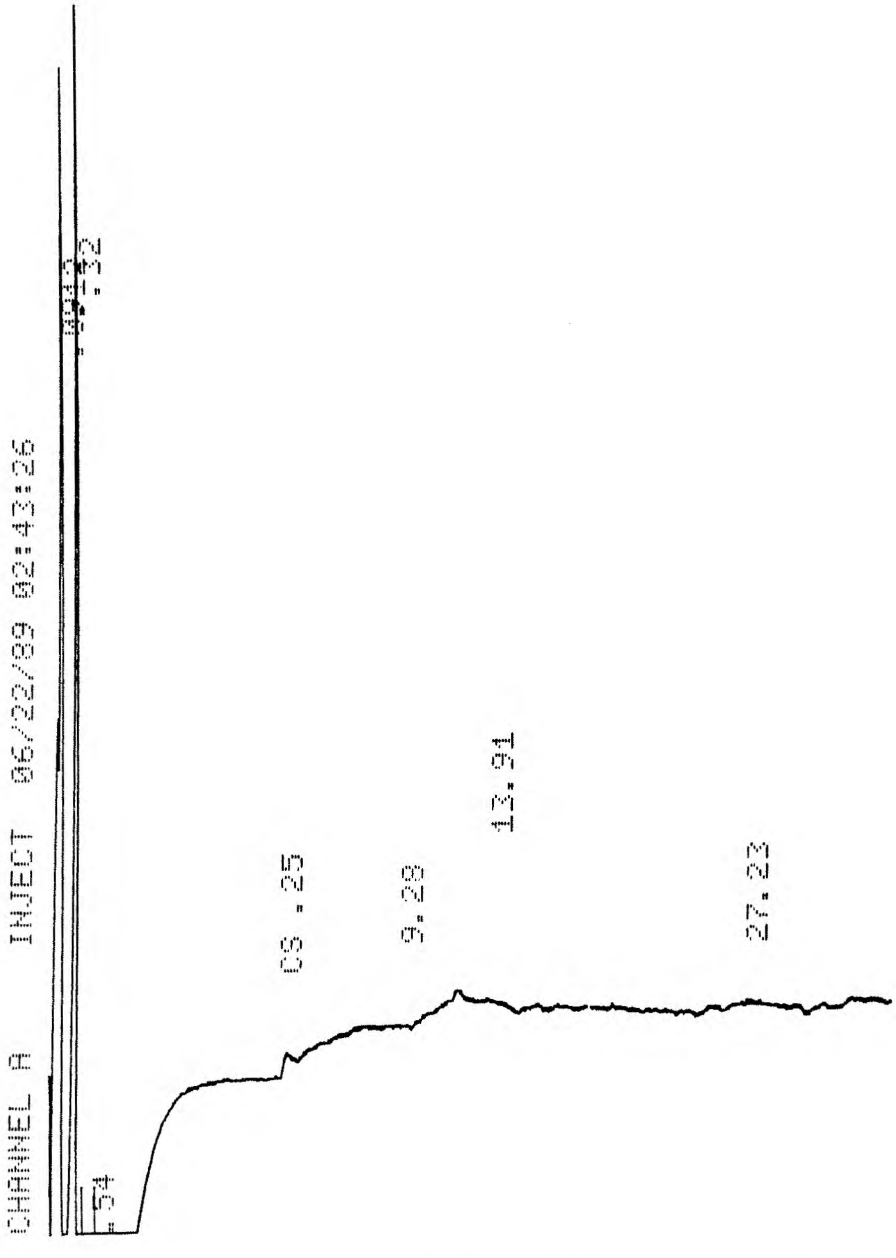


Figure 3-4 The GC Chromatogram of lank Test After Three Cycles Cleaned

Inject Volume : 1177 ml

TABLE 3-1

RESULTS OF STANDARD GAS MIXTURE ANALYSIS --- REPRODUCIBILITY

I. CRYOGENIC INJECTION

COMPOUND	CONC. PPM	RUN 1 PA	ERROR %	RUN 2 PA	ERROR %	RUN 3 PA
ACETYLENE	18.55	183113	0.48	183354	0.62	188338
ETHYLENE	20.00	198099	0.56	200288	1.67	195570
ETHANE	19.99	199575	0.44	199636	0.47	196579
PROPYNE	19.99	210000	-5.23	234185	5.69	237771
PROPYLENE	20.07	279672	-1.92	321608	12.78	281879
PROPANE	19.99	309758	-0.06	319093	2.95	305706

COMPOUND	ERROR %	RUN 4 PA	ERROR %	CONC. PPM	RUN 5 PA	ERROR %
ACETYLENE	3.35	189178	3.81	18.55	171096	-6.11
ETHYLENE	-0.73	205201	4.16	20.00	191170	-2.96
ETHANE	-1.07	212303	6.85	19.99	192235	-8.25
PROPYNE	7.31	229458	3.56	19.99	191304	-13.66
PROPYLENE	-1.15	292303	2.51	20.07	260252	-8.73
PROPANE	-1.37	320853	3.52	19.99	293377	-5.35

COMPOUND	RUN 6 PA	ERROR %	AVERAGE PA	RELATIVE STANDARD DEVIATION %
ACETYLENE	178307	-2.15	182231	3.70
ETHYLENE	191662	-2.71	196998	2.72
ETHANE	191853	-3.44	198697	3.77
PROPYNE	226752	2.33	221578	7.97
PROPYLENE	275220	-3.48	285156	7.25
PROPANE	310887	0.30	309946	3.21

* ERROR % RELATIVE TO AVERAGE

TABLE 3-2

RESULTS OF STANDARD GAS MIXTURE ANALYSIS --- REPRODUCIBILITY

II. NON-CRYOGENIC INJECTION

COMPOUND	CONC. PPM	RUN 1 PA	ERROR %	RUN 2 PA	ERROR %	RUN 3 PA
ACETYLENE	18.55	178457	0.79	185071	4.52	179996
ETHYLENE	20.00	179617	-0.03	186845	3.99	183236
ETHANE	19.99	181586	-0.34	192171	5.47	186019
PROPYNE	19.99	240381	0.43	249538	4.25	252108
PROPYLENE	20.07	255367	0.06	264406	3.60	266809
PROPANE	19.99	297524	-0.24	309350	3.73	323271

COMPOUND	ERROR %	RUN 4 PA	ERROR %	CONC. PPM	RUN 5 PA	ERROR %
ACETYLENE	1.66	172767	-2.43	18.55	173465	-2.03
ETHYLENE	1.99	176034	-2.02	20.00	176312	-1.87
ETHANE	2.09	178629	-1.96	19.99	177178	-2.76
PROPYNE	5.33	228042	-4.73	19.99	229659	-4.05
PROPYLENE	4.54	241305	-5.45	20.07	246062	-3.59
PROPANE	8.40	283029	-5.10	19.99	281430	-5.63

COMPOUND	RUN 6 PA	ERROR %	AVERAGE PA	RELATIVE STANDARD DEVIATION %
ACETYLENE	172609	-2.51	177061	2.83
ETHYLENE	175966	-2.06	179668	2.52
ETHANE	177630	-2.51	182202	3.23
PROPYNE	236401	-1.23	239355	4.17
PROPYLENE	257380	0.85	255222	3.92
PROPANE	294774	-1.16	298230	5.36

* ERROR % RELATIVE TO AVERAGE

3.21%. For non-cryo cooling analysis the relative standard deviation of acetylene is 2.83%, ethylene is 2.52%, ethane is 3.23%, propyne is 3.23%, propylene is 4.17%, propane is 5.36%. The analysis error of each run is also listed in the table and presented by percent (%) error. The results show that both of the cryo focusing and non-cryo focusing injections are in an acceptable reproducibility.

b. Reproducibility of ambient air analysis

Several air samples are selected to illustrate the reproducibility of our experiments in a time frame of one sampling period. Five to six analysis runs are made on every selected sample as part of our routine work. The error is calculated and illustrated by the relative standard deviation for six points. A calculation working sheet and results are listed in table 3-3 (February 1989) and table 3-4 (March 1989).

The results show that each target compound has its own error range. C_2 compounds usually have smaller standard deviations than C_3 compounds. This because the GC peaks of C_2 compounds have better resolution than the C_3 compounds on our GC column.

Table 3-3

Calculation sheet of canister air samples

		Standard		GC parameter
Sample pick up date :	02/03/89			
Site, Canister no. :	Carteret #D	Std ID	C1-C4	Range 10
Analysis date :	2/13/89	STD' VOL	0.39 ml	FID 250 C
Evacuated chamber vol (ml) :	2200	temp(C)	95.00	ECD 280 C
Laboratory temperature (C) :	25	P (psia)	14.70	Att 16 - integrator

LH0289 LH0203 standard :2/13/89			Run 1		Run 2		Run 3		Run 4	
			ΔP(inHg)	14.00	ΔP(inHg)	11.00	ΔP(inHg)	11.00	ΔP(inHg)	11.00
Compound	Std ppm	Std' PA	PA	ppb	PA	ppb	PA	ppb	PA	ppb
1. Acetylene	18.55	59545	26402	3.12	28980	4.35	30446	4.57	29872	4.49
2. Ethylene	20	63886	39922	4.73	34224	5.17	35257	5.32	35819	5.41
3. Ethane	19.99	63218	28397	3.40	34919	5.32	35248	5.28	38184	5.82
4. Propyne	19.99	80517	0	0.00	0	0.00	0	0.00	0	0.00
5. Propylene	20.07	87618	17540	1.52	21164	2.34	21078	2.33	14117	1.56
6. Propane	19.99	109993	68139	4.69	59382	5.20	59098	5.18	56935	4.99

			Run 5		Run 6			
			ΔP(inHg)	10.00	ΔP(inHg)	7.20	total run no. :	6
Compound	Std ppm	Std PA	PA	ppb	PA	ppb	Avg ppb	relative std dev %
1. Acetylene	18.55	59545	25940	4.29	23341	5.36	4.36	15.11
2. Ethylene	20	63886	30528	5.07	27904	6.44	5.36	9.86
3. Ethane	19.99	63218	31850	5.34	28416	6.62	5.30	18.27
4. Propyne	19.99	80517	0	0.00	0	0.00	0.00	ERR
5. Propylene	20.07	87618	11277	1.37	11701	1.97	1.85	21.00
6. Propane	19.99	109993	45867	4.42	44312	5.93	5.07	9.34

Remark :	Temp prog	Loop
	135(3)-6-195	ID 1/8" , 9" length filled with inert glass beads

FID Air: 495 ml/min
H2 : 47 ml/min
PA : peak area
Δ P : pressure difference into sandard volume
volume calculated from P1V1 = P2V2 (ideal gas)

Table 3-4

Calculation sheet of canister air samples

Sample pick up date : 03/17/89
Site, Canister no. : Elizabeth #A
Analysis date : 03/23/89
Evacuated chamber vol (ml) : 2200
Laboratory temperature (C) : 25

Standard		GC parameter
Std ID	C1-C4	Range 10
Std vol	0.39 ml	FID 250 C
temp(C)	95.00	ECD 280 C
P (psia)	14.70	Att 16 - integrator

		Run 1		Run 2		Run 3		Run 4	
03/23/89		ΔP(inHg)	8.00	ΔP(inHg)	12.00	ΔP(inHg)	9.60	ΔP(inHg)	8.80
Std ppm	Std PA	PA	ppb	PA	ppb	PA	ppb	PA	ppb
18.55	56428	39699	7.69	56137	8.16	50851	7.39	48394	8.44
20	63297	57484	10.70	89081	12.44	84263	11.77	69513	11.65
19.99	63792	109663	20.25	183030	25.35	180354	24.98	151449	25.17
19.99	78457	0	0.00	0	0.00	0	0.00	0	0.00
20.07	92437	266923	34.15	406798	39.04	342529	32.87	307123	35.37
19.99	109069	750072	81.02	1200711	97.27	982860	79.62	904133	87.89

total run no. : 5

		Run 5		Run 6			
		ΔP(inHg)	8.00	ΔP(inHg)	0.00		
Std ppm	Std PA	PA	ppb	PA	ppb	Avg ppb	relative std dev %
18.55	56428	41711	8.08	0	0.00	7.95	4.64
20	63297	66076	12.30	0	0.00	11.77	5.22
19.99	63792	131057	24.20	0	0.00	23.99	7.96
19.99	78457	0	0.00	0	0.00	0.00	ERR
20.07	92437	277712	35.54	0	0.00	35.39	5.82
19.99	109069	791447	85.49	0	0.00	86.26	7.26

Temp prog	Loop
135(3)-6-195	ID 1/8" , 9" length filled with inert glass beads

FID Air: 495 ml/min
H2 : 47 ml/min
PA : peak area
Δ P : pressure difference into standard volume
volume calculated from P1V1 = P2V2 (ideal gas)

C. Recovery Rate

The recovery rate of our analysis was determined by two types of injections: one was routine sample injection and another was routine sample spiked with known volume standard gas. The analysis of the sample only injections and the sample plus standard gas injection allow calculation of the recovry rate. Table 3-5 lists the result of this determination.

TABLE 3-5 RECOVERY RATE OF OUR TARGET COMPOUNDS

COMPOUND	STANDARD *CONC.	STANDARD PEAK AREA 1	SAMPLE PEAK AREA 1	SAMPLE PEAK AREA 2	SPIKE PEAK AERA 1
acetylene	18.55	41041	25234	24848	93400
ethylene	20.00	56062	24027	21529	79624
ethane	19.99	54714	23359	22216	93743
propylene	20.07	104958	36006	43874	232333
propane	19.99	83804	48899	64949	464989

* CONC. PPMV
STANDARD GAS INJECT 0.3 ML
AIR SAMPLE INJECT 463.2 ML

The recovery rate was calculated by comparing the volume of target compounds injected with the volume of the target compound plus standard gas injected. The calculation is presented only for acetylene.

0.3 ml of standard gas was concentrated in cryo loop and injected into the GC, the concentration of acetylene in the standard gas is 18.55 ppmv. Thus, the volume of acetylene in this injection is:

$$18.55 \text{ ppmv} = 18.55 \ (\text{ml}/\ 10^{6} \text{ ml})$$

$$\frac{18.55 \text{ ml}}{10^{6} \text{ ml}} * 0.3 \text{ ml} = 5.565*10^{-6} \text{ ml}$$

of acetylene injected

The injecting volume of acetylene from the ambient air is (data from table 3-5) :

$$\frac{\overset{\text{(sample)}}{(25234 + 24848)/2}}{\underset{\text{(STD')}}{41041}} * 0.3 \text{ ml} * \frac{18.55 \text{ ml}}{10^{6} \text{ ml}}$$

$$= 3.40 * 10^{-6} \text{ ml}$$ of acetylene injected

--- in sample using above standard to calculate ppm of sample

The injecting volume of acetylene of the sample plus 0.3 ml standard gas is:

$$\frac{93400}{41041} * 0.3 \text{ ml} * \frac{18.55 \text{ ml}}{10^{6} \text{ ml}}$$

$$= 12.66*10^{-6} \text{ ml}$$ of acetylene in the injection of sample plus standard gas

The recovery rate of acetylene in our analysis is:

$$\frac{(12.66*10^{-6} - 5.565*10^{-6})\ \text{ml}}{3.40*10^{-6}\ \text{ml}} * 100\% = 208.2\ \%$$

* Note this is only one estimate --- it is in process of being repeated

The recovery rate of our target compounds are listed in table 3-6.

TABLE 3-6 RECOVERY RATE OF TARGET COMPOUND

COMPOUND	RECOVERY RATE %
acetylene	208.2
ethylene	103.3
ehtane	171.2
propylene	449.8
propane	670.0

Table 3-6 shows the recovery rate of our target compounds and only ethylene is in the acceptable range (80 % to 120 %). The reason why We can not have a good recovery rate may result from the difference between the concentration of our standard gas and the concentration of air sample.

CHAPTER 4 ANALYSIS DETAILS

1. Cryotrap Volume Estimation

Initially, the 1 ml standard loop have been used for analyzing the standard gases and a separate 1/8" OD loop (filled with glass beads) is used as a cryotrap to analyze the air samples respectively. With this two loop operation, we need to change the loop whenever we changed analysis. This is not convenient for routine analysis and causes the excessive wear on the tube fittings of the 6-port valve. We therefore, calibrate the sampling cryo loop volume (filled with glass beads) so that we could use it for both analysis. If we know the volume of the packed cryo trap, we can use only one loop for both standard gas analysis without cryotrapping and for sample analysis with cryotrapping.

The volume of the loop which filled with glass beads is unknown. The unknown volume is calculated by the loop of standard volume, 1 ml. The unknown volume loop is installed on the 6-port valve and inject the mixed standard gas as usual. Then, the mixed standard gas is also injected by the standard volume loop. The estimation of the unknown volume is done by comparing the peak area of 1 ml standard loop with the peak area of unknown volume loop. The result of these studies are listed in table 4-1 and 4-2 the unknown volume is 0.368 ml.

2. Calculation of Hydrocarbon Concentration in Canister Sample

Three assumptions are included :

i. 100 % cryo trap collection efficiency.

ii. 100 % thermal release efficiency from the cryo trap into the GC column.

iii. All the sample gases obey the ideal gas law.

The quantitation of each target compound is calculated by comparing the peak area of each compound in the standard with the peak area of the respective compound in the air sample. The ratio of the peak area of sample to the peak area of standard gas on the chromatogram equals the ratio of the number of moles injected. The number of moles of each specie equals to total moles of the injected air or gas times its mole fraction concentration. The unit of ppb by volume is used for moles is proportion to volume.

For a Y compound :

$$\frac{\text{peak area of Y compound in the air } (PA_Y)}{\text{peak area of Y compound in standard gas } (PA_{std})}$$

TABLE 4-1

ESTIMATION OF UNKNOWN VOLUME CYRO TRAP WITH STANDARD TRAP

The unknown volume is measured by comparing the peak area of 1 ml standard gas injection with the peak area of unknown.

Volume of Standard Trap: 1ml
Volume of Unknown Trap: ?ml

I. Unknown Volume Trap

COMPOUND	CONC. PPM	RUN 1 PA	ERROR %	RUN 2 PA	ERROR %	RUN 3 PA
ACETYLENE	18.55	75150	-0.86	75394	-0.54	76750
ETHYLENE	20.00	83038	-1.42	84127	-0.13	85063
ETHANE	19.99	84253	-1.28	85243	-0.12	86238
PROPYNE	19.99	104487	1.23	103362	0.14	100807
PROPYLENE	20.07	112283	2.54	110914	1.29	107071
PROPANE	19.99	135304	0.81	132633	-1.18	134202

COMPOUND	ERROR %	RUN 4 PA	ERROR %	CONC. PPM	RUN 5 PA	ERROR %
ACETYLENE	1.25	76659	1.13	18.55	75073	-0.97
ETHYLENE	0.98	85647	1.68	20.00	83293	-1.12
ETHANE	1.05	87029	1.97	19.99	83966	-1.62
PROPYNE	-2.34	110410	6.97	19.99	97034	-5.99
PROPYLENE	-2.22	113652	3.79	20.07	103607	-5.39
PROPANE	-0.01	140347	4.57	19.99	128566	-4.21

COMPOUND	AVERAGE PA	RELATIVE STANDARD DEVIATION %
ACETYLENE	75805	1.10
ETHYLENE	84234	1.33
ETHANE	85346	1.52
PROPYNE	103220	4.78
PROPYLENE	109505	3.75
PROPANE	134210	3.19

ERROR % RELATIVE TO AVERAGE

TABLE 4-2

ESTIMATION OF UNKNOWN VOLUME CYRO TRAP WITH STANDARD TRAP

The unknown volume is measured by comparing the peak area of 1 ml standard gas injection with the peak area of unknown.

II. 1 ml Standard Trap

COMPOUND	CONC. PPM	RUN 1 PA	ERROR %	RUN 2 PA	ERROR %	RUN 3 PA
ACETYLENE	18.55	206202	0.03	205954	-0.09	206311
ETHYLENE	20.00	225067	-0.83	227726	0.37	227240
ETHANE	19.99	224564	-2.64	232473	0.78	232918
PROPYNE	19.99	277348	0.18	275681	-0.43	277718
PROPYLENE	20.07	304241	-0.43	305104	-0.15	306889
PROPANE	19.99	360207	-1.63	366487	0.08	369873

COMPOUND	ERROR %	RUN 4 PA	ERROR %	AVERAGE PA	RELATIVE STD' DEV. %
ACETYLENE	0.08	206123	-0.01	206148	0.07
ETHYLENE	0.16	227483	0.27	226879	0.54
ETHANE	0.98	232695	0.88	230663	1.76
PROPYNE	0.31	276699	-0.06	276862	0.32
PROPYLENE	0.44	305996	0.14	305558	0.37
PROPANE	1.01	368179	0.54	366187	1.15

COMPOUND	RATIO PA OF STD/PA OF UNKNOWN
ACETYLENE	0.368
ETHYLENE	0.371
ETHANE	0.370
PROPYNE	0.373
PROPYLENE	0.358
PROPANE	0.367
AVERAGE	0.368 ml

ERROR % RELATIVE TO AVERAGE

$$= \frac{\text{moles of Y compound in the air } (N_y)}{\text{moles of Y compound in standard gas } (N_y)}$$

$$= \frac{N_{air} * X_y}{N_{std} * X_{y,std}}$$

N_{air} : total moles of air sample

N_{std} : total moles of standard gas

X_y : moles fraction of Y compound in the air

$X_{y,std}$: moles fraction of Y compound in the air

according to ideal gas law :

$$\text{moles } (N) = \frac{\text{pressure } (P) * \text{volume } (V)}{\text{constant } (R) * \text{temperature } (T)}$$

so, for Y compound, we have :

$$\frac{PA_y}{PA_{std}} = \frac{\dfrac{P_{air} * V_{air}}{R * T_{air}} * X_{air}}{\dfrac{P_{std} * V_{std}}{R * T_{std}} * X_{std}} \qquad \text{(a)}$$

X_{air} : mole fraction of Y compound in the air

X_{std} : mole fraction of Y compound in the standard

PA_y : peak area of Y compound in the air

PA_{std}: peak area of Y compound in standard gas

An evacuated cylinder is used to draw air sample through cryo trap from the canister. The pressure in the cylinder rises from P_i to P_f. The moles of loaded air sample gas are equal to the moles of compound condensed on the trap plus the moles of gas which accumulate in the standard volume cylinder.

total moles of the loaded air =

total moles of compounds condense on the trap + total moles of air evacuated into the cylinder

Because the concentrations of the organic compounds in the analyzed air are very low, around several ppb, the moles of compounds which are condensed on the trap can be neglected. Then,

total moles of the loaded air

= total moles of gas increased in the cylinder (N_{air}) (b)

Then, according to the ideal gas law,

$$N_{air} = \frac{P_f * V_{cyl}}{R * T_{cyl}} - \frac{P_i * V_{cyl}}{R * T_{cyl}}$$

$$= \frac{(P_f - P_i) * V_{cyl}}{R * T_{cyl}} \qquad (c)$$

V_{cyl} : volume of the evacuated cylinder

T_{cyl} : temperature of the evacuated cylinder

Substitute (c) into equation (a) and (b) for Y compound, we have

$$\frac{PA_Y}{PA_{std}} = \frac{\dfrac{(P_f - V_i) * V_{cyl}}{R * T_{cyl}} * X_{air}}{\dfrac{(P_{std} * V_{std})}{R * T_{std}} * X_{std}}$$

Therefore, the concentrations of Y compound in the air sample, C_{air}, are equal to

$$C_{air} = \frac{PA_{sample}}{PA_{standard}} * \frac{\dfrac{(P_{std} * P_{std})}{R * T_{std}} * C_{std}}{\dfrac{(P_f - P_i) * V_{cyl}}{R * T_{cyl}}}$$

cancelling the ideal gas law constant, R, we get

$$C_{air} = \frac{PA_{sample}}{PA_{standard}} * \frac{\dfrac{(P_{std} * V_{std})}{T_{std}} * C_{std}}{\dfrac{(P_f - P_i) * V_{cyl}}{T_{cyl}}}$$

Applying the formula to our work, we use a standard gas mixture containing C_1 to C_4 standard with their concentrations around 20 ppm +/- 2 ppb. The gases are purged through a 1 ml (or 0.368 ml) sampling loop to 14.7

psi, at 25° C. The volume of the evacuated cylinder is 2200 ml, at 25° C. The actual operation and calculation, units and values of the parameters are :

PA : peak area in mv sec (millivolt second), from chromatograms and calculated by the integrator.

P_{std} : 14.7 psi, atmosphere pressure

V_{std} : 1 ml (or 0.368 ml)

T_{std} : 25° C, sampling loop in room temperature

C_{std} : concentration of standard gas, ppm

V_{cyl} : 2200 ml

T_{cyl} : 25° C

$P_f - P_i$: reading from pressure gauge, inch-Hg

C_{air} : concentration of air sample, ppb

* Accuracy : +/- 10 % according to Standard Gas
20 +/- 2 ppb

CHAPTER 5 RESULTS AND DISCUSSION

1. Analysis Results

The analysis results of ambient air sample collections from 1988 September through 1989 July, 32 samples at Carteret and 38 samples at Elizabeth are presented in tables 5-1 to 5-8. The seasonal and year-round averages are calculated for each compound at both sites. Those data are listed in tables 5-9 to 5-16.

Acetylene, Ethylene, Ethane, Propylene, and Propane were always detected. Propyne was usually below detection limit or sometimes observed but at concentrations lower than 1 ppbv. Methylene chloride was often detected at the site of Elizabeth (note: We think that the pump at Elizabeth is contaminated with Methylene Chloride). Freon 12 was also routinely detected in both sampling sites, but we did not quantify this because we did not have a standard.

Plots of concentration verses time for the year, September 1988 through July 1989, at both sites, Carteret and Elizabeth, are presented in figures 5-1 to 5-4 by segmental lines.

To compare the C_2 compounds, we put acetylene,

TABLE 5-1

CONCENTRATION OF VOLATILE ORGANIC COMPOUNDS IN AMBIENT AIR

SAMPLING SITE: CARTERET
SAMPLING PERIOD: FALL, SEPT. 1988 TO NOV. 30, 1988
DAILY AND MONTHLY AVERAGES

DATE	DETECTED CONCENTRATION (PPB)v					
	Acetylene	Ethylene	Ethane	Propyne	Propylene	Propane
09/12	14.27	28.43	37.19	ND	14.99	9.87
10/06	3.62	13.52	8.34	ND	3.09	5.21
10/12	8.82	4.89	4.51	ND	1.61	3.00
10/18	6.93	7.31	4.23	ND	2.16	4.89
AVERAGE	3.87	5.41	3.42	ND	1.37	2.62
11/05	2.77	3.96	3.23	ND	0.29	1.76
11/23	4.55	6.66	6.00	ND	4.30	10.88
AVERAGE	3.66	5.31	4.62	ND	2.30	6.32
THREE MONTH AVERAGE	7.27	13.05	15.08	ND	6.22	6.27

TABLE 5-2

CONCENTRATION OF VOLATILE ORGANIC COMPOUNDS IN AMBIENT AIR

SAMPLING SITE: ELIZABETH
SAMPLING PERIOD: FALL, SEPT. 1988 TO NOV.30, 1988
DAILY AND MONTHLY AVERAGES

DATE	DETECTED CONCENTRATION (PPB)v					
	Acetylene	Ethylene	Ethane	Propyne	Propylene	Propane
09/12	6.17	7.03	7.93	ND	20.31	11.45
09/24	8.69	6.24	3.15	ND	2.19	3.09
09/30	7.16	6.21	4.92	ND	5.18	12.56
AVERAGE	7.34	6.49	5.33	ND	9.23	9.03
10/06	9.16	6.30	4.65	ND	1.50	2.93
10/12	7.87	4.22	2.60	ND	1.33	1.92
10/18	3.42	7.78	11.57	ND	11.45	19.32
AVERAGE	6.82	6.10	6.27	ND	4.76	8.06
11/05	1.67	4.42	7.53	ND	38.18	84.02
11/11	6.81	6.18	6.17	ND	3.22	5.02
11/17	8.96	10.96	15.75	ND	2.93	10.98
AVERAGE	5.81	7.19	9.82	ND	14.78	33.34
THREE MONTHS AVERAGE	6.42	6.59	7.14	ND	9.59	18.61

TABLE 5-3

CONCENTRATION OF VOLATILE ORGANIC COMPOUNDS IN AMBIENT AIR

SAMPLING SITE: CARTERET
SAMPLING PERIOD: WINTER, DEC. 1989 TO FEB.28, 1989
DAILY AND MONTHLY AVERAGES

DATE	DETECTED CONCENTRATION (PPB)v					
	Acetylene	Ethylene	Ethane	Propyne	Propylene	Propane
12/05	6.71	9.30	10.63	ND	3.08	1.74
12/17	6.47	7.49	6.63	ND	2.99	6.18
12/23	7.05	11.17	11.85	0.98	5.90	8.13
AVERAGE	6.74	9.32	0.97	0.98	3.99	7.35
01/04	2.97	3.08	4.02	ND	0.36	1.6
02/03	4.36	5.36	5.30	ND	1.85	5.07
02/09	4.52	7.35	7.40	ND	1.56	4.79
02/27	9.39	11.15	14.24	ND	4.48	13.81
AVERAGE	6.09	7.95	8.98	ND	2.63	7.89
THREE MONTHS AVERAGE	5.27	6.78	7.57	ND	2.34	5.61

TABLE 5-4

CONCENTRATION OF VOLATILE ORGANIC COMPOUNDS IN AMBIENT AIR

SAMPLING SITE: ELIZABETH
SAMPLING PERIOD: WINTER, DEC. 1989 TO FEB.28, 1989
DAILY AND MONTHLY AVERAGES

DATE	DETECTED CONCENTRATION (PPB)v					
	Acetylene	Ethylene	Ethane	Propyne	Propylene	Propane
12/05	6.56	9.53	12.45	ND	11.76	29.88
12/11	1.98	1.83	3.38	ND	1.23	3.06
AVERAGE	4.27	5.68	7.92	ND	6.50	16.47
01/04	3.05	2.74	4.48	ND	0.79	1.93
01/10	5.48	10.52	13.43	ND	11.64	31.02
01/22	11.25	19.10	34.53	0.43	17.23	27.11
01/28	1.73	4.58	10.15	ND	6.61	12.79
AVERAGE	5.38	9.24	15.65	0.43	9.07	18.21
02/03	4.39	3.83	5.26	ND	0.74	2.92
02/09	4.29	5.62	8.55	0.42	2.56	6.60
02/27	2.87	3.18	6.69	ND	ND	3.94
AVERAGE	5.38	4.21	6.83	0.42	1.65	4.49
THREE MONTHS AVERAGE	5.01	6.38	10.13	0.42	5.74	13.06

TABLE 5-5

CONCENTRATION OF VOLATILE ORGANIC COMPOUNDS IN AMBIENT AIR

SAMPLING SITE: CARTERET
SAMPLING PERIOD: SPRING, MAR. 1989 TO MAY.30, 1989
DAILY AND MONTHLY AVERAGES

DATE	DETECTED CONCENTRATION (PPB)v					
	Acetylene	Ethylene	Ethane	Propyne	Propylene	Propane
03/05	6.94	8.18	9.23	ND	6.54	13.02
03/17	3.39	1.99	6.76	ND	0.54	5.79
03/23	3.95	2.46	4.96	ND	ND	ND
03/29	6.28	6.32	7.47	ND	1.47	3.62
AVERAGE	5.14	4.74	7.11	ND	2.85	7.48
04/04	6.00	6.64	6.90	ND	3.58	13.76
04/10	6.00	3.06	4.29	ND	0.84	3.11
04/16	13.98	15.15	14.78	ND	4.36	10.62
04/28	2.56	1.51	2.92	ND	ND	1.52
AVERAGE	7.14	6.59	7.22	ND	2.93	7.25
05/04	7.22	8.71	7.22	ND	4.76	7.12
05/10	5.71	7.35	7.02	ND	ND	ND
05/28	3.93	1.52	1.35	ND	3.49	3.25
AVERAGE	5.62	5.86	5.20	ND	4.13	5.19
THREE MONTHS AVERAGE	5.97	5.73	6.51	ND	3.30	6.64

TABLE 5-6

CONCENTRATION OF VOLATILE ORGANIC COMPOUNDS IN AMBIENT AIR

SAMPLING SITE: ELIZABETH
SAMPLING PERIOD: SPRING, MAR. 1989 TO MAY 31, 1989
DAILY AND MONTHLY AVREAGES

DATE	DETECTED CONCENTRATION (PPB)v					
	Acetylene	Ethylene	Ethane	Propyne	Propylene	Propane
03/11	5.67	7.47	12.20	ND	10.05	17.44
03/17	7.95	11.77	23.99	ND	35.39	86.26
03/23	3.95	2.16	4.96	ND	ND	ND
03/29	6.28	6.32	7.47	ND	1.47	3.62
AVERAGE	5.96	6.93	12.16	ND	15.64	35.77
04/04	13.60	21.46	22.82	0.61	21.24	27.38
04/10	4.66	2.68	3.36	ND	1.14	2.46
04/22	3.65	2.08	3.78	ND	0.26	2.42
04/28	1.87	1.74	2.03	ND	3.41	5.53
AVERAGE	5.95	6.99	8.00	0.61	6.51	9.45
05/04	4.18	4.96	7.33	2.61	45.64	43.77
05/10	5.83	8.05	7.64	ND	2.20	2.96
05/28	5.42	1.74	1.59	ND	2.43	3.74
AVERAGE	5.14	4.92	5.52	2.61	16.76	16.82
THREE MONTHS AVERAGE	5.68	6.07	8.58	1.61	12.97	20.86

TABLE 5-7

CONCENTRATION OF VOLATILE ORGANIC COMPOUNDS IN AMBIENT AIR

SAMPLING SITE: CARTERET
SAMPLING PERIOD: SUMMER, JUNE 1989 TO JULY 31, 1989
DAILY AND MONTHLY AVERAGES

DATE	DETECTED CONCENTRATION (PPB)v					
	Acetylene	Ethylene	Ethane	Propyne	Propylene	Propane
06/03	3.32	2.25	1.61	ND	2.15	3.37
06/09	8.64	5.03	2.06	ND	7.83	10.31
06/16	7.79	7.41	3.14	ND	8.58	16.31
06/27	9.01	12.44	11.37	ND	1.02	2.73
AVERAGE	7.19	6.78	4.55	ND	4.90	8.18
07/09	14.07	12.63	14.32	ND	1.66	7.03
07/15	3.20	4.36	4.11	ND	ND	3.24
07/21	5.72	4.94	ND	ND	ND	8.30
07/27	3.36	6.24	6.42	ND	ND	ND
AVERAGE	8.78	7.04	8.28	ND	1.66	6.19
TWO MONTHS AVERAGE	7.98	6.91	6.4	ND	3.28	7.18

TABLE 5-8

CONCENTRATION OF VOLATILE ORGANIC COMPOUNDS IN AMBIENT AIR

SAMPLING SITE: ELIZABETH
SAMPLING PERIOD: SUMMER, JUNE 1989 TO JULY 31, 1989
DAILY AND MONTHLY AVERAGE

DATE	DETECTED CONCENTRATION (PPB)v					
	Acetylene	Ethylene	Ethane	Propyne	Propylene	Propane
06/03	4.72	4.21	3.10	ND	15.99	41.91
06/09	10.35	7.97	2.69	ND	10.91	12.96
06/16	13.02	15.11	8.31	ND	5.73	8.15
06/21	6.50	6.29	2.39	2.86	16.48	16.31
06/27	5.74	5.05	1.36	2.17	3.72	4.20
AVERAGE	8.07	7.73	3.57	2.52	10.57	16.71
07/04	6.76	4.49	4.53	ND	3.37	22.47
07/09	4.76	4.87	3.94	ND	3.75	9.27
07/21	5.64	7.50	1.54	1.86	5.74	7.21
07/27	16.78	17.96	14.98	ND	11.86	13.46
AVERAGE	8.48	8.70	6.24	1.86	6.18	13.10
TWO MONTHS AVERAGE	8.27	8.21	4.90	2.19	8.37	14.90

ethylene, and ethane in figure 5-1 and 5-2, and C_3 compounds, propylene, and propane in figures 5-3 and 5-4 for Carteret and Elizabeth respectively. We can readily observe that the distribution of the three C_2 and two C_3 compounds track very well. Fluctuations of all five compounds are similar through out the entire year.

The compounds, in figures 5-1 to 5-4 show some concentration peaks almost every month and these occur consistently for the three C_2 VOCs. The C_3 compounds also show similar results to the C_2 compounds.

2. Seasonal Concentration Changes of Target Compounds

The seasonal concentraion changes are discussed separatly. The year is divided into four seasons, fall (Sep. to Nov. 1988), winter (Dec. 1988 to Feb. 1989), spring (Mar. to May 1989), and summer (June to July 1989).

The three months average concentrations of acetylene, ethylene, ethane, propylene, and propane are : 7.27, 13.05, 15.08, 6.22, 6.27 ppbv, at Carteret in the fall. The average, highest and lowest concentrations in fall at Carteret are shown in table 5-9.

The three months average concentrations of acetylene,

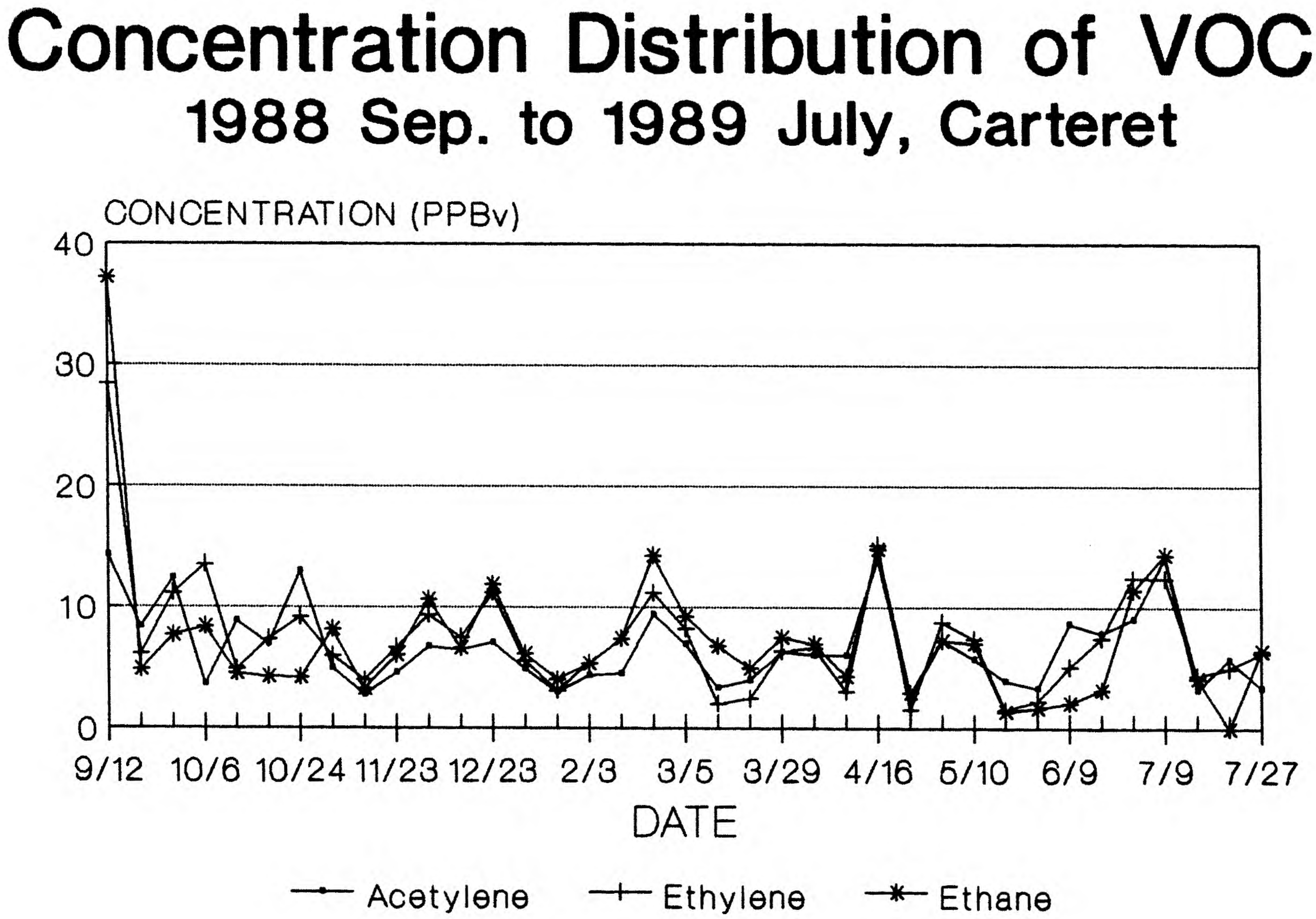


Figure 5-1 Concentration Distribution of Acetylene Ethylene, and Ethane at Carteret

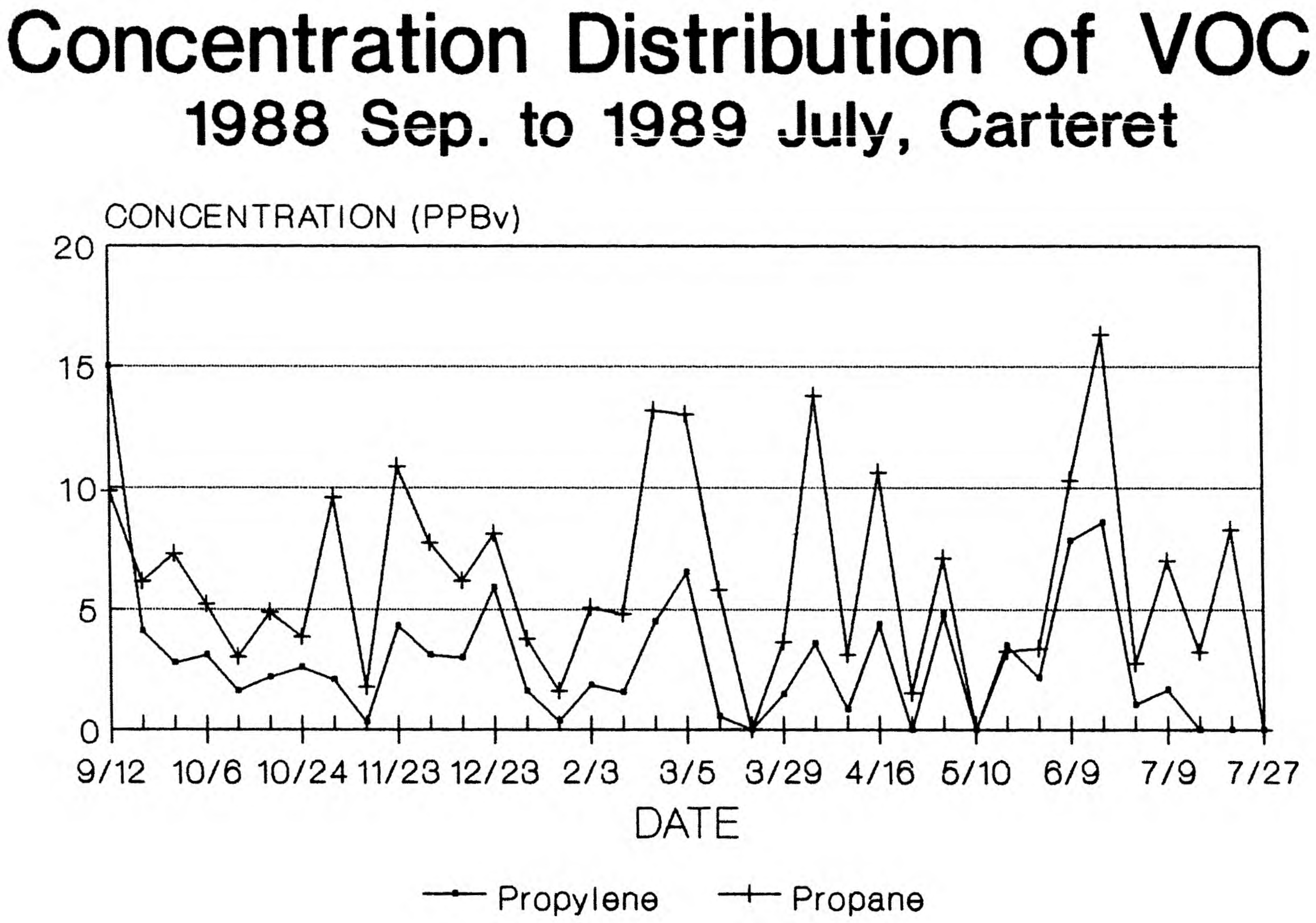


Figure 5-2 Concentration Distribution of Propylene and Propane at Carteret

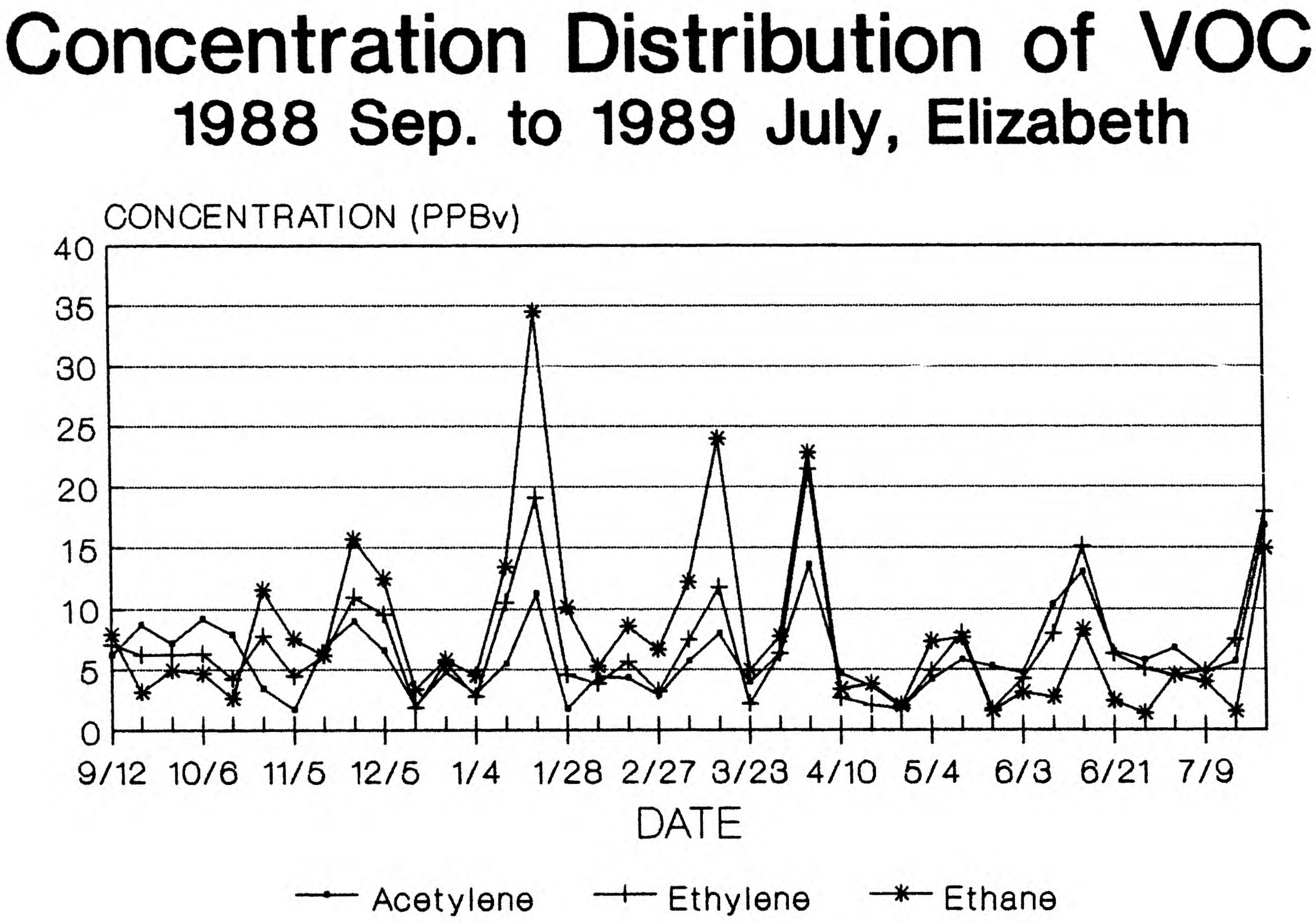


Figure 5-3 Concentration Distribution of Acetylene Ethylene, and Ethane at Elizabeth

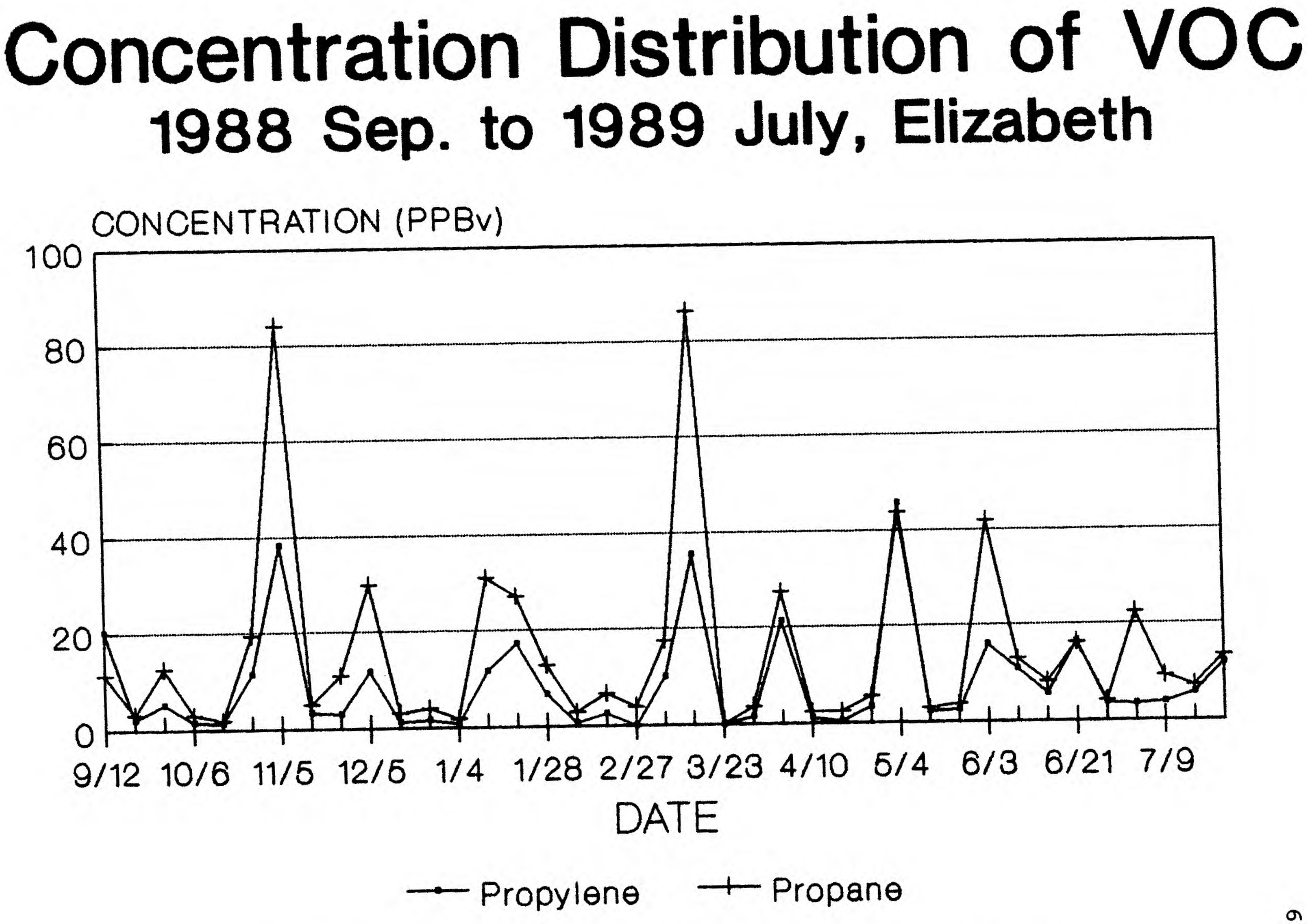


Figure 5-4 Concentration Distribution of Acetylene Ethylene, and Ethane at Elizabeth

ethylene, ethane, propylene, and propane are: 6.42, 6.59, 7.14, 9.59, and 18.61 ppbv, at Elizabeth in the fall. The average, highest, and lowest concentrations in fall at Elizabeth are shown in table 5-10.

The three months average concentrations of acetylene, ethylene, ethane, propylene, and propane are: 5.27, 6.78, 7.57, 2.34, and 5.61 ppbv, at Carteret in the winter. The average, highest, and lowest concentrations in fall at Carteret are shown in table 5-11.

The three months average concentrations of acetylene, ethylene, ethane, propylene, and propane are: 5.01, 6.38, 10.13, 6.74, and 13.0 ppbv, at Elizabeth in the winter. The average, highest, and lowest concentrations in fall at Elizabeth are shown in table 5-12.

The three months average concentrations of acetylene, ethylene, ethane, propylene, and propane are: 5.97, 5.73, 6.51, 3.30, and 6.64 ppb, at Carteret in the spring. The average, highest, and lowest concentrations in spring at Carteret are shown in table 5-13

The three months average concentrations of acetylene, ethylene, ethane, propylene, and propane are: 5.68, 6.07, 8.58, 12.97, and 20.86 ppbv, at Elizabeth in the spring.

TABLE 5-9 SEASONAL AVERAGE, LOWEST, AND HIGHEST CONCENTRATION OF AMBIENT AIR

compounds	average	concentration (ppb) lowest	month	highest	month
Acetylene	7.27	2.77	Nov.	14.27	Sept.
Ethylene	13.05	3.96	Nov.	28.43	Sept.
Ethane	15.08	3.23	Nov.	37.19	Sept.
Propylene	6.22	0.29	Nov.	14.99	Sept.
Propane	6.27	1.76	Nov.	10.88	Nov.

* sampling site: carteret , 1988 Fall

TABLE 5-10 SEASONAL AVERAGE, LOWEST, AND HIGHEST CONCENTRATION OF AMBIENT AIR

compounds	average	concentration (ppb) lowest	month	highest	month
Acetylene	6.42	1.67	Nov.	9.16	Oct.
Ethylene	6.59	4.22	Oct.	10.96	Nov.
Ethane	7.14	2.60	Oct.	15.75	Nov.
Propylene	9.59	1.33	Oct.	38.18	Nov.
Propane	18.61	1.92	Oct.	84.02	Nov.

* sampling site: elizabeth, 1988 Fall

TABLE 5-11 SEASONAL AVERAGE, LOWEST, AND HIGHEST CONCENTRATION OF AMBIENT AIR

compounds	average	concentration (ppb) lowest	month	highest	month
Acetylene	5.27	2.97	Jan.	9.39	Feb.
Ethylene	6.78	3.08	Jan.	11.17	Dec.
Ethane	7.57	4.02	Jan.	14.24	Feb.
Propylene	2.34	0.36	Jan.	5.90	Dec.
Propane	5.61	1.60	Jan.	13.81	Feb.

* sampling site: carteret, 1988 winter

The average, highest, and lowest concentrations in spring at Elizabeth are shown in table 5-14.

The three months average concentrations of acetylene, ethylene, ethane, propylene, and propane are: 7.98, 6.91, 6.40, 3.28, and 7.18 ppbv, at Carteret in the summer. The average, highest, and lowest concentrations in summer at Carteret are shown in table 5-15.

The three months average concentrations of acetylene, ethylene, ethane, propylene, and propane are: 8.27, 8.21, 4.90, 8.37, and 14.90 ppbv, at Elizabeth in the summer. The average, highest, and lowest concentrations in summer at Elizabeth are shown in table 5-16.

The yearly average concentration of each compound is listed in table 5-17.

The results show that sometimes the lowest and highest concentration of some of the compounds occured in the same month but in different sampling week. If the lowest concentration of the different compounds occured in the same month, they usually occured in the same sampling week. The highest concentration of the different compounds fluctuated as well. The weather conditions including, on site temperature, humidity, rain, wind direction and speed could

TABLE 5-12 SEASONAL AVERAGE, LOWEST, AND HIGHEST CONCENTRATION OF AMBIENT AIR

	concentration (ppb)				
compounds	average	lowest	month	highest	month
Acetylene	5.01	1.73	Jan.	11.25	Jan.
Ethylene	6.38	1.83	Dec.	19.10	Jan.
Ethane	10.13	3.38	Dec.	34.53	Jan.
Propylene	6.74	1.23	Dec.	17.23	Jan.
Propane	13.00	3.06	Dec.	31.02	Jan.

* sampling site: Elizabeth, 1988 winter

TABLE 5-13 SEASONAL AVERAGE, LOWEST, AND HIGHEST CONCENTRATION OF AMBIENT AIR

	concentration (ppb)				
compounds	average	lowest	month	highest	month
Acetylene	5.97	2.56	Apr.	13.98	Apr.
Ethylene	5.73	1.52	May	15.15	Apr.
Ethane	6.51	1.35	May	14.78	Apr.
Propylene	3.30	0.54	Mar.	6.54	Mar.
Propane	6.64	1.52	Apr.	13.76	Apr.

* sampling site: Carteret , 1989 spring

TABLE 5-14 SEASONAL AVERAGE, LOWEST, AND HIGHEST CONCENTRATION OF AMBIENT AIR

	concentration (ppb)				
compounds	average	lowest	month	highest	month
Acetylene	5.68	1.87	Apr.	13.60	Apr.
Ethylene	6.07	1.74	Apr.	21.46	Apr.
Ethane	8.58	1.59	May	23.99	Mar.
Propylene	12.97	0.26	Apr.	45.64	May
Propane	20.86	2.42	Apr.	86.26	Mar.

* sampling site: Elizabeth, 1989 spring

TABLE 5-15 SEASONAL AVERAGE, LOWEST, AND HIGHEST CONCENTRATION OF AMBIENT AIR

	concentration (ppb)				
compounds	average	lowest	month	highest	month
Acetylene	7.98	3.20	July	14.07	July
Ethylene	6.91	2.25	June	12.63	July
Ethane	6.40	1.61	June	14.32	July
Propylene	3.28	1.02	June	8.58	June
Propane	7.18	2.73	June	16.31	June

* sampling site: Carteret, 1989 summer

TABLE 5-16 SEASONAL AVERAGE, LOWEST, AND HIGHEST CONCENTRATION OF AMBIENT AIR

	concentration (ppb)				
compounds	average	lowest	month	highest	month
Acetylene	8.27	4.72	June	16.78	July
Ethylene	8.21	4.21	June	17.96	July
Ethane	4.90	1.36	June	14.98	July
Propylene	8.37	3.72	June	16.48	June
Propane	14.90	4.20	June	22.47	July

* sampling site: Elizabeth , 1989 summer

TABLE 5-17 ONE YEAR AVERAGE LEVELS OF DETECTED AMBIENT AIR COMPOUNDS

COMPOUND	YEAR AVERAGE LEVELS (PPBV) CARTERET(32)	 ELIZABETH(38)[a]
ACETYLENE	6.61	6.34
ETHYLENE	8.12	6.81
EHTANE	8.89	7.69
PROPYLENE	4.53	9.42
PROPANE	6.67	16.84

a. number of samples from site

all be the factors in the results. And the emission condition of the local industries and highways in the area are also a factor to cause the changes of highest and lowest concentration.

Generally, the concentration of the five target compounds at Elizabeth were higher than the respective concentrations at Carteret. This is probably indicative of the different locations of the air sampler. At the Elizabeth site, the air sampler was north of the heavier traffic area and refining and chemical industries (downwind for dominant New Jersey wind directions). The air sampler, in Carteret, was located in lower traffic area and lower density chemical industries.

3. Concentration Trends of Target Compounds

Analysis trends for each detectable compound are observed by a moving average of each compound over a year period. The averages were calculated using the following procedures : the first moving average contains the first three weekly data point for each compound. Then the first weekly data point is dropped, and the second through fourth weekly data is averaged. The calculation proceeds this way until the last moving average is calculated, containing the last three weekly data points of the series. In the actual calculation an adjustment was made in order to center the moving average figures so their reported data corresponds to that of the central week of the three. The first moving average (average of the first, second, and third weeks) is thus plotted at the second sampling week. The results are plotted in figures 5-5 to 5-14. These figures demonstrate that the trend of our target compounds appear to follow cyclical fluctuations.

The average concentration of acetylene over the year of analysis is 6.61 ppbv +/- 10.2%. Another part of our research in the Air Pollution Laboratory detects the concentration of benzene and toluene in the ambient air samples at Elizabeth and Carteret. Usually, the concentration of benzene is around 1-3 ppbv and toluene is 3-4 ppbv. The toxicities of the acetylene and benzene are somewhat similar but the concentration of acetylene in the whole year is about three times that of benzene and two times that of toluene.

4. Analysis Error and Detection Limit

i. Precision

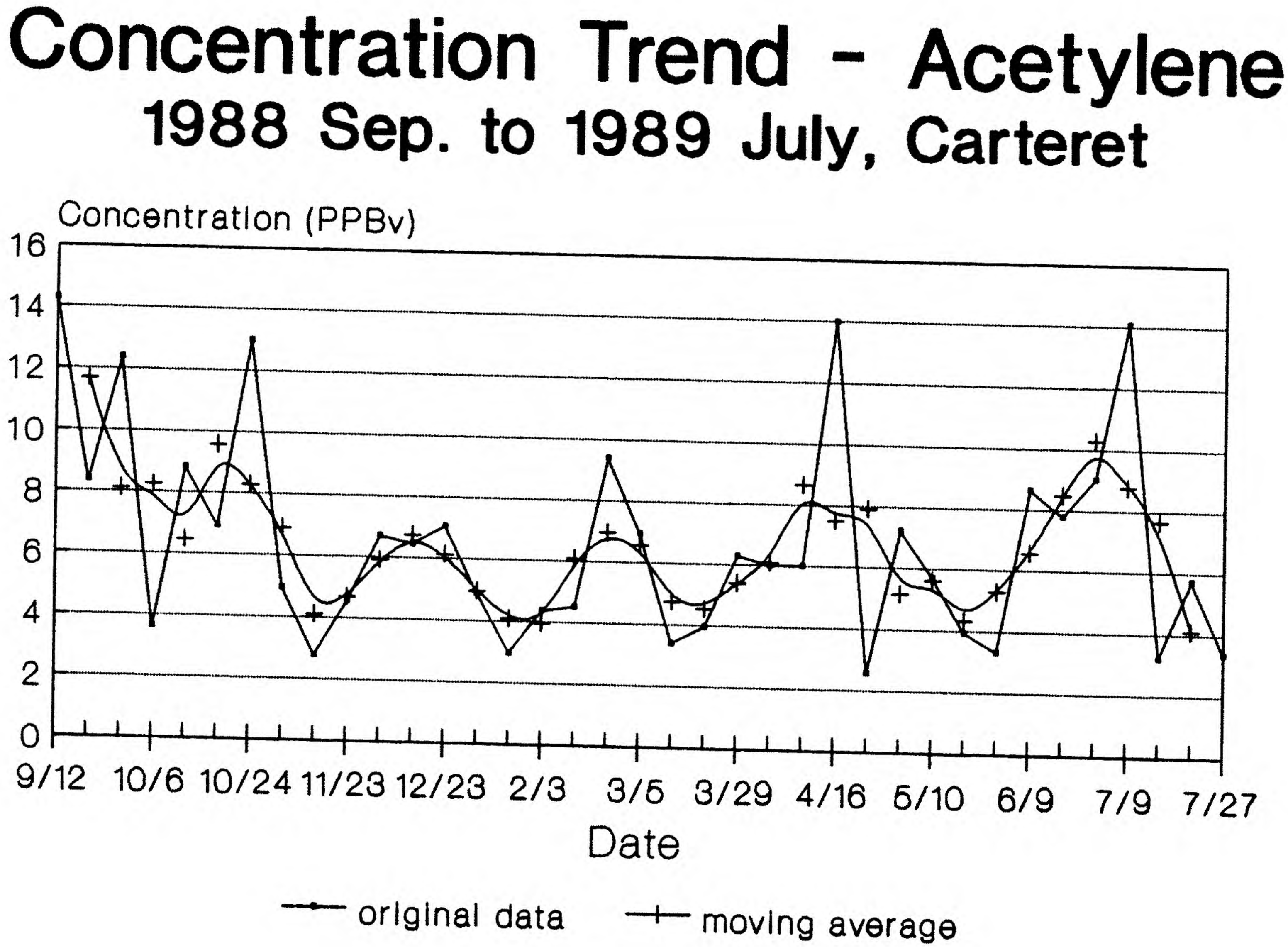

Concentration Trend - Acetylene
1988 Sep. to 1989 July, Carteret
Concentration (PPBv)
16
14
12
10
8
6
4
2
0
9/12
10/6
10/24
11/23
12/23
2/3
3/5
3/29
4/16
5/10
6/9
7/9
7/27
Date
original data
moving average

Figure 5-5

Concentration Trend - Ethylene

1988 Sep. to 1989 July, Carteret

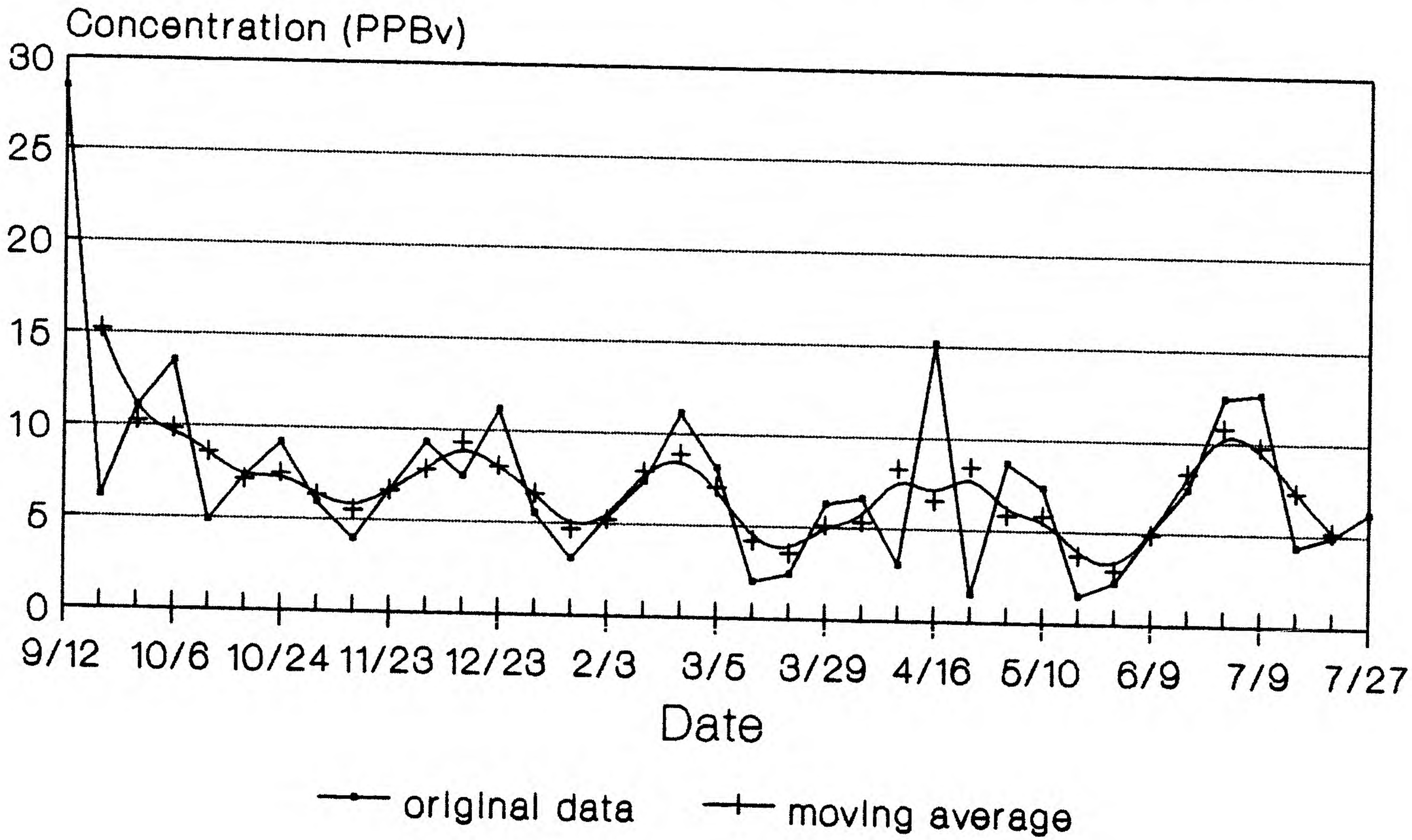
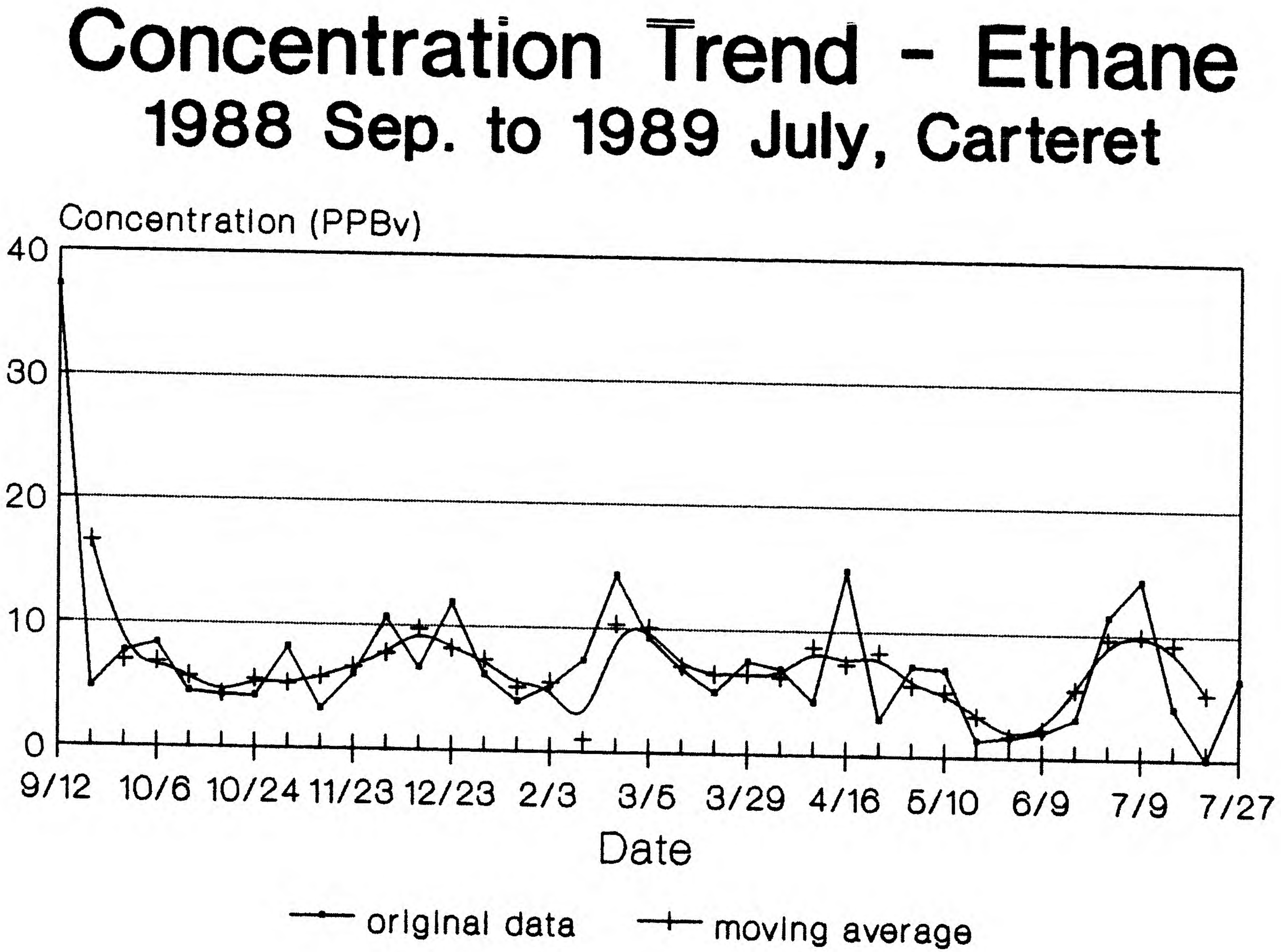


Figure 5-6



Concentration Trend - Ethane
1988 Sep. to 1989 July, Carteret

Figure 5-7

Concentration Trend - Propylene

1988 Sep. to 1989 July, Carteret

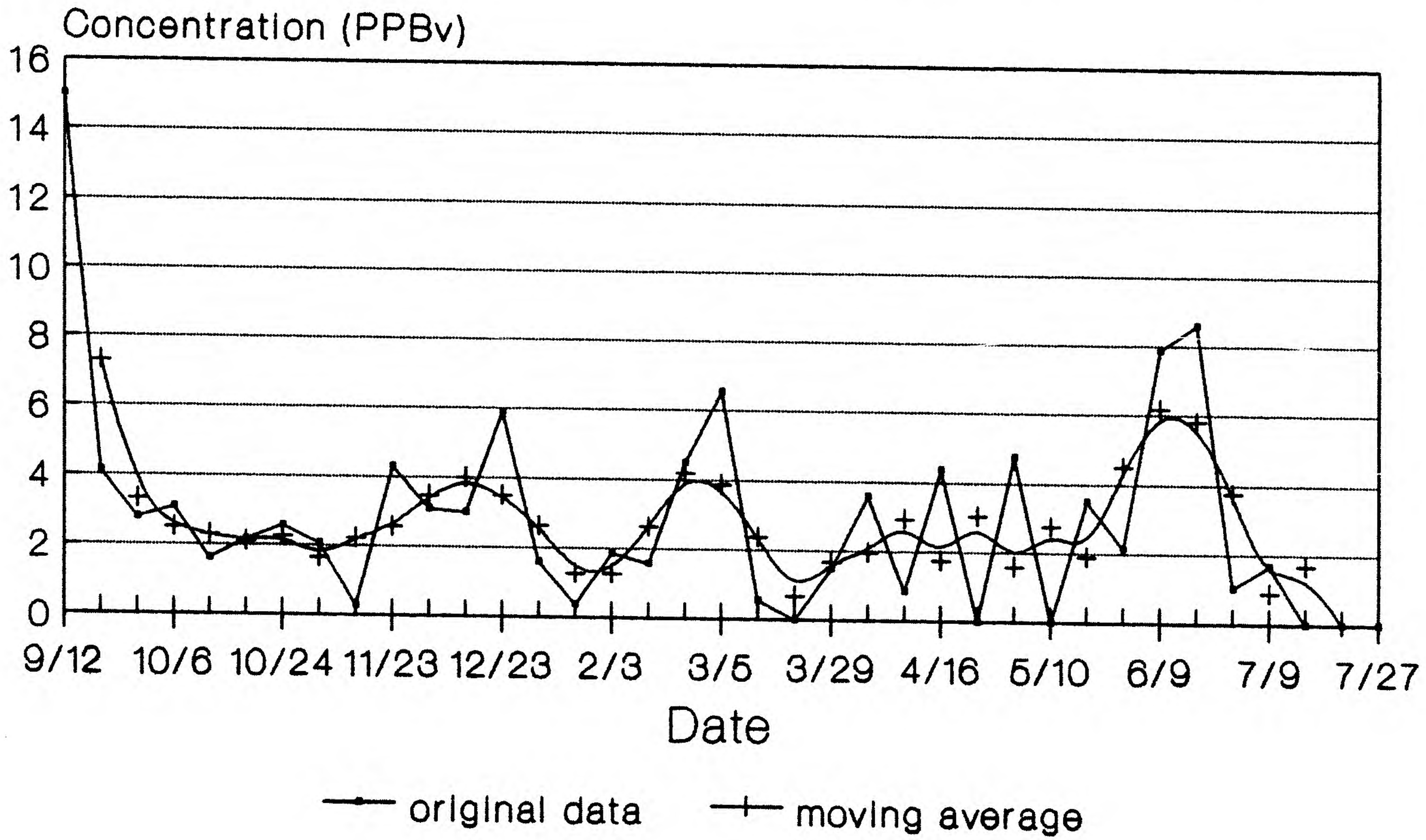


Figure 5-8

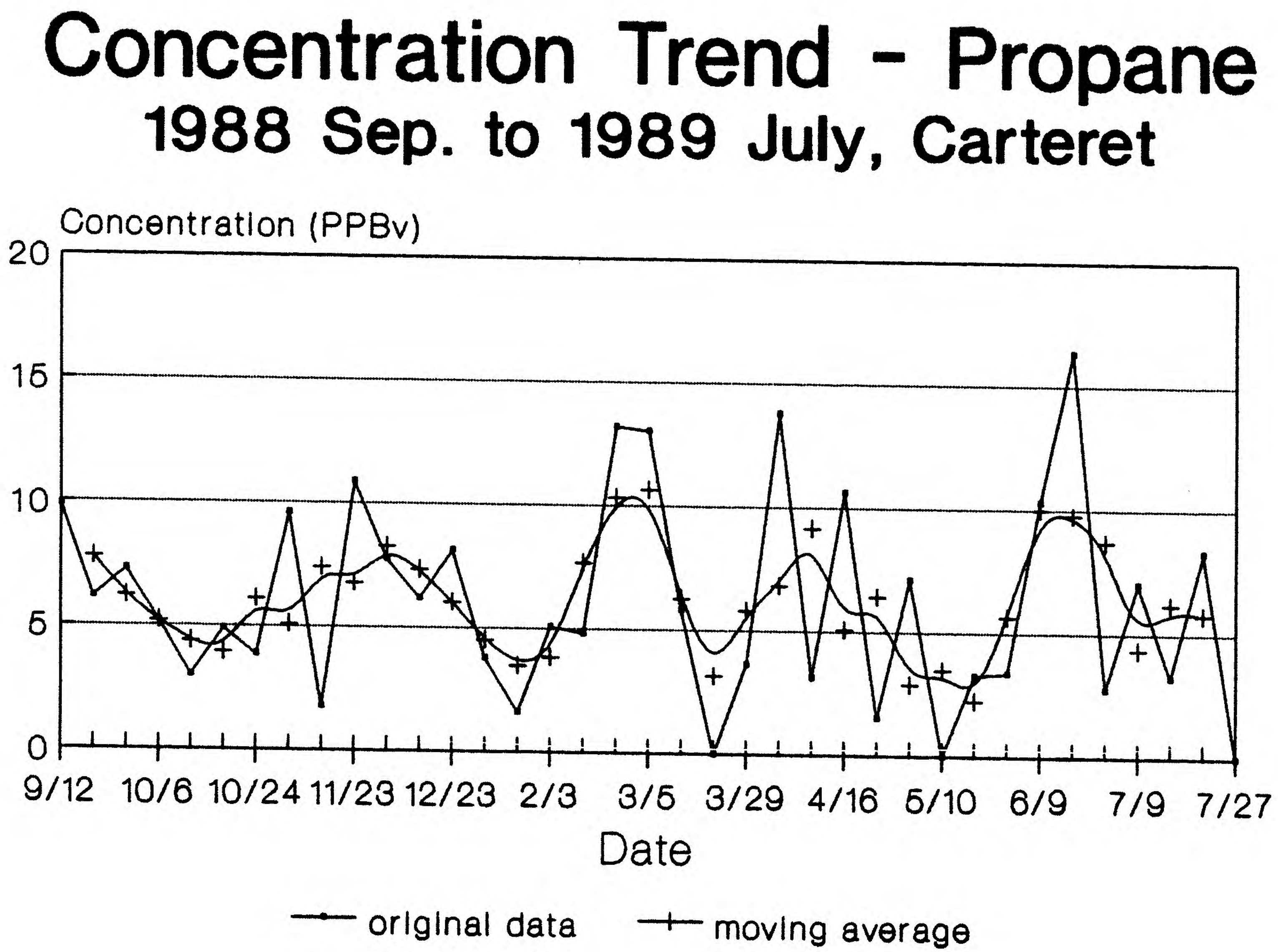

Concentration Trend - Propane
1988 Sep. to 1989 July, Carteret
Concentration (PPBv)
20
15
10
5
0
9/12
10/6
10/24
11/23
12/23
2/3
3/5
3/29
4/16
5/10
6/9
7/9
7/27
Date
original data
moving average

Figure 5-9

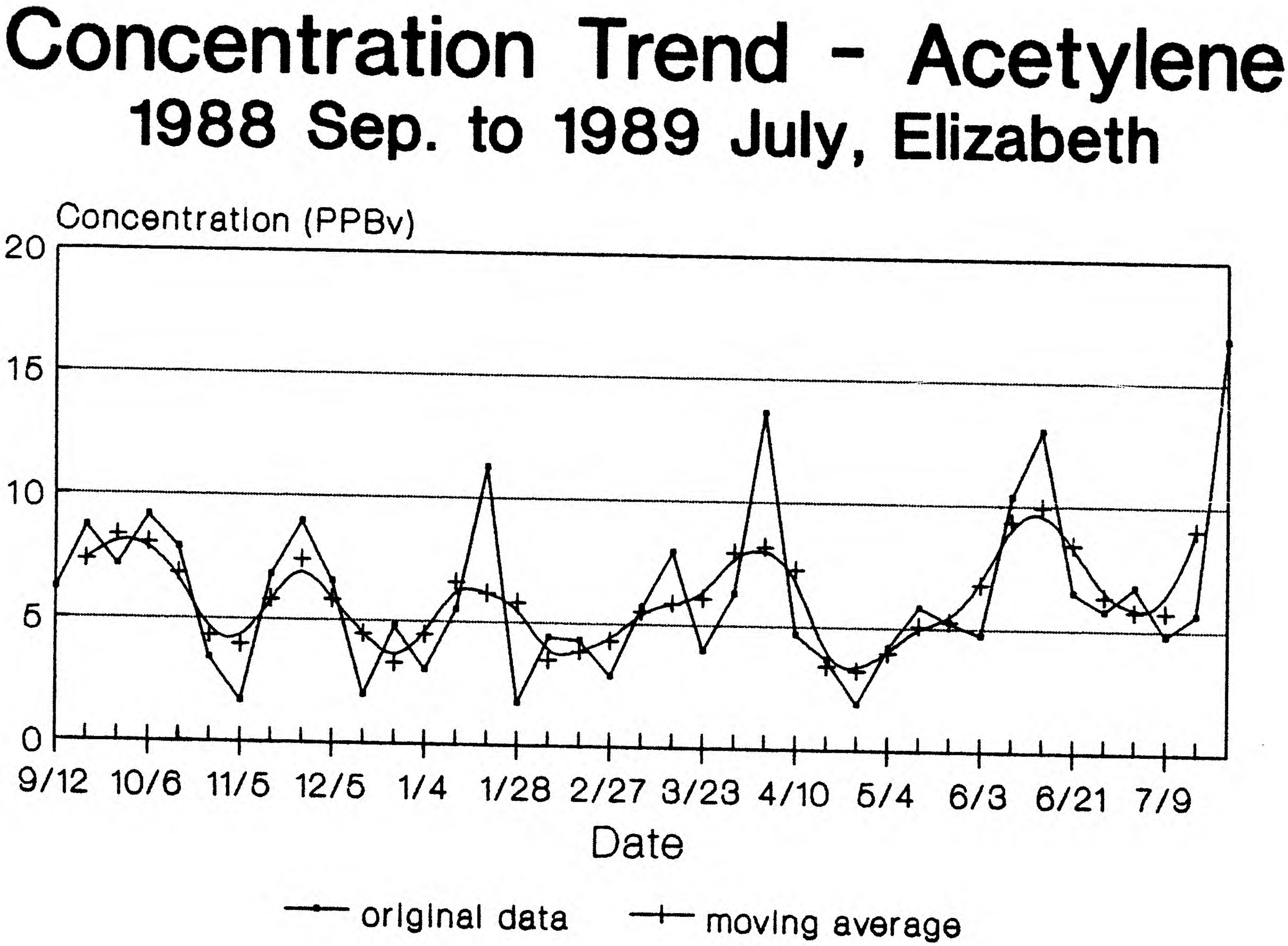

Concentration Trend - Acetylene
1988 Sep. to 1989 July, Elizabeth
Concentration (PPBv)
20
15
10
5
0
9/12
10/6
11/5
12/5
1/4
1/28
2/27
3/23
4/10
5/4
6/3
6/21
7/9
Date
original data
moving average

Figure 5-10

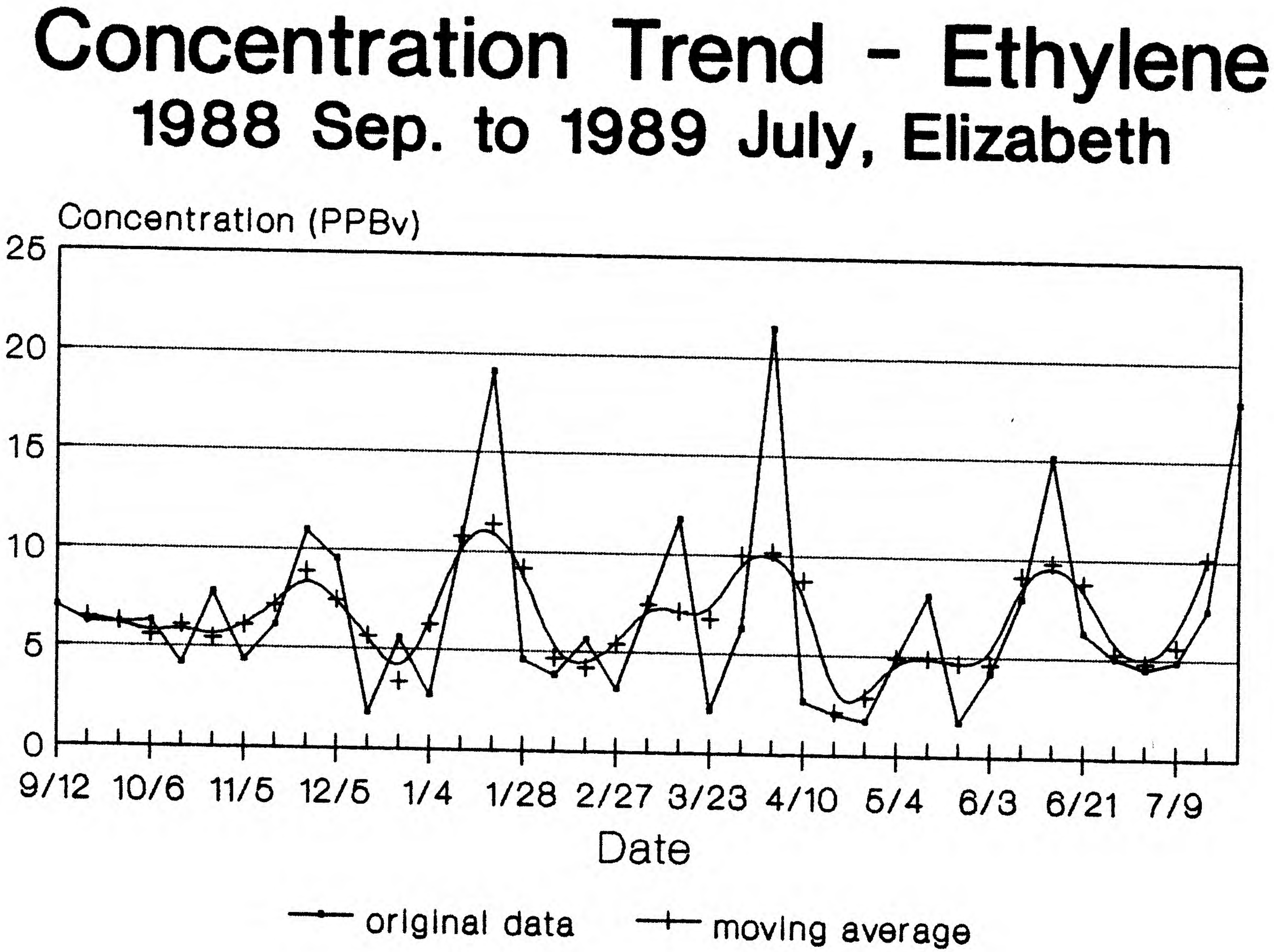

Concentration Trend - Ethylene
1988 Sep. to 1989 July, Elizabeth
Concentration (PPBv)
25
20
15
10
5
0
9/12
10/6
11/5
12/5
1/4
1/28
2/27
3/23
4/10
5/4
6/3
6/21
7/9
Date
original data
moving average

Figure 5-11

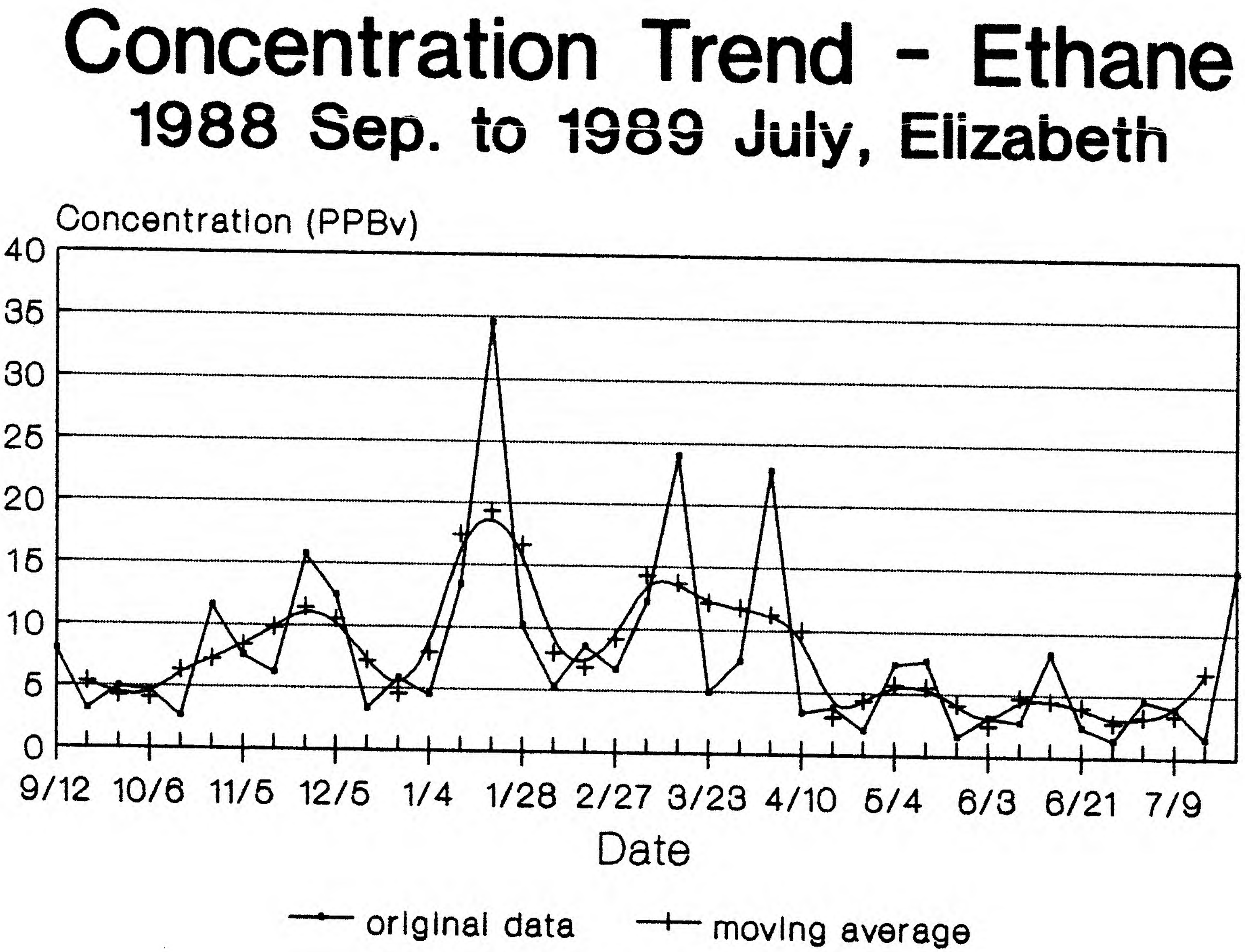

Concentration Trend - Ethane
1988 Sep. to 1989 July, Elizabeth
Concentration (PPBv)
40
35
30
25
20
15
10
5
0
9/12
10/6
11/5
12/5
1/4
1/28
2/27
3/23
4/10
5/4
6/3
6/21
7/9
Date
original data
moving average

Figure 5-12

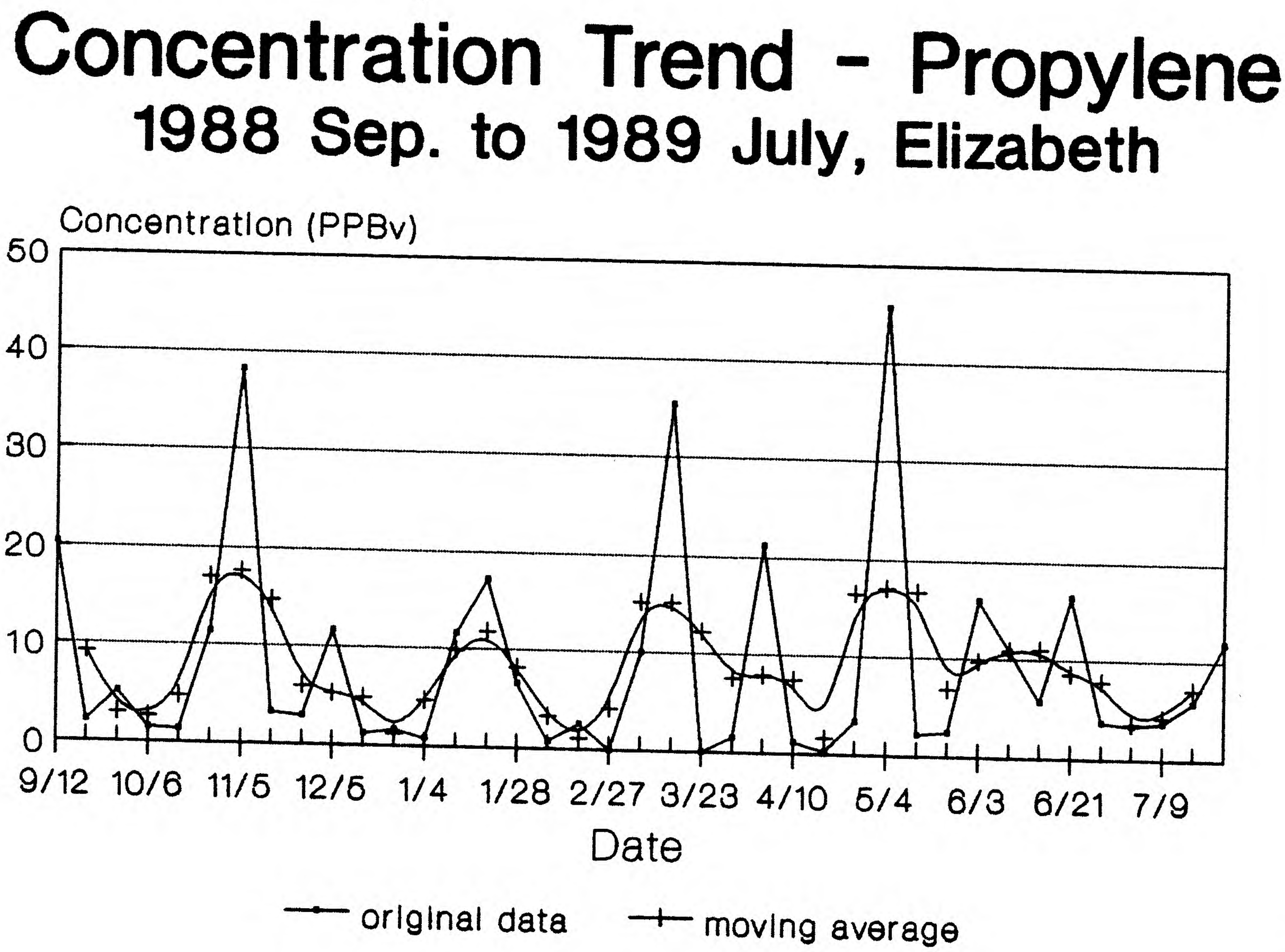
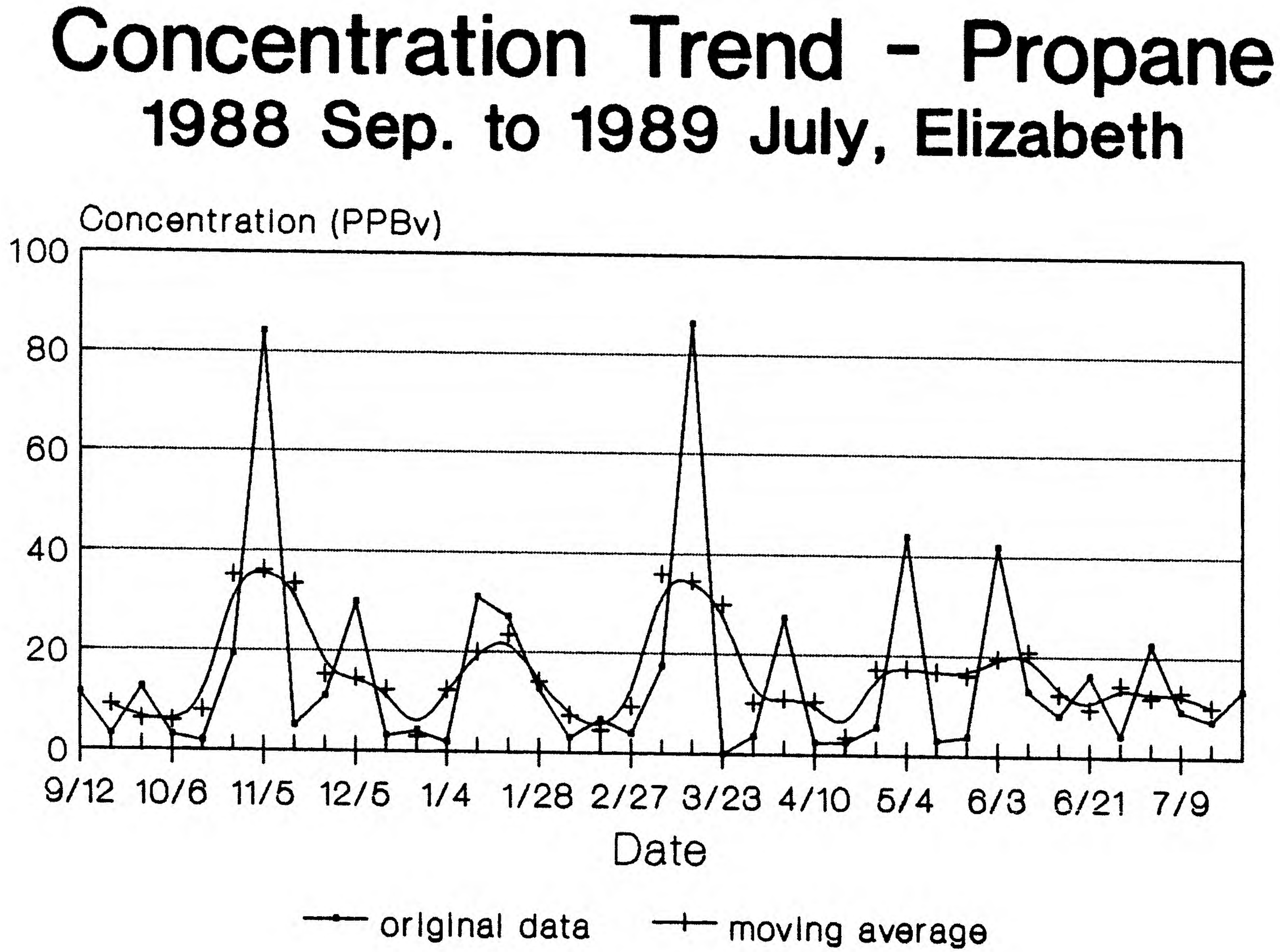

Concentration Trend - Propylene
1988 Sep. to 1989 July, Elizabeth
Concentration (PPBv)
50
40
30
20
10
0
9/12
10/6
11/5
12/5
1/4
1/28
2/27
3/23
4/10
5/4
6/3
6/21
7/9
Date
original data
moving average

Figure 5-13



Concentration Trend - Propane
1988 Sep. to 1989 July, Elizabeth
Concentration (PPBv)
100
80
60
40
20
0
9/12
10/6
11/5
12/5
1/4
1/28
2/27
3/23
4/10
5/4
6/3
6/21
7/9
Date
original data
moving average

Figure 5-14

The analysis precisions were calculated as percent relative standard deviation. Each sample was analyzed 3 to 6 times (injection into GC) and the standard deviation was calculated. The average relative standard deviation of each compound was calculated from the standard deviations of 70 data sets. The results are listed in table 5-17.

Table 5-18 The average Standard Deviation of Five Target Compounds

compound	relative standard deviation (%)
Acetylene	10.2
Ethylene	13.5
Ethane	21.0
Propylene	27.3
Propane	14.6

* Standard Gas (Scott Specialty Gas) has +/- 10 % error

ii. Detection Limits

The detection limit of our target compounds is performed by injecting a small amount of standard gas, for example, 10 ul, into the GC and observing the signal. Each compound has its own detection limit calculated. The detection limits are listed in table 5-19 and the concentration of each standard gas are illustrated. The result are calculated by assuming the injection of each standard gas are concentrated from 1 liter sample volume.

Table 5-19 Detection Limit of Target Compounds When Target Compounds From 1 Liter sample volume

compound	concentration (ppbv)
Acetylene	1.8
Ethylene	1.5
Ethane	1.5
Propyne	1.0
Propylene	1.0
Propane	1.0

2. Research Problems

i. Water Vapor Plugging Problem

The percent humidity in the atmosphere effected our analysis. In the cold dry winter time, December 1988 to March 1989, the humidity in the atmosphere was low. We could load more volume of the air sample through the cryo trap before it plugged with water. The loaded volume was often 1 liter. On raining days or more humid weather, late March to June, the cryo trap was easily plugged and the average loaded volume was often only 300 to 500 ml. These volume limitations were due to the frozen water (ice) plugging the cryo-trap and it limited our precision in the analysis.

To try and reduce the ice plugging problem, we used the desiccants, K_2NO_3 and Calcium sulfate, in 2 mm ID and 0.3

meter long stainless steel tube[1]. The desiccator tube was connected between the sample canister and the inlet 6-port valve. The air sample can pass through the tube to remove the wwater vapor and then be concentrated in the cryogenic loop. Two runs with the dryer pretreatment and two runs without dryer pretreatment were taken and analyzed to compare the lose of the sample after the drying procedure. The results were presented in the table 5-21. The results showed that the desiccator adsorbed not only water but also some of our target compound. The loss of target compounds, up 60 % illustrated in table 5-21, produced even large errors than with the reduced volume and so we did not use the drying trap.

TABLE 5-21 COMPARISON OF THE DRYING VS NONDRYING PRETREATMENT EFFECTS

COMPOUND	SAMPLE RUNS CONCENTRATION (PPBV) WITH DRYER	WITHOUT DRYER	LOSE and GAIN %
acetylene	3.35	9.01	- 62.8
ethylene	3.61	12.44	- 70.9
ethane	2.80	11.37	- 75.4
propylene	4.17	1.02	+ 308.8
propane	5.32	2.73	+ 94.8

ii. Problem of Qualitative and Quantitative VOC

Initially, we desired to have qualitative and quantitative analysis on several chlorinated hydrocarbons these include chloromethane and vinyl chloride which elute from the GC column in the time frame of our conditions. However, we did not observe vinyl chloride and chloromethane above our 1 ppbv detection limit at any time in the sampling period. In addition, we found that there was one Freon in the air samples, it was identified as Freon 12 and the chromatogram showed in figure 2-8 (c).

3. Analysis Improvement Suggestion

a. Remove the water vapor

In the previous studies (including literature review), some researchers used a desiccant to solve the problem of plugging, but we were not successful in that. Some materials that we did not try, like Perma-Pure dryer (1985)[18] and Nafion Dryer (1987)[19] are a possibility. Those dryers were successfully used by researchers where there were much higher levels of pollutant and were suggestions to use in the furture research. The only uncertain points were that those researchers focused their analysis on higher concentration of chlorinated compounds, they did not report effects relative to our target compounds, acetylene, ethylene, ethane, and etc. An effective dryer before the cryotrap which did not elimiate or reduce our target compound concentration would certainly increase our analysis capability.

2. The Identification Ability of Our GC

Under our GC condition, we were not able to identify and quantitate some of our desired target chlorinated compounds. We suggest to use the Durapak column (Octane/Porasil C, 6.1 m * 1.5 mm OD stainless steel, 1982)[19] to separate C_2-C_6 hydrocarbons or a capillary capillary column (50 m * 0.32 mm fused silica PLOT (Al_2O_3/KCl) to separate and improve analysis of C_1-C_5 hydrocarbons. For the Durapak column, temperature programing starts from -50 ^{o}C for 4 minutes and then increased 16 C per minutes to +60 ^{o}C. The Capillary column is reported to start form 70 C to 200 C and a temperature program rate is 3 ^{o} C per minutes.

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SECTION II

DEVELOPMENT OF SIMPLE ANALYSIS FOR POLYCYCLIC AROMATIC HYDROCARBONS

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SECTION II DEVELOPMENT OF SAMPLE ANALYSIS FOR POLYCYCLIC AROMATIC HYDROCARBONS

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CHAPTER 1 INTRODUCTION

Polycyclic Aromatic Hydrocarbons [PAH, equivalent name Polynuclear Aromatic Hydrocarbons (PNA)] are a group of chemical compounds that are known as human carcinogens[1]. The chief emission sources of the PAH are related combustion. The combustion of fossil fuels and biomass, be it in utility power plants, trucks, and automobiles or in home fireplaces, usually introduces finely divided particulate matter into the environment.

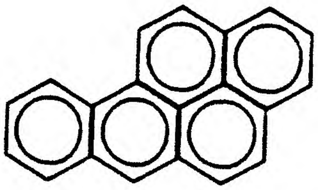
The carcinogenic PAH are relatively nonvolatile and are found overwhelmingly on particulate matter rather than in the vapor phase[1]. Furthermore, roughly 90 percent of the mass of these PAH are present on particulate smaller than 2 uM in diameter[2,3], which are those sizes considered to be capable of penetrating the lungs. PAH are often found in soils, waters, process streams from fuel and chemical plants, fly and bottom ash, airborne particulate, etc,.

A variety of methods for PAH analysis have been developed. The gas chromatograph-mass spectrometry (GC-MS) and high-pressure liquid chromatographic (HPLC) systems with UV absorption and fluorescence detection are applied to separation, identification, and measurement of PAH in a variety of sample types. Because of sample complexity, many of these methods are tedious, manipulation-intensive, and not practical for large-scale environmental surveillance or energy process monitoring[4].

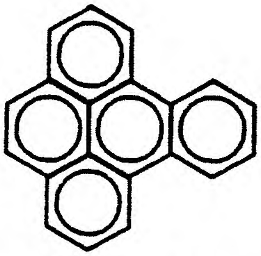
In the group of PAH compounds, benzo(a)pyrene [B(a)P] is measured most frequently as a representative or surrogate compound for the class (The structures of frequently measured PAH are ploted in Figures 1-1 to 1-3). This simpler analysis based on BaP only can help in judging how a given source contributes to the total amount of PAH. The B(a)P is, however, only a minor component, usually less than 5 % of the total PAH[5]. The old procedure for analysis of B(a)P includes a six-hour Soxhlet extraction, concentration of the extract (reduction of solvent volume), separation by thin layer chromatography, of a fraction of the extract and detection by fluorescence. This process is quite lengthy. Swanson and Walling (1981)[6] developed a modification to the extraction step which depends on ultrasonics thus, shortening the extraction time, furthermore, they eliminated the concentration step, further significantly shortening the procedure. Now, most researchers and routine analysis procedure apply this ultrasonic extraction step, but the remaining analysis is still very time consuming. A simple,

Examples of Some Polycyclic Aromatic Hydrocarbons (PAH) and Some Single Ring Aromatic Hydrocarbons

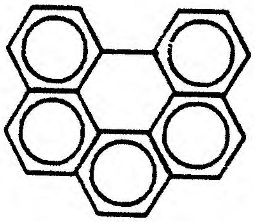
(o) non carcinogenic
(+++) very carcinogenic



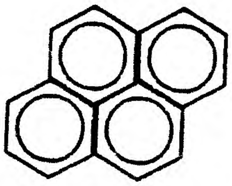
Benzo (a) pyrene
(+++)



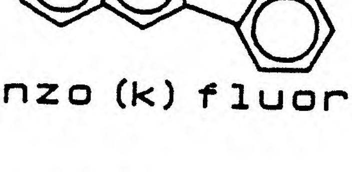
Benzo (e) pyrene
(o)



Benzo (ghi) perylene
(o)



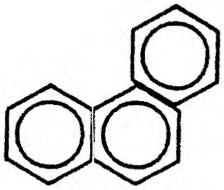
pyrene (o)



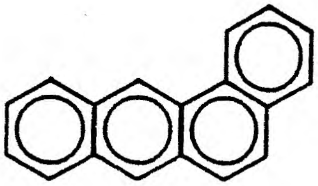
(O)
Benzo (k) fluoranthene

anthacene (o)

Figure 1-1 Structure of Polycyclic Aromatic Hydrocarbons

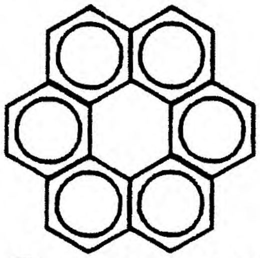


Phenanthrene (0)

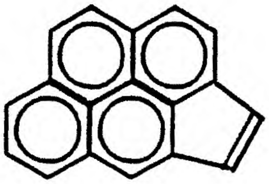


(+)

Benz (a) Anthracene

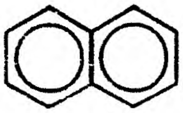


Coronene (o)

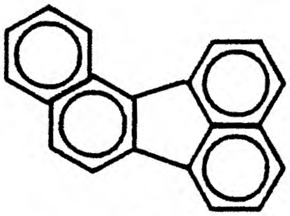


?
(++)

Cylopenta (cd) pyrene

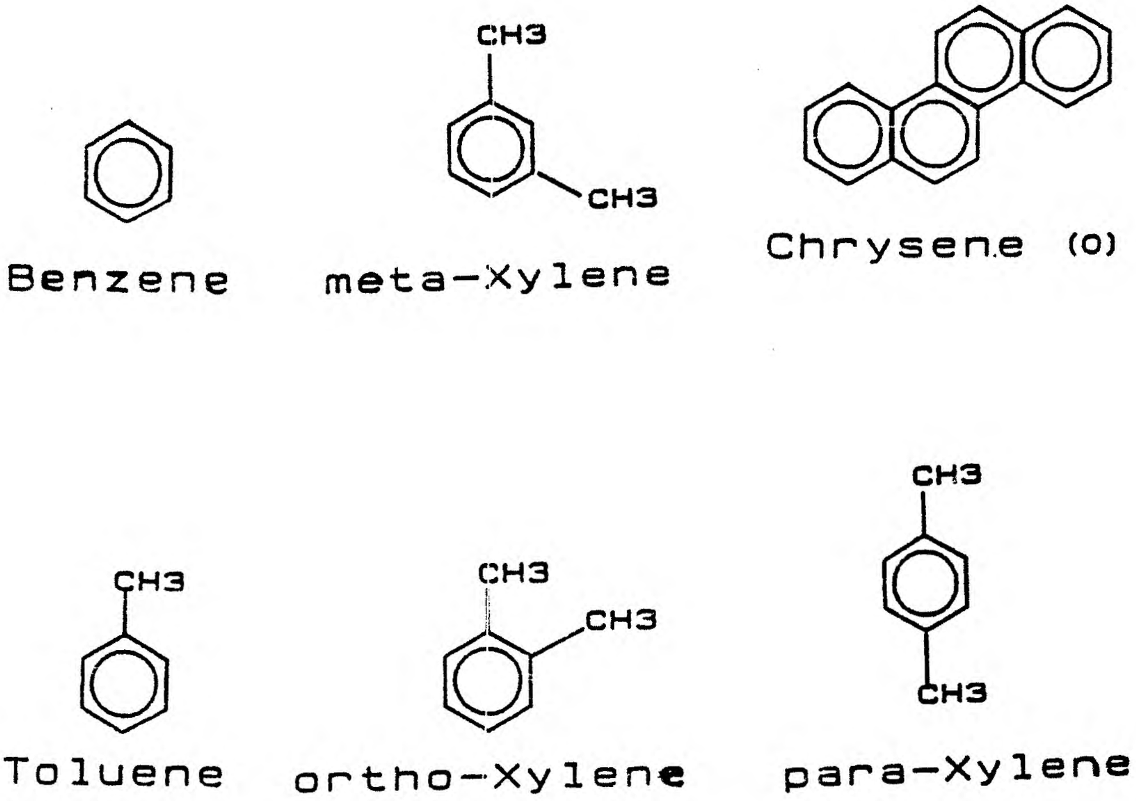


Naphthalene
(O)



Benzo (j) fluoranthene
(++)

Figure 1-2 Structure of Polycyclic Aromatic Hydrocarbons



Benzene meta-Xylene Chrysene (O)

Toluene ortho-Xylene para-Xylene

Figure 1-3 Structure of Polycyclic Aromatic Hydrocarbons And Some Single Ring Aromatic Hydrocarbons accurate, and rapid method of analysis of PAH is needed for routine air pollutant and other source measurements.

In 1988, LEE[7] developed a fast and convenient alternative to other more complex methods of analysis for PAH. His study was directed to serve as an initial guide to source origins of PAH. In the study, sample clean-up was confined to silica gel and Sephadex column chromatography to isolate, first, the PAH fraction, and then to fractionate the individual components according to their ring numbers. The samples were analyzed after the isolation step of Sephadex chromatography. Their research only involved investigation of the four-to seven-ring PAH, since compounds with three rings or fewer are less carcinogenic[8].

The objectives of this experiment were to develop a simpler and semiquantitative method, using ultraviolet absorption and fluorescence spectroscopy, to determine the total polycyclic aromatic hydrocarbons and relate these total number to B(a)P, in air particulate. The reason for basing the analytical methods on both UV absorption and fluorescence spectroscopy is that fluorescence is a relatively specific characteristic of the PAH. The Ultrasonic extraction technique was used to extract the samples from filter collection media, particulate was separated from the extracted solutions by filter discs, and the rresults of total PAH numbers were compared from several different UV absorption and fluorescence analysis against quantitative analysis of B(a)P from thin layer plate fluorescence analysis.

We have not been able to demonstrate that our method of total PAH analysis correlates linearly with BaP measurements. We can not distinguish between the following three conclusions :

i. That BaP does not track total PAH's and that our results then show the inequality of total PAH vs BaP that actually exists.

ii. That BaP may track total PAH but our methods of analysis are not specific to PAH, i.e. we measure additional compounds which absorbance and fluorescence in the regions of the UV where this analysis was performed.

iii. Neither of above.

CHAPTER 2 EXPERIMENTAL PROCEDURES

PNA --- COLLECTION AND ANALYSIS

A. Sample Collection and Storage

Airborne particulate samples are collected by using a high volume samplers for 24 hours (midnight to midnight) in industrial areas.

The sample filter is 8 by 10 inches in size and is composed of glass fiber filter (type A/E, Gelman Sciences Inc, Ann Arbor, Michigan). Typical air flow of high volume pump is 40-45 cfm (1.13 to 1.27 m^3/min), particle size cut off 0.3 micron (Gelman) and particles above 35 uM diameter do not enter the covered sampler. The filters are brought back to laboratory (NJIT) to analyze the polycyclic aromatic hydrocarbons (PAH). The sample filter is wrapped in an aluminum foil before analyzing to keep away from light.

B. Sample Preparation

1. Sample Extraction

The total area of sample filter is 8 by 10 inches and the particle exposure area is 7 by 9 inches. A 1 by 8 inches strip (exposure area is 1 by 7 inches) is cut from the sample filter and further cut into smaller pieces. The filter pieces are placed into a graduated glass vial (Volume of the vial is about 24 ml). 10 ml of solvent is added and the vial is capped with a teflon lined screw-cap. Four different organic solvents: ethanol, hexane, cyclohexane, and methylene chloride, are used to extract the PAH from the air sample filter.

An ultrasonic bath is used to perform the sample extraction. The glass vial with filter pieces and solvent is placed in an ultrasonic bath. The bath is 2/3 filled with hot water. The temperature of the water is controlled for different solvents, 70°C for ethanol, hexane and cyclohexane, and 40 °C for methylene chloride. The samples are extracted in the bath for 20 minutes.

2. Purification and Separation (Isolation)

i. Purification Procedure

The solvents contain pieces of filter strips and particulates after the extraction procedure. The particulates in the solution will block or reflect the light and affect the analysis results in the absorption and fluorescence analysis. The solutions, therefore, need a pretreatment procedure to remove the unwanted particulates and leave the solution clear for the analysis.

A filter disc (25 mm filter unit, 0.45 um PTFE, Lida Manufacturing Corp., Bensenville, IL) and a syringe are used to remove the particulates from the solution. The solution for analysis is passed through the filter with the syringe. The filtered solution is then placed into a clean glass vial that is ready for analysis.

The majority of our samples are treated by this extraction/purification procedure only and then analyzed by UV-VIS Spectrometer and Fluorescence Spectrometer. These samples are extracted by ethanol, cyclohexane, or methylene chloride to determine if one solvent works better than another. All the solvents are Photrex, Baker analyzed reagent grade (J.T. Baker Chemical Co., Phillipsburg, N.J.).

ii. Separation Procedure

A small number of our samples are treated by an additional separation procedure before analysis by UV absorbance and fluorescence. Here the extracting solvents are different from the samples treated by extraction/filtration only. The two solvents use to extract the sample in this experiment are hexane and cyclohexane.

After the extraction and filtration procedure, the solutions are clear but still contain many types of chemical compounds, polars, neutrals PAH, that can dissolve in the extracting solvent. It would help to separate the target compound, B(a)P, from the solution before analysis.

Two kinds of commercial absorbent cartridges are used to try and isolate the PAH; Octadecyl C18 column, 300 mg C18 packing material, (Baxter Healthcare Corp., Burdick and Jackson Division, Muskegon, MI) and Florisil, 300 mg florisil packing material. Both cartridges are 4.5 cm long and 1 cm OD filter units. The cartridges are disposable and only one cartridge is used for one sample. Figure 2-1 is a cross section picture of the cartridge. Two sections are included in a small cartridge, one is a small channel (about 0.1 cm ID) and the other is a column, 0.8 ID and 1.5 cm long, with packing material. The solvent can only pass through the small channel and extend into the column section to have a complete interaction.

Two solvents are needed for purification with a cartridge in this procedure : one is for extracting the PAH from the sample filter and then leaving it adsorbed on the cartridge and the second for removing adsorbed B(a)P from the cartridge. The solvents are different for the two kinds of

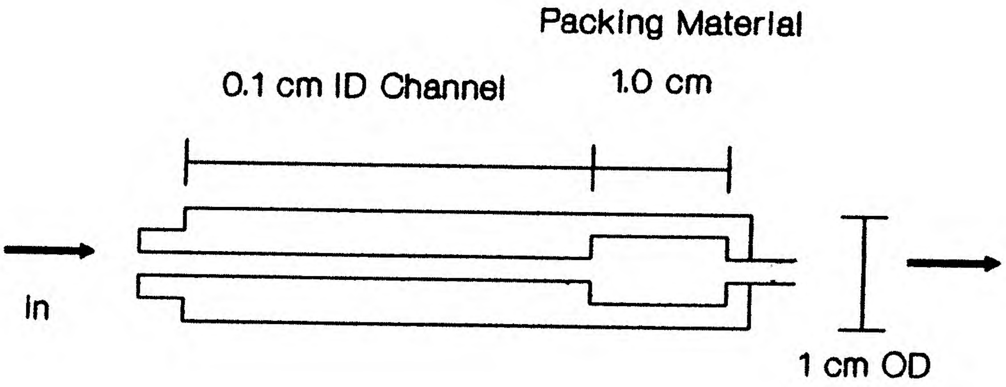


Figure 2-1 Intersection of Cartridge

cartridges.

The C18 column, a non-polar atationary phase, retains non-polar compounds. Ethanol is used to extract the sample and hexane, a less polar solvent, to elute the B(a)P off the C18 adsorbent. B(a)P, a non-polar compound, can be extracted by ethanol from the filter adsorbed on the C18 column. The second solvent, hexane, removes the B(a)P from the column for UV absorption and fluorescence analysis.

For the Florisil column, a relatively polar stationary phase, hexane is used to extract B(a)P from the filter and cyclohexane to carry the B(a)P off the florisil absorbent. The procedure for pretreating the sample by these by these two cartridges are illustrated below :

i. The cartridge is activated by 3 ml of solvent (hexane is used for Florisil; ethanol is used for C18).

ii. Sample from solvent extraction of a filter strip is filtered by the cartridge slowly to prevent incomplete adsorption. The filtered solution is discarded.

iii. Unwanted compounds are washed from the cartridge by a second 5 ml of the extraction solvent.

iv. A second solvent is employed to elute B(a)P (and other PAH compounds) which are retained on the cartridge, flowing the solvent in the same direction. Here cyclohexane is employed for the florisil column and hexane for the C18 column. The eluant is then analyzed by absorbance and fluorescence spectrometries.

C. Sample Analysis

1. Thin-Layer Chromatography Method with Fluorescence

In this part of the experiment cyclohexane is used to extract the sample from the filter. The cyclohexane is Photrex, Baker analyzed reagent, J. T. Baker Chemical Co., Phillipsburg, NJ.

i. A 0.1 ml aliquot of each sample is applied as a spot 2 cm above the bottom edge of a cellulose-acetate thin-layer plate (20 by 20 cm^2). Each plate has 18 such channels, and each sample is spotted into two channels for replication purposes. A series of B(a)P standards (0.1 ml each) such as 5 ng/ml; 10 ng/ml; 20 ng/ml; 40 ng/ml; 70 ng/ml; are applied in duplicate for calibration. After sample spotting, the plate is developed with 150 ml ethanol/dichloromenthane (2:1) in a development tank, with the tank covered with a glass lid within a box to avoid light during development. The developed plate is allowed to air dry in a dark place for about 5 minutes.

ii. Using a plate-scanning spectrofluorometer (Perkin Elmer, model MPF-44B, Fluorescence Spectrometer), B(a)P is identified by the retention time of the standard at excitation wavelength 387 nm and emission wavelength 428.6 nm. Quantitation is done by using the ratio of the sample peak area to that of a standard peak area which is similar in magnitude to the sample.

2. Analyze The Air Sample by UV-Spectrometer (absorbance)

In this part of the experiment, ethanol (anhydrous), methylene chloride and cyclohexane are used to extract the sample filters respectively. All the solvents are Photrex, Baker analyzed reagent, J.T. Baker chemical Co., Phillipsburg, N.J..

i. Standard Solution Preparation

Standard solutions are prepared from 1000 ng/ml standard BaP. The stock solution (1000 ng/ml) is kept at $0^{o}C$. The diluted standard solutions are prepared daily before the analysis. A series of standard solutions, 1, 2, 3, and 5 mg/l are prepared to run on the UV-VIS Spectrometer Spectrometer (Unicam Sp1800 Ultraviolet Spectrophotometer) for calibrating the BaP concentration.

ii. UV-Spectrometer absorption analysis

Two 10 mm light path quartz cuvettes with two polished windows are used for the UV-Spectro analysis : One for the reference and the other for sample beam paths.

To ascertain the optional detection wavelength for the B(a)P with the UV-Spectrophotometer, the standard solutions are scanned. The different standard solutions (ethanol, methylene chloride, cyclohexane) are also scanned, starting from 200 nm to 400 nm. Figure 2-2, 2-3, and 2-4 are the spectra for ethanol, methylene chloride, and cyclohexane respectively, between 200 and 400 nm. The most sensitive wavelength (for the three solvents) occurs at 296 nm. The detecting wavelengh is then set at 296 nm. The UV source is a deuterium lamp, automatic reference, double beam, 0.5 mm slit width and a fixed wavelength 296 nm. The result are recorded as percent absorbance.

3. Fluorescence Spectrometer Analysis

i. Standard Solution Preparation

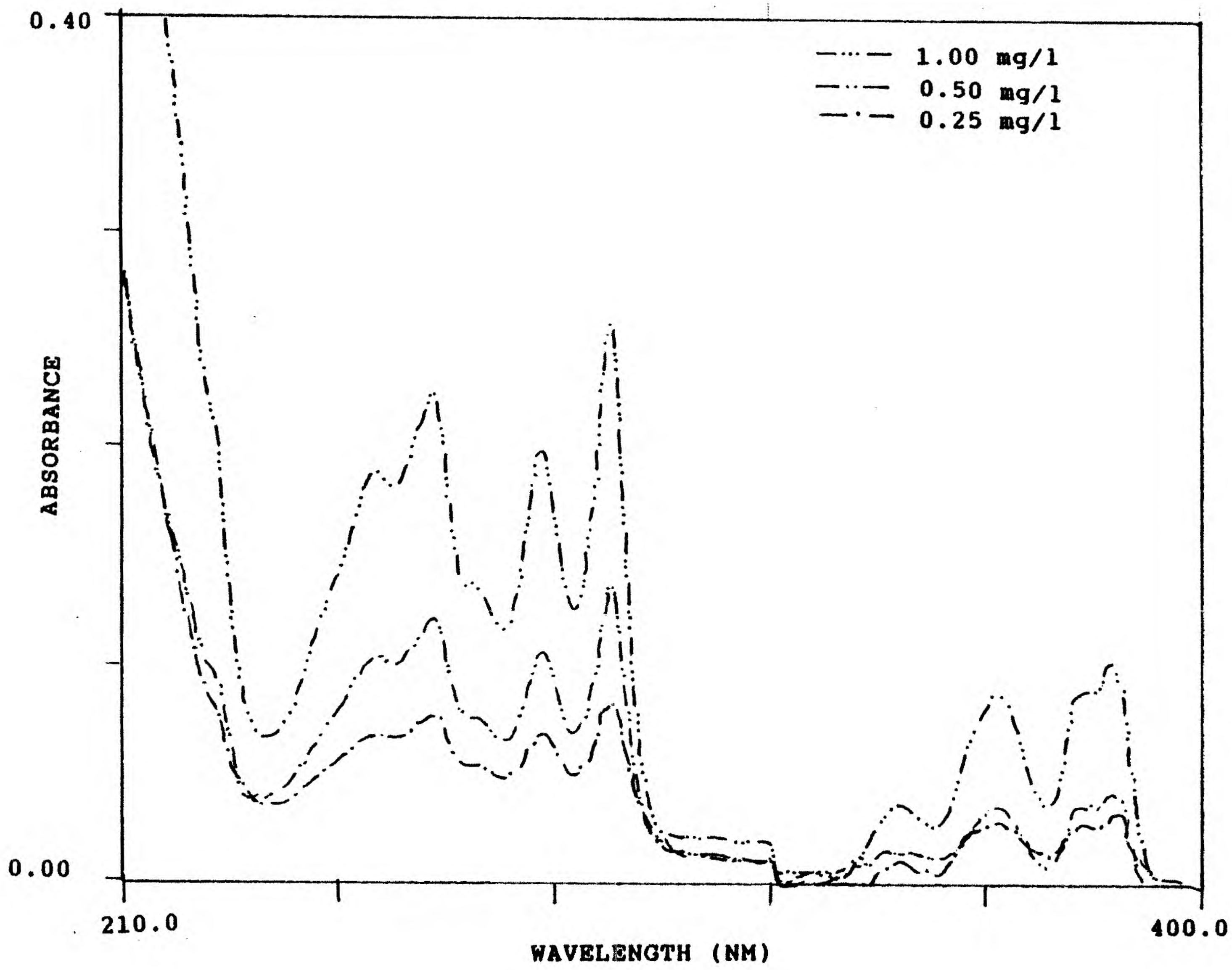


Figure 2-2 UV Absorbance Scanning Spectra of B(a)P Standard Solutions in Ethanol

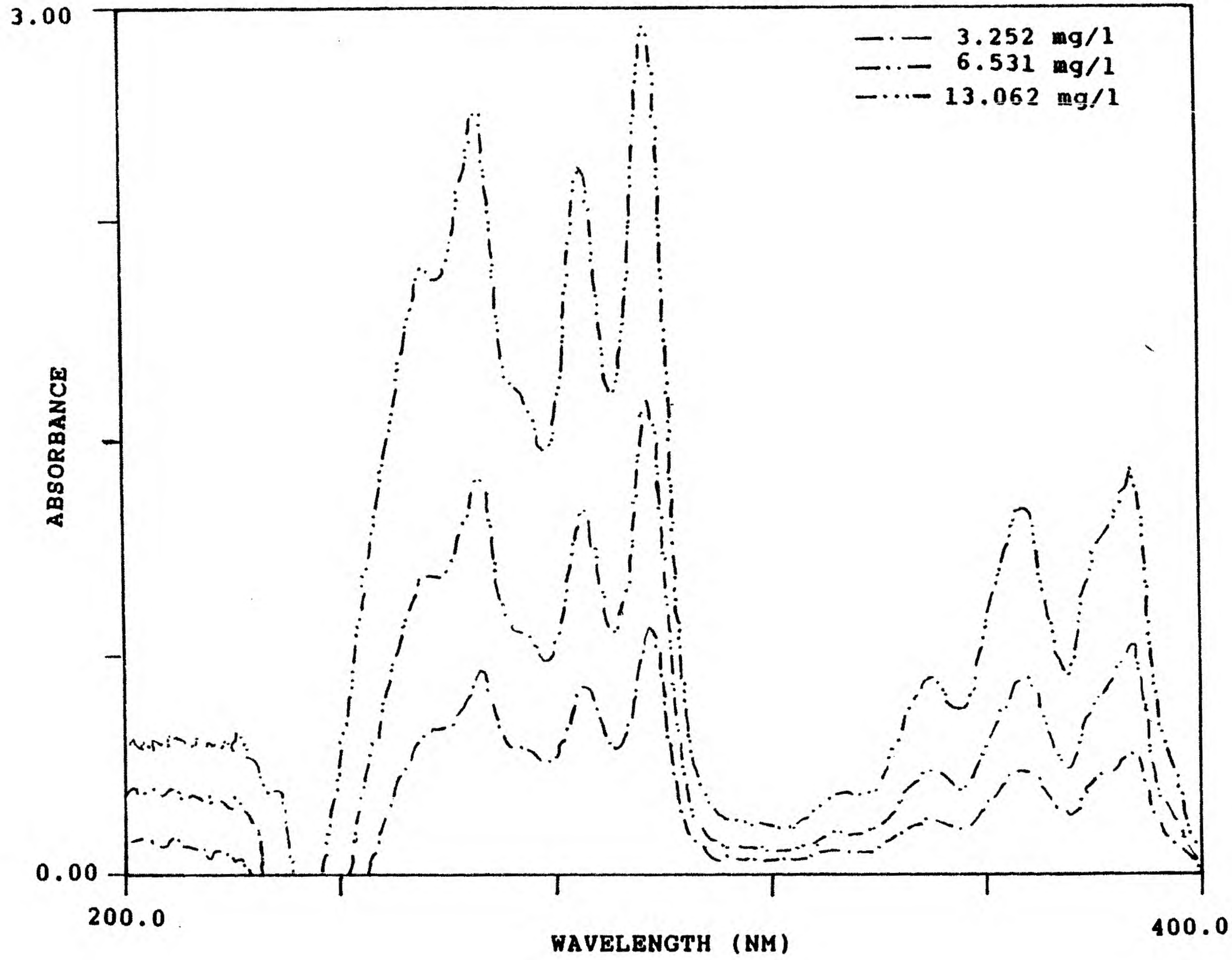
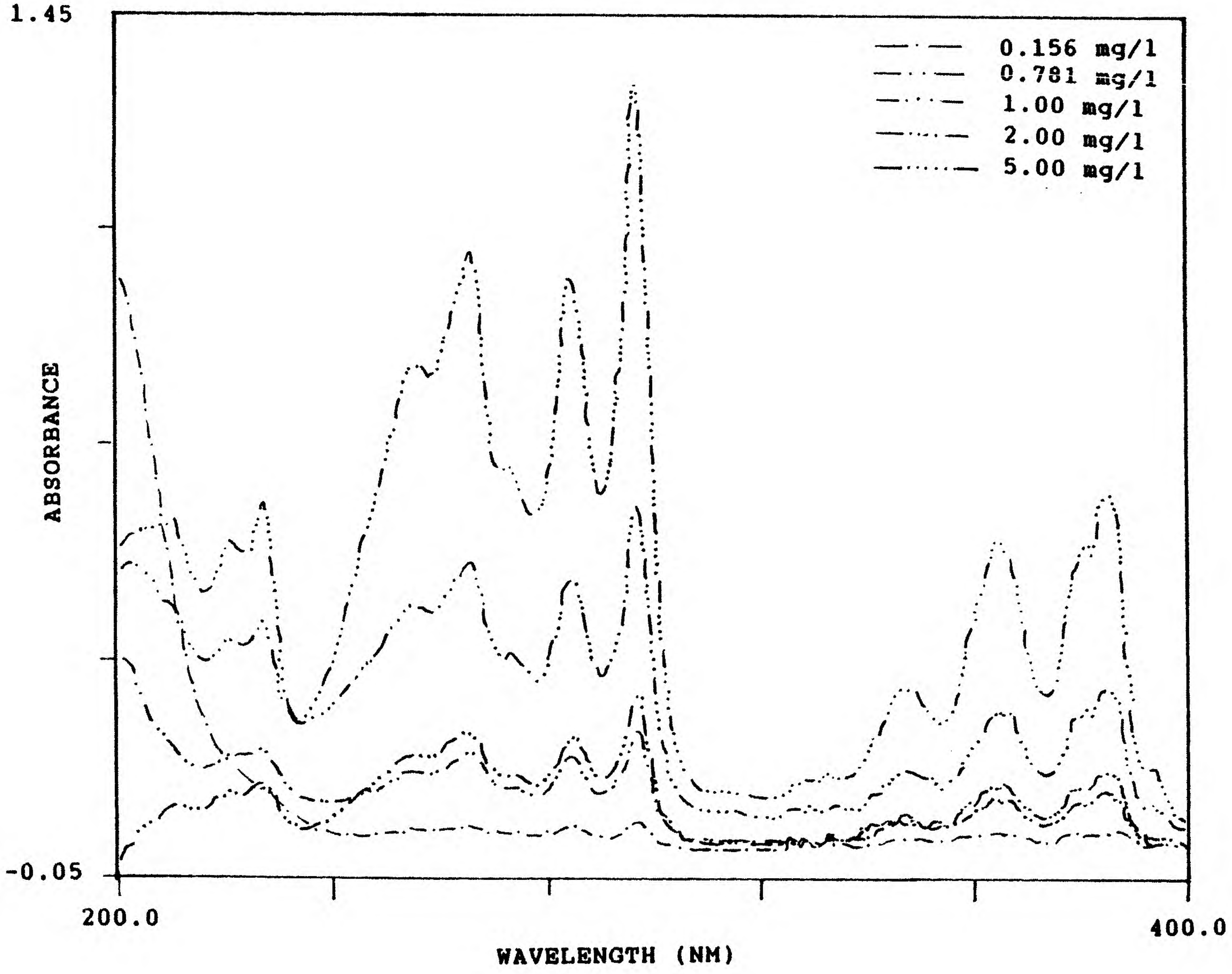


Figure 2-3 UV Absorbance Scanning Spectra of B(a)P Standard in Methylene Chlioride


1.45
-0.05
ABSORBANCE
200.0
400.0
WAVELENGTH (NM)
0.156 mg/l
0.781 mg/l
1.00 mg/l
2.00 mg/l
5.00 mg/l

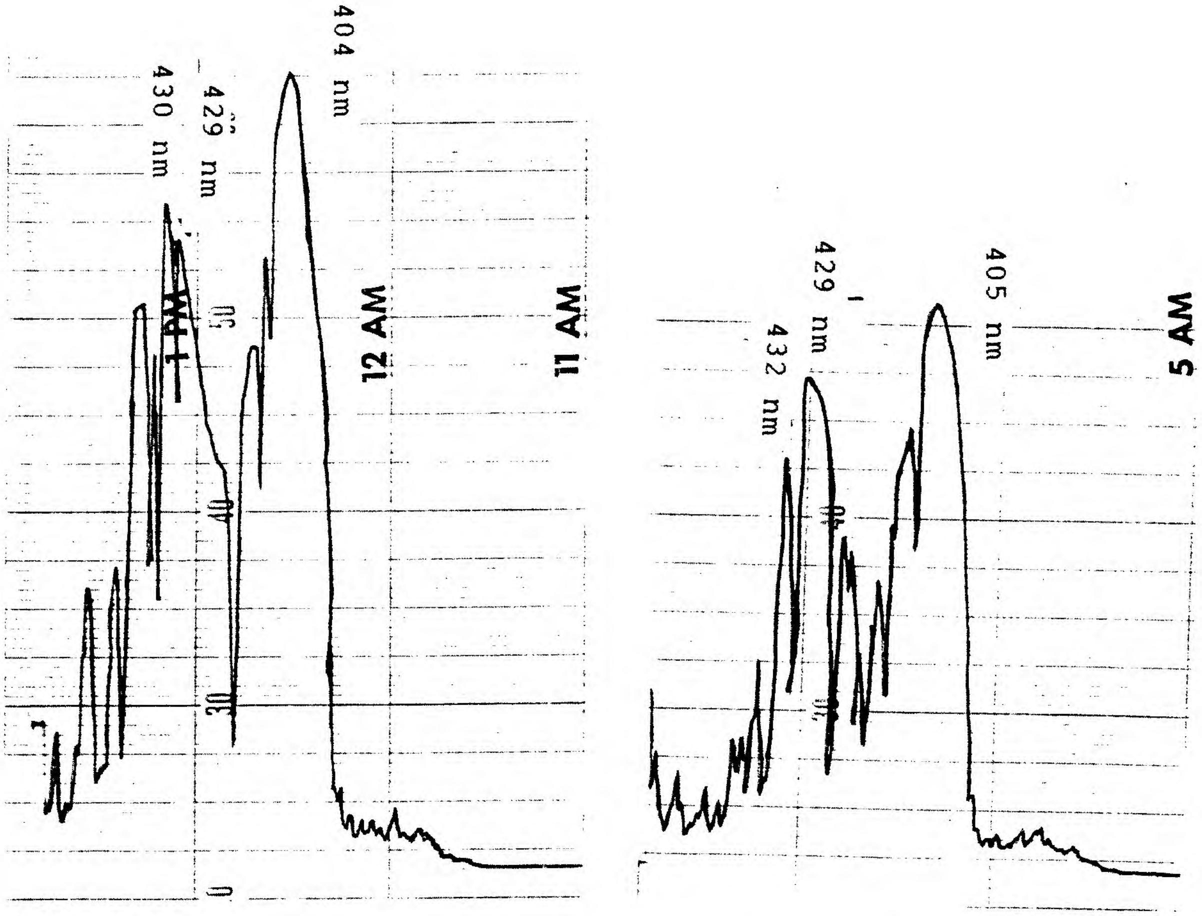
Standard solutions are prepared from the 1000 ng/ml standard solution of B(a)P. The stock solution (1000 ng/ml) is kept at 0 °C. The diluted standard solution are prepared daily before the analysis. A series of standard solutions,, 10, 20, 40, and 60 ng/ml are prepare for calibration using the fluorescence spectrophotometer (Spectrofluo JY3, Jobin Yvon Instruments SA, France) to calibrate the B(a)P concentration of air sample.

ii. Fluorescence Spectrometer analysis

Two 10 mm light path Optical glass cuvettes with four polished windows are used to do the analysis. One cuvette is used for blank solution and another for sample.

The detecting wavelength is also scanned in Fluorescence-Spectrometer. Two wavelengths need to be chosen in this experiment : excitation and emission. The excitation wavelength is varied until fluorescence occurs; often this can be observed visually on the analog meter. The excitation monochromator is then set at this wavelength (or at any point within the excitation wavelength band) and the emission monochromator is allowed to scan, recording the emission spectrum. The emission monochromator is then set at the wavelength at which maximum fluorescence occurred, and the excitation monochromator is now allowed to scan and the excitation spectrum is recorded. In turn, the final emission spectrum is obtained by setting the excitation monochromator at the maximum excitation wavelength and again scanning with the emission monochromator. Through these procedures, we set the excitation wavelength at 380 nm and emission wavelength at 429 nm (or 405 nm optional). Figures 2-5 and 2-6 are the scanning spectra recorded holding the emission wavelength at 380 nm.

The results of the working curves for the standard solutions are close to linear in both UV absorbance and fluorescence analysis. The standard curve (is updated daily) and is regressed on a computer with a linear regression program to calibrate the concentration of samples. Figures 2-7 and 2-8 and tables 2-1 and 2-2 are the results of linear regression using both UV and flourescence detection The concentration levels of samples are under the range of those standard solutions.

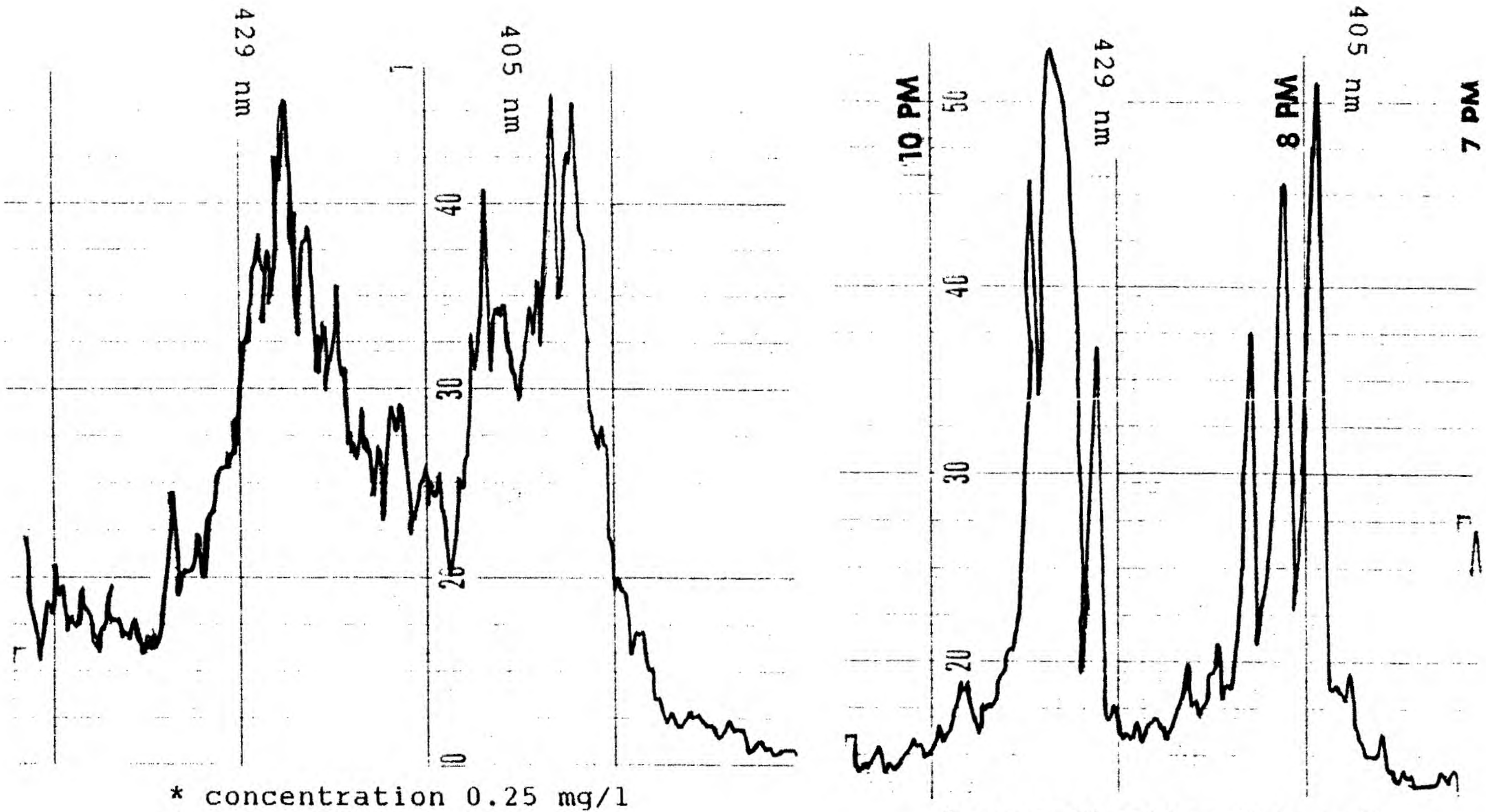


* concentration 2.5 mg/l

* concentration 1.0 ppm

* At Excitation 380 nm
Scanning emission from 350 nm to 500 nm
* Gain x 30

Figure 2-5 Fluorescence Scanning Spectra of B(a)P Standard In Ethanol



* concentration 0.25 mg/l
* Gain x 300

* concentration 0.5 mg/l
* Gain x 300

* At Excitation 380 nm
Scanning emission from 350 nm to 500 nm

Figure 2-6 Fluorescence Scanning Spectra of B(a)P Standard In Cyclohexane

Table 2-1 UV ABSORBANCE OF B(a)P STANDARD SOLUTIONS

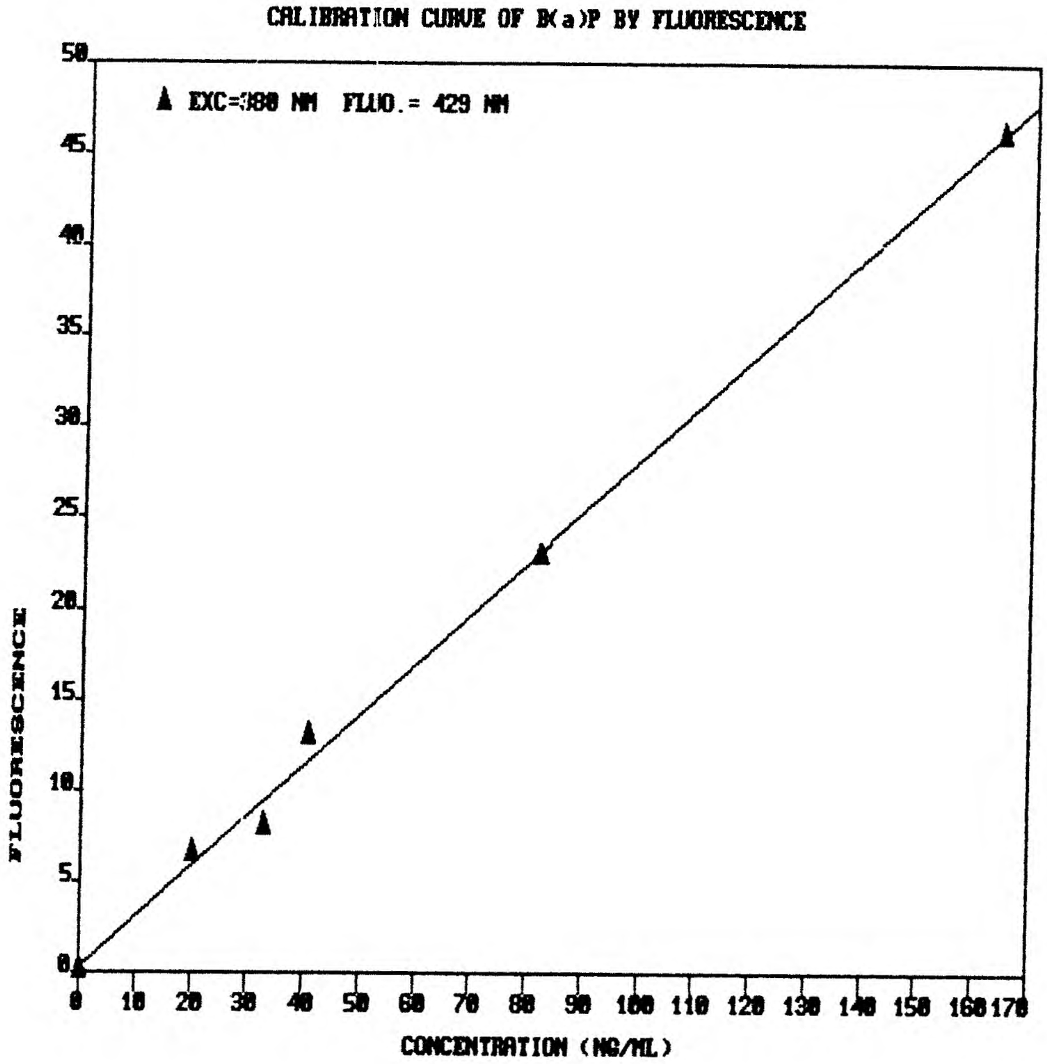
CONCENTRATION X (MG/L)	ABSORBANCE Y (%)
0.00	0.00
1.00	0.24
2.00	0.46
2.50	0.58
5.00	1.20

SLOPE= 0.2395774 +/- 3.348992E-03
INTERCEPT = -7.112551E-03 +/- 1.261997E-02
CORRELATION = 0.9997072

TABLE 2-2 FLUORESCENCE OF B(a)P STANDARD SOLUTION

CONCENTRATION X (NG/ML)	FLUORESCENCE Y (%)
0.0	0.0
20.2	6.5
32.8	8.0
40.5	13.0
81.9	23.0
164.0	46.0

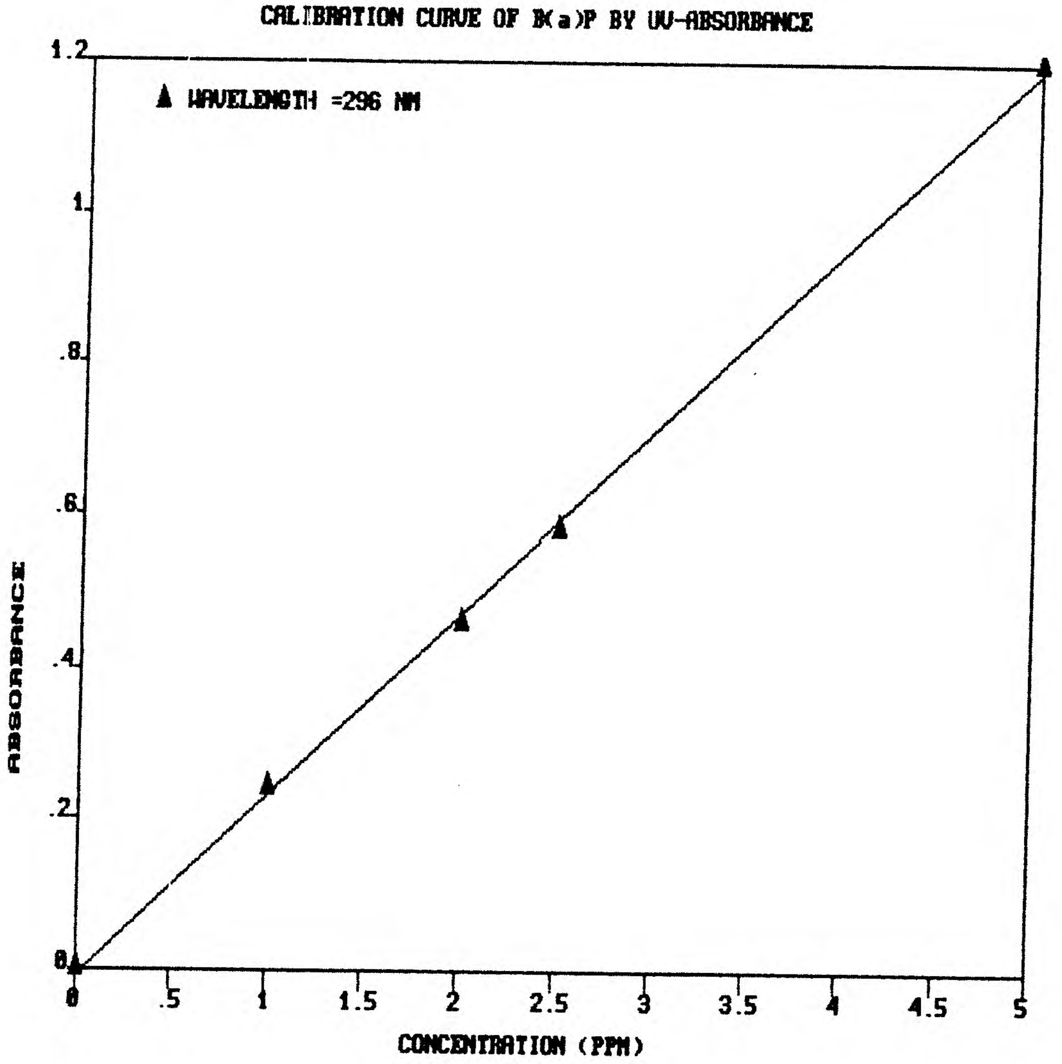
SLOPE = 0.2789214 +/- 8.011986E-03
INTERCEPT = 0.3056806 +/- 1.060764
CORRELATION = 0.9983538



```
THE REGRESSION POLYNOMIAL OF LINE  1 -

        ( 3.057E-01) + ( 2.789E-01)*X
        THE VARIANCE -  7.502E-01
```

Figure 2-7 Calibration Curve of B(a)P standards by Fluorescence



```
THE REGRESSION POLYNOMIAL OF LINE  1 -

    (-7.113E-03) + ( 2.396E-01)*X
    THE VARIANCE -  9.549E-05
```

Figure 2-8 Calibration Curve of B(a)P Standards by UV-Absorbance

CHAPTER 3 RESULTS AND DISCUSSION

1. Calculation of The Amount of PAH on Sample Filter

The amount of the PAH on the 24 hours sample filter was detected by the Spectrometer as the concentration in solvent. A unit conversion factor was needed to calculate the real amount of PAH. Because two different methods of sample pretreatment were used, the calculations were different.

a. Analysis of Sample With Filter Purification Only Pretreatment Procedure

1/9 of the total filter was used, extracted by 10 ml of solvent and analyzed by UV Absorbance and Fluorescence Spectrometry. In comparing the results of UV-Absorbance Spectrometry (results presented as mg/filter) with the result of the TLC analysis (results presented as ng/filter) we needed to convert one set of the units.

The total amount of PAH on the whole filter

= X (ng/filter)

$= C_f \text{ (mg/l)} * 0.01 \text{ (l)} * 10^6 \text{ (ng/mg)} * 9 \text{ (1/filter)}$

C_f : final concentration of the solution
0.01 l : volume of solution (extract)

b. Analysis of Samples With The Isolation Via Absorbent Cartridge Pretreatment

1/9 of the filter was cut and 10 ml of solvent was used to extract. The 10 ml solution was flowed through the chosen cartridge and eluted by only 5 ml of second solvent (flow in reverse direction). The 5 ml of solution was then was then analyzed by fluorescence or absorption

The amount of B(a)P on the whole filter

$$= X \text{ (ng/filter)}$$

$$= C_f \text{ (mg/l)} * 0.005 \text{ (l)} * 10^6 \text{ (ng/mg)} * 9 \text{ (1/fillter)}$$

2. Analysis Results And Discussion

a. Analysis results

Figures 3-1 to 3-2 are UV absorption spectras of samples and and standard. Figure 3-1 was the spectra of the samples which were extracted by methylene chloride. The spectra of two samples in figure 3-1 did not trace the spectra of standard well and both of the sample spectra had the peak around wavelengh 240 nm to 280 nm. The Figure told that a large amount of compounds were extracted from the filter by methylene chloride and detected at wavelength 296 nm but they were not only B(a)P or PAH. Even though they had

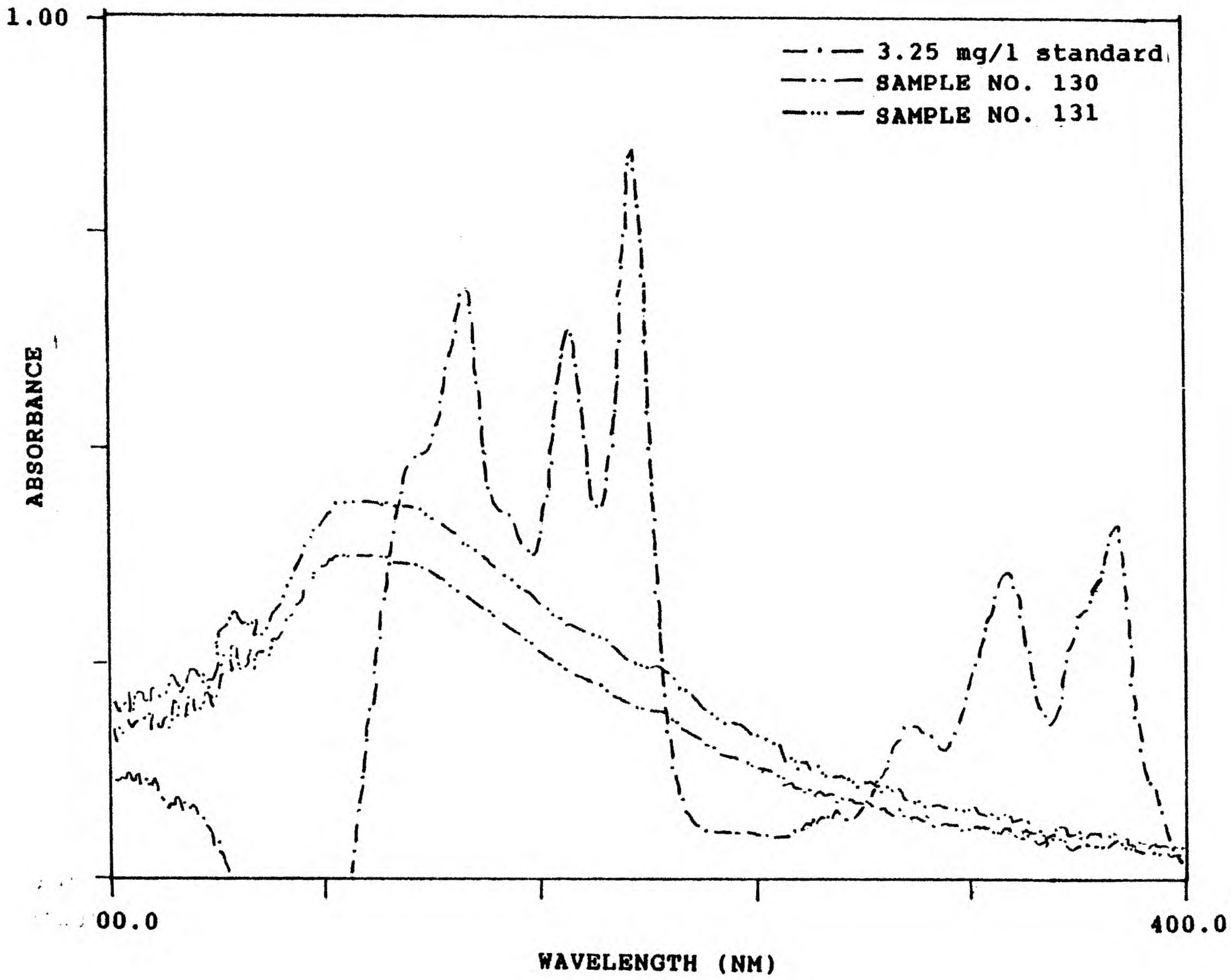


Figure 3-1 UV Absorbance Scanning Spectra of B(a)P Standard And Air Samples in Methylene Chloride

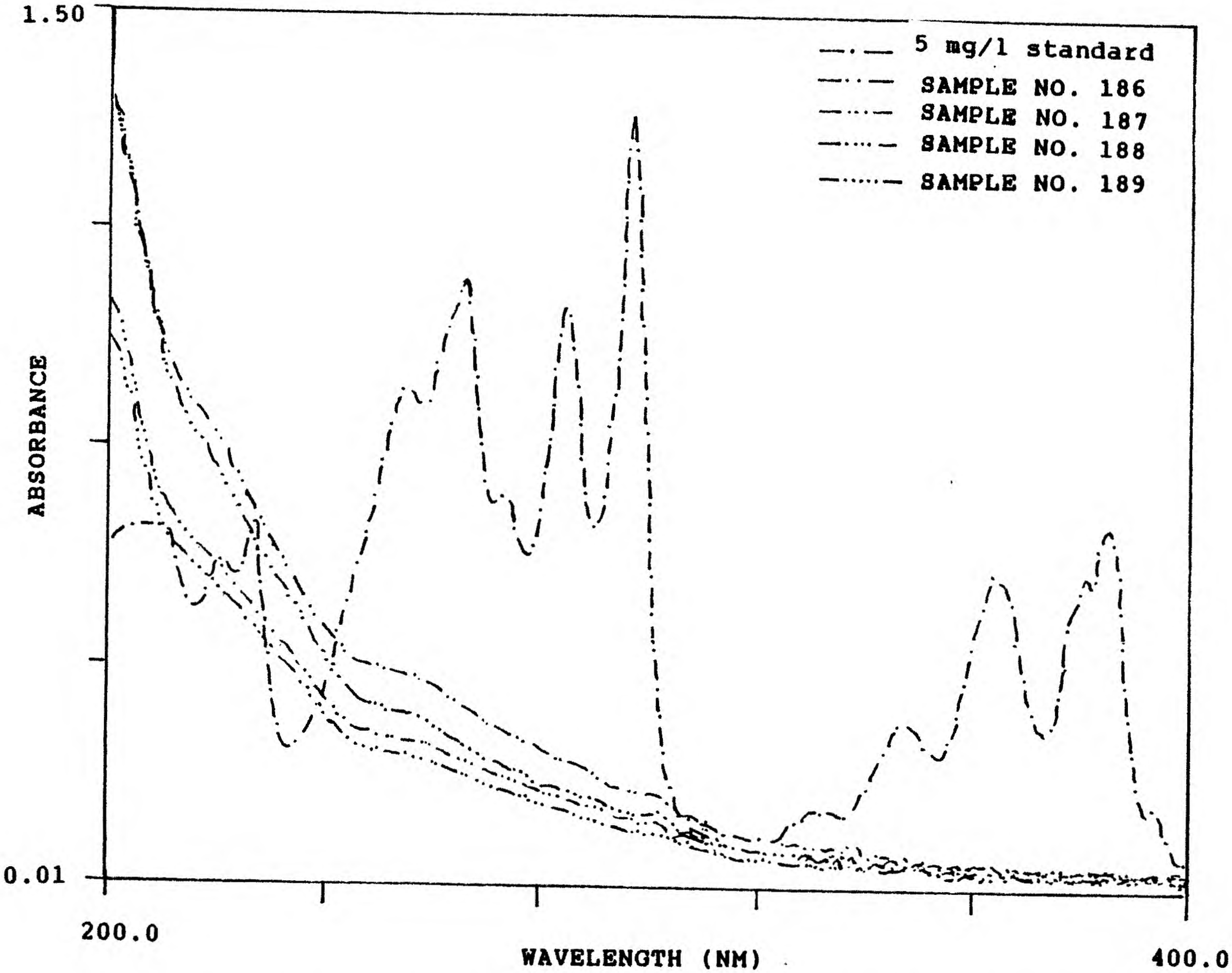
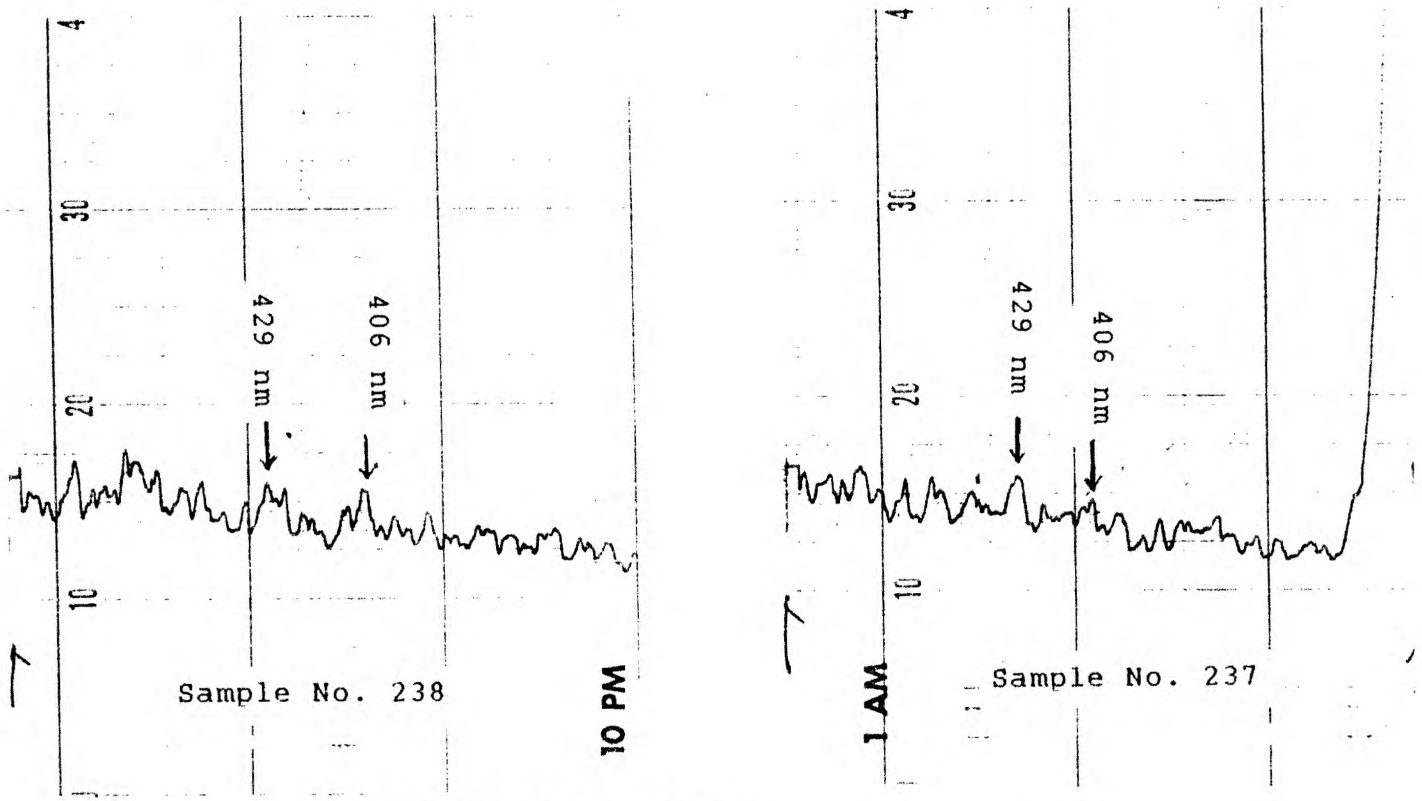


Figure 3-2 UV Absorbance Scanning Spectra of B(a)P Standard And Air Samples in Cyclohexane

some smooth peaks at 296 nm that could not be identified as B(a)P or PAH. Figure 3-2 was the spectra of the samples which were extracted by cyclohexane. Same conditions as Figure 3-1 were happened in Figure 3-2. Here, the extracted compounds by cyclohexane were less than by methylene chloride. Thought these two figures did not have the specific character of PAH, they gave the same characters in a sampling location and the same extraction solvent.

Figure 3-3 was the fluorescence spectra (at excitation wavelength 380 nm and scanning the fluorescence from 350 nm to 500 nm) of sample which were extracted by cyclohexane. The detecting peaks of fluorescence were indicated. The detecting signals here were too low (The smallest fluorescence scale were used to detect the samples.) to identify the characters of the B(a)P or PAH. However, the character of fluorescence was more specific than UV-absorbance. The results of fluorescence were of cause smaller than the results of UV-absorbance (compare to the result in Figures 3-1 and 3-2).

The analysis results were listed in tables 3-1 to 3-4. The data include the results of analysis by TLC and absorbance/fluorescence. Four solvents, hexane, ethanol, cyclohexane, and methylene chloride, were used to extract



* At Excitation 380 nm
Scainning emission from 350 to 500 nm

* Gain x 1000

Figure 3-3 Fluorescence Scanning Spectra of Air Samples in Cyclohexane

TABLE 3-1

Total PAH (as BAP) Analysis of Air Sample
Analyzed by UV-Spectrometer and Fluoro-Spectrometer
Compared to TLC, Sample Extracted by 10 ml Cyclohexane

	TOTAL PAH ANALYSIS		BaP ANALYSIS
sample no.	UV ng/filter	Fluorescence ng/filter	TLC ng/filter
186	55252	5217	1045.82
187	38993	3140	758.84
188	43211	3964	878.99
189	33177	2442	888.53
190	31544	3248	458.97
191	21952	1458	331.10
204	24469	1637	790.23
205	42395	2890	734.87
206	79095	6112	1361.21
207	38789	1816	842.87
209	55218	1887	368.96
210	56612	2424	328.09
211	76170	3355	535.24
212	42667	1494	321.40
213	47837	2174	288.93
214	23993	1458	307.67
215	38449	1816	389.64
216	40830	2174	378.72
217	32905	1923	246.95
219	25864	1637	519.19

TABLE 3-2

Total PAH (as BAP) Analysis of Air Sample Analyzed by UV-Spectrometer and Fluoro-Spectrometer Compared to TLC, Sample Extracted by 10 ml Methylene Chloride

	TOTAL PAH ANALYSIS		BaP ANALYSIS
sample no.	UV ng/filter	Flurescence ng/filter	TLC ng/filter
130	68121	---	961.00
131	84483	---	2461.48
132	4649	---	28.50
133	110803	6396	1190.34
134	76429	5270	1267.26
135	77428	5720	1543.46
136	64500	4143	973.32
137	69642	3692	1012.92
138	94860	---	1205.73
139	57060	3467	1124.80
140	111105	5270	1230.18
141	---	6846	1370.46
142	---	5270	1295.80
144	93870	4368	883.94
145	89790	---	681.76
146	73440	5044	593.87
147	93880	5044	708.35
148	89790	4819	530.54
149	89790	---	715.68
150	57110	---	530.54
151	81620	4594	480.17
152	40700	---	410.64
153	77500	---	436.57
154	40700	---	617.52
155	53020	---	411.60
156	102050	---	783.40
157	36680	---	665.20

TABLE 3-3.1

Total PAH(as BAP) Analysis of Air Sample
Analysed by UV and Fluoro-Spectrometer
Sample Extracted by 10 ml Ethanol (Anhydrous)

	TOTAL PAH ANALYSIS		BaP ANALYSIS
sample no.	UV ng/filter	Fluorescence ng/filter	TLC ng/filter
143	145871	11417	1263.22
144	183830	8487	883.94
145	145871	9952	681.76
146	123096	10440	593.87
147	183830	9708	708.35
149	161055	10196	715.68
150	153463	6387	530.54
151	85137	7266	480.17
152	107913	5557	410.64
153	69954	4092	436.57
154	153463	7022	617.52
155	123096	6534	411.60
156	176238	10196	783.41
157	123096	8731	655.20
158	86830	5618	547.00
159	78844	4810	416.68
160	190645	10066	1227.15
162	98808	6022	430.57
173	150716	8853	602.95
174	186652	9661	554.80
176	154709	9257	912.67
177	166688	9944	832.60
182	118773	6225	601.34
183	198631	10874	645.29
184	134744	5416	805.38
185	118773	7842	743.09
186	191352	10672	1045.82
187	167500	7640	758.84
188	175451	7842	878.89
189	143649	7033	888.53
190	135698	9055	458.97
191	111846	9863	331.10
192	119797	6022	291.28
194	103896	5820	262.21
195	87995	6225	359.72
196	80044	4082	232.25
197	167500	11279	384.93
198	80044	4001	249.06
199	87995	5012	370.31
201	135698	6225	706.71
202	175451	10066	758.12

TABLE 3-3.2 (CONTINUE)

Total PAH (as BaP) analysis of Air Sample
Analysed by UV and Fluoro-Spectrometer
Sample Extracted by 10 ml Ethanol (Anhydrous)

	TOTAL PAH ANALYSIS		BaP ANALYSIS
sample no.	UV ng/filter	Fluorescence ng/filter	TLC ng/filter
204	139373	7520	790.23
205	139373	10207	734.87
206	92518	17998	1361.21
207	194036	9401	842.87
209	162800	5747	368.96
210	100327	4834	328.09
211	92518	9132	535.24
212	154991	7789	321.40
213	182323	8326	288.93
214	139373	8058	307.67
215	131564	6983	389.64
216	139373	5747	378.72
217	115945	5264	246.95
231	---	10082	445.77
234	---	10082	315.60
235	---	6134	308.27
236	---	6589	1282.76
238	---	9171	725.49
240	---	9930	691.63
241	---	9171	418.50
242	---	6589	376.81
243	---	5526	295.04
244	---	5526	287.72
245	---	4463	217.37
246	---	6893	240.49
247	---	6134	263.28
248	---	7045	321.92
249	---	5071	239.95
250	---	8867	564.68
256	---	4159	150.72
257	---	3552	110.15
258	---	4463	116.72
259	---	3400	115.24

TABLE 3-3.3 (CONTINUE)

Total PAH (as BaP) analysis of Air Sample
Analysed by UV and Fluoro-Spectrometer
Sample Extracted by 10 ml Ethanol (Anhydrous)

	TOTAL PAH ANALYSIS	BaP ANALYSIS
sample no.	Fluorescence ng/filter	TLC ng/filter
260	3786	50.44
261	4131	164.26
262	3786	133.39
263	5047	470.98
264	3613	170.93
265	1309	167.66
266	7925	544.20
267	7753	713.84
268	9650	1018.24
269	7408	535.22
270	8443	619.03
271	7063	411.04
272	5511	284.01
273	5683	291.65
274	3377	305.01
275	3253	143.61
277	5620	224.64
278	6492	254.98
279	6617	373.38
280	6118	260.92
281	4000	264.35

TABLE 3-4

Analysis of B(a)P in Ambient Air Sample
By UV-Spectrometer and Fluoro-Spectrometer and Compared to TLC
Sample Pretreated by Cartridge --- C18 Column

SAMPLE	BaP Fluorescence ng/filter	ANALYSIS TLC ng/filte	RATIO FLUORO/TLC
608	924.84	1476.12	0.63
610	279.10	951.55	0.29
611	171.48	1717.81	0.10
612	709.59	1585.90	0.45
613	386.73	1116.85	0.35
		AVERAGE	0.36

TABLE 3-4.1

Analysis of B(a)P in Ambient Air Sample
By UV-Spectrometer and Fluoro-Spectrometer and Compared to TLC
Sample Pretreated by Cartridge --- Florisil

SAMPLE	BaP Fluorescence ng/filter	ANALYSIS TLC ng/filte	RATIO FLUORO/TLC
616	71.66	41.76	1.72
617	40.95	320.50	0.13
618	225.22	315.10	0.71
619	194.51	330.36	0.59
620	194.51	279.85	0.70
		AVERAGE	0.63

different sample filters. Cyclohexane was the only solvent used for TLC. Ninety-three samples were extracted by ethanol and 20 samples were extracted by cyclohexane. Twenty-four samples were extracted by methylene chloride and analyzed by UV-Spectrometer, but only 14 samples were run by Fluorescence Spectrometer. Five samples were pretreated by C18 and fluorisil cartridges and analysed by fluorescence. These data were all run by TLC to analyze the B(a)P. The units of those data were all coverted into ng/filter for comparing with three different analysis methods.

The comparisons were processed by calculating the ratio of PAH (or B(a)P units) (the samples were analyzed by UV-Spectrometer and Spectrofluometer) and BaP (the samples were analyzed by TLC). The comparison of UV-absorbance and fluorescence by ratio of these two data were also calculated. Those calculation could observe the range of deviation of the data. A possible minor reference factor of PAH to B(a)P may be calculated by a statistical data analysis. The results of comparison were listed in tables 3-5 to 3-10.

The ratio average, standard deviation, and relative standard deviation of each comparative data point was calculated. The population standard deviation was calculated for the sample number over 20. The sample standard deviation was calculated for the sample number under 20. The relative standard deviation was calculated for each data set and presented by percent(%).

The ratio of PAH/B(a)P (or B(a)P units/B(a)P) meant ratio of the result of UV absorbance/fluorescence to the result of TLC. The average ratio, population standard deviation, and relative standard deviation of the samples which were extracted by cyclohexane were: 87.45, 44.91, and 51 % for UV absorbance analysis, and 4.88, 1.65, and 33.8 % for fluorescence analysis. The data were listed in table 3-5.

The average ratio, population standard deviation, and relative standard deviation of the samples which were extracted by methylene chloride and analyzed by UV-Spectrometer were: 98.0, 38.40, and 39%. The average ratio, sample standard deviation, and relative standard deviation of the samples which were extracted by methylene chloride and analyzed by Fluorescence were : 5.28, 1.92, and 36.4 %. The data were listed in table 3-6.

The average ratio, population standard deviation, and relative standard deviation of the samples which were extracted by ethanol were : 263.62, 108.42, and 41.1 % for UV absorbance, and 17.4, 8.93, and 51.6 % for

TABLE 3-5

Analysis of Total PAH (as B(a)P) in Ambient Air Sample By UV-Spectrometer and Fluoro-Spectrometer and Compared to TLC [B(a)P] analysis,

sample	PAH/BaP UV	PAH/BaP Fluorescence	UV/Fluo.
186	52.83	4.99	10.59
187	51.39	4.14	12.41
188	49.16	4.51	10.90
189	37.34	2.75	13.58
190	68.73	7.08	9.71
191	66.30	4.40	15.07
204	30.96	2.07	14.96
205	57.69	3.93	14.68
206	58.11	4.49	12.94
207	46.02	2.15	21.40
209	149.66	5.12	29.23
210	172.55	7.39	23.35
211	142.31	6.27	22.70
212	132.75	4.65	28.55
213	165.57	7.52	22.02
214	77.98	4.74	16.45
215	98.68	4.66	21.18
216	107.81	5.74	18.78
217	133.24	7.79	17.10
219	49.82	3.15	15.82
ratio average	87.45	4.88	17.57
sample std dev	46.08	1.69	
population std dev	44.91	1.65	
rel. std dev.	51%	33.8%	

* Sample No. = 20

* Sample Extracted by 10 ml Cyclohexane

Table 3-6

Analysis Total PAH (as B(a)P) of Ambient Air Sample By UV-Spectrometer and Fluoro-Spectrometer Compared to TLC [B(a)P] analysis

sample	PAH/BaP UV	PAH/BaP Fluorescence	UV/Fluoro
130	70.88	---	---
131	43.32	---	---
132	163.12	---	---
133	93.80	5.37	17.47
134	60.31	4.15	14.53
135	50.16	3.70	13.56
136	66.26	4.25	15.59
137	68.75	3.64	18.89
138	76.67	---	---
139	50.72	3.08	16.47
140	90.31	4.28	21.10
141	---	4.99	---
142	---	4.06	---
144	106.19	4.94	21.50
145	131.70	---	---
146	123.66	8.49	14.57
147	132.52	7.12	18.61
148	117.08	6.26	18.70
149	125.46	---	---
151	107.61	9.5	11.26
152	169.98	---	---
153	99.11	---	---
154	177.52	---	---
155	65.90	---	---
156	128.81	---	---
157	130.26	---	---
ratio average	98.00	5.28	14.45
sample std dev	39.20	1.92	
population std dev	38.40	1.85	
rel. std dev	39%	36.4%	

* Sample No. of UV = 20
Sample No. of Fluo. = 14
Sample Extracted by 10ml Methylene Chloride

Fluorescence. The data were listed in tables 3-7, 3-8, and 3-9.

The average ratio, sample standard deviation, and relative standard deviation of the samples which were pretreated by C18 cartridges were 0.36, 0.196, and 54 %. The samples were pretreated by fluorisil cartridge were 0.77, 0.58, and 75 %. The data were listed in table 3-10.

The results showed that the ratio of PAH to BaP was not a constant. The ratio fluctuated around 30 to 75 % of the average. The average ratio of the samples which were extracted by cyclohexane and methylene chloride were similar. Also they had the better relative standard deviations less than 50%. The results of cartridges were not so good as expected. The possible reason could be the extraction solvents and elution solvent. The extraction efficiency of the first and second solvents could be not so high as expected.

The results showed that the analysis of fluorescence had less interference than the analysis of UV-absorbance. However, the analysis of BaP by fluorescence had some interference also. The interference could be some PAH compounds including: Benz(b)fluoranthene, Benzo(α)pyrene, 3-

Table 3-7

Analysis of Total PAH (as B(a)P) in Ambient Air Sample By UV-Spectrometer anf Fluoro-Spectrometer and Compared to TLC [B(a)P] analysis

sample	PAH/BaP UV	PAH/BaP Fluorescence	UV/ Fluorescence
143	115.48	9.04	12.77
144	207.97	9.60	21.66
145	213.96	14.60	14.65
146	207.28	17.58	11.79
147	259.52	13.70	18.94
149	225.04	14.25	15.79
150	289.26	12.04	24.02
151	177.31	15.13	11.72
152	262.79	13.53	19.42
153	160.24	9.37	17.10
154	248.52	11.37	21.86
155	299.07	15.87	10.84
156	224.96	13.02	17.28
157	187.88	13.13	14.31
158	158.74	10.27	15.46
159	189.22	11.46	16.51
160	155.36	8.20	18.95
162	229.48	13.99	16.40
173	249.96	14.69	17.02
174	336.43	17.41	19.32
176	169.51	10.14	16.72
177	200.20	11.94	16.77
182	197.51	10.35	19.08
183	307.82	16.85	18.27
184	167.31	6.72	24.90
185	159.84	10.55	15.15
188	199.60	8.92	22.38
189	161.67	7.92	20.41
191	337.80	29.79	11.34
192	411.28	20.68	19.89
194	396.23	22.20	17.85
195	244.62	17.30	14.14
196	344.65	17.57	19.62
197	435.14	29.30	14.85
198	321.39	16.06	20.01
199	237.62	13.53	17.56
		AVERAGE	17.58

* Sample extracted by 10 ml Ethanol (Anhydrous)

Table 3-8 (CONTINUE 3-7)

Analysis of Total PAH (as B(a)P) in Ambient Air Sample By UV-spectrometer and Fluoro-Spectrometer and Compared to TLC [B(a)P] analysis

sample	PAH/BaP UV	PAH/BaP Fluorescence	UV/ Fluorescence
201	192.01	8.81	21.79
202	231.43	13.28	17.43
204	176.37	9.52	18.53
205	189.66	13.89	13.65
206	67.97	13.22	5.14
207	230.21	11.15	20.65
209	441.24	15.58	28.32
210	305.79	14.73	20.76
211	172.85	17.06	10.13
212	482.24	24.23	19.90
213	631.03	28.82	21.90
214	452.99	26.19	17.30
215	337.65	17.92	18.84
217	469.51	21.31	22.03
219	268.44	22.62	11.87
234	---	31.95	---
235	---	19.90	---
236	---	5.14	---
238	---	12.64	---
240	---	14.36	---
241	---	21.91	---
242	---	17.49	---
243	---	18.73	---
244	---	19.21	---
245	---	20.53	---
246	---	28.66	---
247	---	23.30	---
248	---	21.88	---
249	---	21.13	---
250	---	15.70	---
256	---	27.60	---
257	---	32.25	---
258	---	38.24	---
259	---	29.50	---
		AVERAGE	17.88

* Sample Extracted by 10ml Ethanol (anhydrous)

Table 3-9 (CONTINUE 3-7 & 3-8)

Analysis of Total PAH (as B(a)P) in Ambient Air Sample By UV-Spectrometer and Fluoro-Spectrometer and Compared to TLC [B(a)P] analysis

sample	PAH/BaP UV	PAH/BaP Fluorescence
260	---	75.06
261	---	25.15
262	---	28.38
263	---	10.72
264	---	21.14
266	---	7.81
267	---	14.56
268	---	10.86
269	---	9.48
270	---	13.84
271	---	13.64
272	---	17.18
273	---	19.4
274	---	19.49
275	---	11.07
276	---	22.65
277	---	25.02
278	---	25.46
279	---	17.72
280	---	23.45
281	---	15.13
ratio average	263.62	17.52
population std dev	108.42	8.93
rel. std dev	41.1%	50.9%

* Sample No. of UV. = 52
Sample No. of Fluo. = 93
Sample Extracted by 10 ml Ethanol (anhydrous)

TABLE 3-10

LIST OF STATISTICAL RESULTS

ITEM	SAMPLE#	AVERAGE RATIO	SAMPLE STD' DEV.	POPULATION STD' DEV.	RELATIVE STD' DEV. (%)
ETHANOL					
UV	52	263.62	---	108.42	41.1
FLUO	93	17.52	---	8.93	50.9
CYCLOHEXANE					
UV	20	87.45	---	44.91	51.0
FLUO	20	4.88	---	1.65	33.8
METHYLENE CHLORIDE					
UV	20	98.00	---	38.40	39.0
FLUO	14	5.28	---	1.85	36.4
C18 CARTRIDGE					
FLUO	5	0.36	0.19	---	54.0
FLORISIL CARTRIDGE					
FLUO	5	0.77	0.58	---	75.0

Methylcholnantrene, Anthracene, Benzathrone, 1-Aminopyrene, 2-Metylanthracene, 9-Methylanthracene, 9-Phenylanthracene, 9,10-Diphenylanthracene, and 5,6-Benzoquinoline which excitation and emission wavelengths are in the neighbor of BaP. The excitation and emission wavelengh of these compounds are listed in table 3-11.

Table 3-11

Screening of Possible Interfering Compounds
TLC Plates -- 20 % Acetylated Cellulose

organic compound	Exiciation nm	Emission nm
Benzo(α)pyrene	386	429
Benz(b)fluoranthene	352	432
1-Aminopyrene	362	421
3-Methylpyrene	364	421
Anthracene	358	404
Benzanthrone	374	470
2-Methylanthracene	358	410
9-Methylanthracene	368	416
9-Phenylanthracene	366	414
9,10-Diphenylanthracene	396	432
5,6-Benzoquinoline	362	408

3. Conclusion

We have not been able to demonstrate that our method of total PAH analysis correlates with BaP measurements. We can not distinguish between the following three conclusions :

i. That BaP does not track total PAH and that our results then show the inequality of total PAH vs BaP which actually exists.

ii. That BaP may track total PAH but our methods of analysis are not specific to PAH, i.e. we measure additional compounds which absorption and fluorescence in the regions of the UV where this analysis was performed.

iii. Neither of above.

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