DOE/ER/60100--T1

"Characterization of Polynuclear Aromatic Compounds in Petroleum-Refining Localities"

Progress Report for the Period
September 1, 1982 to November 30, 1983

Department of Energy
Contract No: DE-AS05-82ER60100

DOE/ER/60100--T1

DE83 017471

Isiah M. Warner, Principal Investigator

Department of Chemistry
Emory University
Atlanta, GA 30322

DISCLAIMER

This progress report, prepared for the Department of Energy, Oakridge Operation, summarizes work performed from September 1, 1982 and projected to November 30, 1983. The studies identified in this report were performed by the research group of Isiah M. Warner at Emory University under Contract No: DE-AS05-82ER60100.

1. Objective

The overall objective of this project is to identify and determine the amounts of polynuclear aromatic compounds that are possibly associated with oil refineries. Our research also involves developing the analytical and air sampling procedures which will be used in our proposed study. In order to obtain the polynuclear aromatic (PNA) content of our samples, several complementary analytical methods have been identified and are being developed to yield the maximum information about the PNA content of our samples. These methods include separation techniques such as gas and liquid chromatography (GC and LC), detection techniques such as mass spectroscopy (MS), video fluorometry (VF), as well as combined techniques such as GC/MS and LC/VF. The air sampling techniques include particle sampling using high volume air samplers with and without cascade impactors and vapor phase sampling using solid adsorbing resins. The combination of air sampling techniques and selective analytical methods should yield new levels of sensitivity and selectivity for the analysis of PNAs in environmental samples.

2. Studies in Oil Refining Localities

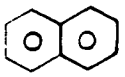
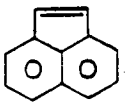
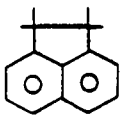
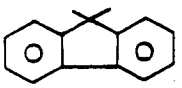
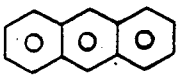
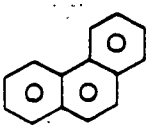
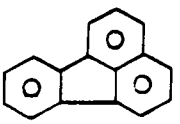
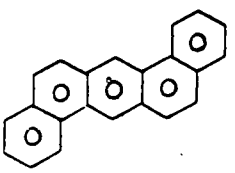
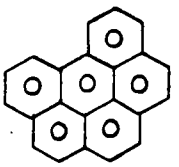
As a follow up to the initial work performed in the Port Arthur - Beaumont area, two additional sampling trips were made to Site B to collect more samples (see previous reports from Texas A&M University under contract DE-AS05-80EV10404). The data reported here is from the first of those two trips. Samplers were placed on two sites within the oil refinery. The first was at a vacuum distillation unit (VD), and a second at the catalytic cracking unit (CC). Two 24-hour high volume air samples were collected at each site. Another high volume air sampler containing a cascade impactor was also set up to collect a 48-hour sample at each site. The use of this impactor allowed size-graded particle fraction collection. The cascade impactor is a multi-stage sampler which separates the particles collected into six size ranges. The top filter collects all particles greater than 10μm. The next stage collects particles with sizes between 10 and 4.9μm. The next three stages collect particle size ranges, 4.9-2.7μm, 2.7-1.3μm and 1.3-.61μm, respectively. The final filter collects particles sized between .61-.3μm. All cascade impactor samples were collected on paper filters and high volume samples were collected on glass fiber filters. In all cases the sampling rate was 40 ft^3/min and precise sampling times were recorded. Vapor phase samples were collected at the vacuum distillation unit using a sampling apparatus of our own design (see previous report). The sampled air passes through a glass fiber filter to remove any suspended particles larger than .3μm. The air is then split and channeled through five different resins: charcoal, Tenax GC,

XAD-2, Chromosorb 105, and Chromosorb LC-9. We were also able to collect some high volume air samples at a Texas State Air Control Sampling Station (AC) in the town of Port Arthur for use as a control. Four 24-hour samples were collected and the results compared to samples collected within the refinery.

Sample Handling - After the samples were collected, the spent filters were wrapped in aluminum foil and refigerated until analysis. The tubes containing the adsorbing resin samples were also wrapped in aluminum foil and refrigerated. All of the high volume air sample filters were soxhlet extracted with 300 mL cyclohexane for 24 hours with the solvent recycling approximately once every 10 minutes. Half of this sample was submitted for GC/MS analysis. A Hewlett Packard 5985 model GC/MS data system under the following conditions was used for the analysis. Separation was obtained using a DB-5 fused silica bonded phase capillary column. Splitless injection was used and helium was the carrier gas. The GC oven initial temperature was 30° C and then programmed to 280° C at 8° C/min. To increase sensitivity and minimize background, selective ion monitoring was used for mass detection. Since the mass spectra of these compounds are relatively simple, the parent ion for each of the 16 priority pollutant PNAs was used for selective scanning.

Results - Table I provides the name, structure and abbreviations for the PNAs to be determined. Table II gives a summary of the pollutants detected in the different 24 hour samples collected both outside the refinery (labeled air control station) and inside the refinery at the vacuum distillation unit, and the catalytic cracking

TABLE I - PNAs of Interest

Compound	Structure	Abbreviation
Naphthalene		NAPH
Acenaphthylene		ACYNE
Acenaphthene		ACENE
Fluorene		FLUR
Anthracene		ANTH
Phenanthrene		PHEN
Fluoranthene		FLAN
1,2,5,6-Dibenzanthracene		DBA
Benzo(ghi)perylene		BghiP

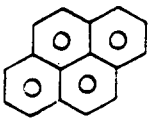
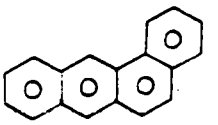
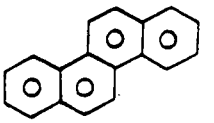
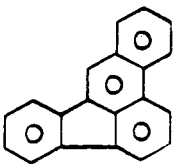
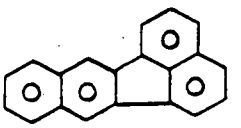
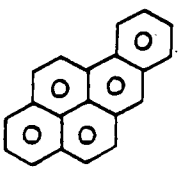
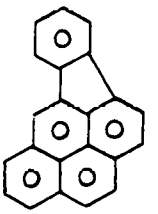
Compound	Structure	Abbreviation
Pyrene		PYRE
1,2Benzanthracene		1,2-BA
Chrysene		CHRY
Benzo(b)Fluoranthene		BbF
Benzo(k)Fluoranthene		BkF
Benzo(a)Pyrene		BaP
Indeno(1,2,3-c,d)pyrene		INDENO

TABLE II - ng Compound/100m^3 Air Sampled

	Air Control Station				Vacuum Distillation Unit		Catalytic Cracking Unit	
Sample #	#1	#4	#6	#9	#2	#5	#7	#10
Compound								
NAPH	1.30	.806	.937	.539	1.36	1.98	1.72	2.74
ACYNE	.266	*	.285	*	*	.385	.472	.403
ACENE	.376	*	*	*	*	.951	.878	.899
FLUR	.721	*	*	*	*	1.44	1.32	1.62
ANTH	1.17	.403	.403	.325	.884	3.03	2.15	3.34
PHEN	*	.511	*	.478	1.13	2.13	1.75	2.19
FLAN	5.86	.842	.904	.578	2.27	7.69	2.43	3.22
PYRE	1.89	.672	.857	.732	2.46	6.28	3.76	3.90
1,2-BA	4.02	.870	17.3	6.91	4.42	16.6	17.0	5.25
CHRY	*	2.96	*	*	3.53	8.25	.605	4.63
BbF and BkF	3.14	*	3.92	*	*	8.74	5.46	4.17
BaP	7.21	*	*	*	*	11.7	7.58	5.51
DBA	*	*	*	*	*	*	*	*
INDENO	*	1.56	2.97	*	*	8.25	*	*
BghiP	*	2.33	6.12	*	3.84	10.6	5.68	*
Wind Direction	Southwest	Southwest	South	Southwest	Southwest	Southwest	South	Southwest
Wind Speed	12mph	7mph	8mph	6mph	12mph	7mph	8mph	6mph
% Humidity	77	56	64	87	77	56	64	87
Barometric Pressure	30.06	29.95	29.97	30.04	30.06	29.95	29.97	30.04

* not detectable

unit (labeled respectively). The numbers shown are nanogram amounts per 100 cubic meters of air sampled. Generally, the amounts found inside the refinery are higher than the amounts found at the Texas Air Control Sampling Station (TACSS). The average wind speed and direction, the average percent humidity, and the average barometric pressure for the 24 hours that the samples were collected is also recorded in each table. Although the data shown are too limited for conclusive results, the difference in concentration of the PNAs in the air at the TACSS may be a result of any or several of these weather conditions.

When sampling with single stage collectors as described above, the total mass concentration for compounds of interest may not be a true indication of the amount of pollutant to which a worker is exposed. For example, if the aerosol being sampled consists of large particles which are "non-respirable", then the total mass concentration for the compounds of interest will not be indicative of the amount actually inhaled. The U.S. Atomic Energy Commission (AEC) has defined respirable dust as "that portion of the inhaled dust which penetrates to the non-ciliated portions of the lung." The Commission set up a standard for insoluable particles in January 1961 (1). They set up the following relationship:

Particle Size vs Respirability

Size* (μm)	10	5	3.5	2.5	2
% Respirable	0	25	50	75	100

*Sizes referred to are equivalent to an aerodynamic diameter having the properties of a unit density sphere.

Other standards have been set by different groups, but they do not differ significantly from the AEC standard.

We used the cascade impactor to get a better estimate of air concentration data related to health hazard. This multistage sampler allows the acquisition of overall size-mass distribution data from which we can determine the mass concentration of the components of interest in specific size range fractions. Tables III and IV are a summary of the data which were collected using the cascade impactor. The mass concentrations for the PNAs which were detected via GC/MS are in units of nanograms per 100 cubic meters of air. The particle size range and the percent mass distribution for each fraction are provided as well as the average wind speed and direction, percent humidity and barometric pressure for both 24-hour periods in which each sample was collected. Although the total amount of PNAs found in both samples varies, the highest concentration of pollutant was found in the fraction which contained the size range 1.3-2.7μm. The difference in concentration of PNAs in both samples might be related to the weather conditions, or possibly activity in the plant itself since the percent mass distribution in both samples is different.

The other half of the soxhlet extract was set aside for HPLC analysis. Because these samples are in a complicated matrix, it is necessary to find a suitable cleanup procedure which will separate the PNAs from the matrix without substantial sample loss. In the past, we have used an extraction procedure proposed by Natusch and Tomkins (2) which uses DMSO and pentane. Recently, Analytichem has introduced a

TABLE III - ng Compound/100m^3 Air Sampled

Sample #	#13	#14	#15	#16	#17	#3
Compound						
NAPH	.585	.940	.948	186	.627	2.01
ACYNE	*	*	.569	446	*	.445
ACENE	*	*	*	646	*	*
FLUR	*	*	*	131	*	1.41
ANTH	*	*	*	1.85	.218	2.00
PHEN	*	*	*	*	*	*
FLAN	.397	*	1.16	380	.500	4.40
PYRE	.314	*	1.90	247	4.56	4.36
1,2-BA	*	*	*	439	1.91	14.7
CHRY	*	1.29	*	5.65	1.15	4.44
BbF and BkF	*	*	*	*	1.29	7.40
BaP	*	.956	*	5.07	*	15.1
DBA	*	*	*	*	*	*
INDENO	*	*	*	*	*	8.33
BghiP	*	*	*	*	*	9.40
Particle Size Range (μm)	>10	10-4.9	4.9-2.7	2.7-1.3	1.3-.61	.61>
% Mass Distribution	2	26	12	25	11	24

The above was collected over a 48-hour period. Weather data are as follows.
Day 1: Average wind speed and direction - Southwest at 12mph; Percent humidity - 77; Barometric pressure - 30.06.
Day 2: Average wind speed and direction - Southwest at 7mph; Percent humidity - 56; Barometric pressure - 29.95.

* not detectable

TABLE IV - ng Compound/100m^3 Air Sampled

Sample #	#18	#19	#20	#21	#22	#8
Compound						
NAPH	1.60	2.51	2.55	2.54	2.03	2.50
ACYNE	*	*	*	*	*	*
ACENE	*	*	*	.950	*	*
FLUR	*	*	1.69	1.58	*	1.11
ANTH	1.48	2.17	2.24	2.70	1.50	4.42
PHEN	*	*	*	1.89	*	4.52
FLAN	1.23	2.18	2.05	2.89	2.12	3.26
PYRE	1.94	3.80	3.68	4.81	2.38	*
1,2-BA	*	5.19	5.59	7.83	*	3.35
CHRY	5.06	6.92	6.07	7.42	3.93	*
BbF and BkF	*	*	*	*	*	9.27
BaP	*	*	*	*	*	*
DBA	*	*	*	*	*	*
INDENO	*	*	*	*	*	*
BghiP	*	*	*	*	*	*
Particle Size Range (μm)	>10	10-4.9	4.9-2.7	2.7-1.3	1.3-.61	.61>
% Mass Distribution	15	18	10	13	9	35

The above was collected over a 48-hour period. Weather data are as follows.

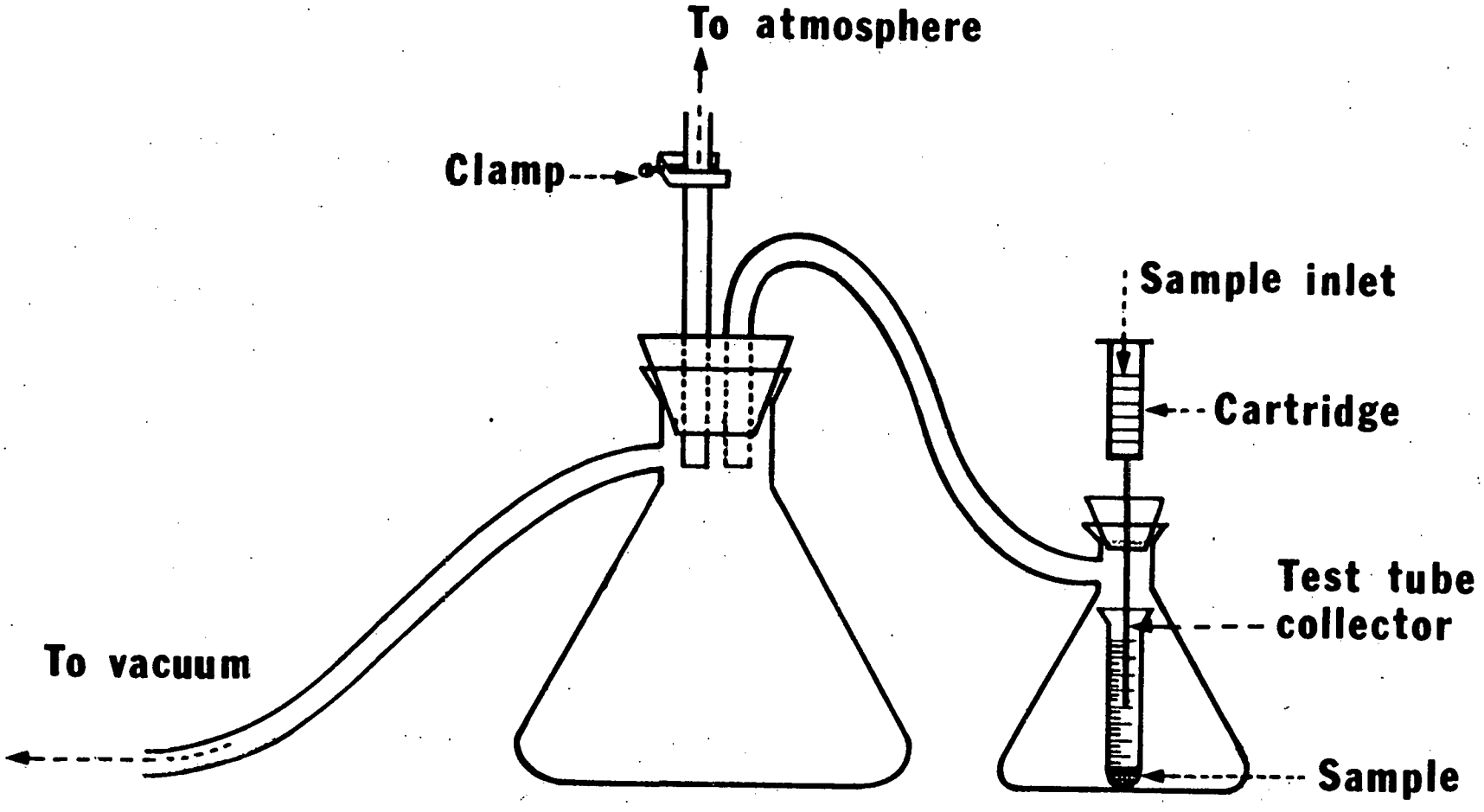
Day 1: Average wind speed and direction - South at 8mph; Percent humidity - 77; Barometric pressure - 29.97.

Day 2: Average wind speed and direction - Southwest at 6mph; Percent humidity - 87; Barometric pressure - 30.04.

* not detectable

new sample cleanup system which uses a small cartridge packed with one of several liquid chromatographic packing materials. Based on some HPLC work done by Chemielowiec and George (3), we decided to apply this system to our problem using a primary-secondary amino bonded phase silica packing material. A diagram of the system we used is shown in Figure 1. The cartridge was packed with approximately 1.5 grams of 30μm amino bonded phase silica. The cartidge was then washed with cyclohexane and any gaps in the cartridge packing were filled. The cartridge fits into a stainless steel needle which goes through a rubber stopper into a test tube which fits in the bottom of the filter flask. This arrangement allows aspirated suction to be applied across the cartridge with the eluent from the column collected in the test tube. The cartridge is prepared by washing with approximately 10 mL cyclohexane. The level of the liquid in the cartridge is brought to the level of the top of the packing material and a clean test tube is placed in the filter flask. A 100μL volume of the soxhlet extract is then pipetted onto the top of the column and the level of the liquid is again aligned with the top of the packing material. An appropriate eluting solvent is then added to the top of the cartridge in 1 mL aliquots. After the addition of each aliquot, vacuum is applied and the eluent collected. After collection, each fraction was analyzed by GC using an FID detector to determine the PNA content. To determine the efficiency of this procedure and to compare it with that of the DMSO/pentane extraction, a spiked PNA sample was added to a glass fiber filter and soxhlet extracted. One aliquot of this concentrated extract was further extracted with DMSO/pentane, while another aliquot was

Figure 1


To atmosphere
Clamp
Sample inlet
Cartridge
Test tube
collector
To vacuum
Sample

cleaned up using the Bondelut cartridge. The overall percent recoveries for the priority pollutant PNAs using both cleanup methods are listed in Table V. Not only is the percent recovery for each PNA better for the Bondelut system, but the total volume of solvent used is also much smaller (30mL total solvent for the Bondelut system versus over 500mL for the DMSO/pentane system).

It is widely recognized that PNAs can also be found as vapors in air. Many of these compounds have relatively low volatilities and consequently low vapor pressures. As a result, these compounds are found in low concentrations in air. For this reason, a very efficient collection scheme must be devised for vapor phase sampling. Many workers use adsorbing resins for collection of organics in the air. In 1973 Zlatkis and coworkers (4) introduced Tenax GC as a resin good for concentrating and analyzing volatile organic vapors. It is a porous polymer particularly stable to heat, and therefore very good for thermal desorption procedures but not necessarily particularly selective for PNAs. However, researchers continue to use Tenax GC as the standard resin for lack of a better resin. Lindgren and others (5) at the Texas State Air Control Board reported the great potential of C_{18} as a selective adsorbant for PNAs. Based on their work and with the advent of several new packing materials for HPLC and GC analysis we decided to use our multistage air sampling system (see previous report) to test the adsorption/desorption capabilities of several resins which might be useful for selective adsorption of PNAs. The resins that were selected for evaluation are listed in Table VI.

These resins were packed into individual cartridges with 100 to

TABLE V

Comparison of Percent Recoveries
for Two Different Extraction Methods

Compound	DMSO/Pentane	Bondelut Cartridge
NAPH		
ACYNE	3	11
ACENE	4	28
FLUR	9	39
ANTH, PHEN	17	41
FLAN	31	50
PYRE	32	68
1,2-BA	33	78
CHRY	36	75
BbF and BkF	31	76
BaP	27	67
DBA	26	51
INDENO	24	62
BghiP	28	42

TABLE VI

Chromosorb LC-9 - Amino Bonded Silica

Chromosorb 105 - Crossed Linked Polyaromatic Resin

Octadecylsilane - Liquid C_{18} Bonded to Silica

Amberlite XAD-2 - Styrene-Divinyl-Benzene Co-Polymer

Tenax GC - 1,6-Diphenyl-p-Phenylene Oxide Polymer

Florisil - Magnesium Silicate

600 mg of adsorbant in a front section and 50 to 100 mg of adsorbant in a back section used to determine breakthrough. The amount of material used was determined by the pressure drop across the cartridge. Enough material was used to provide approximately the same pressure drop across each cartridge. A saturator column was prepared to saturate the air going through it with PNAs since we wanted to sample the PNAs in their vapor phase. The procedure involved weighing an appropriate amount of each PNA to be tested and dissolving it in methylene chloride. A known amount of support (glass beads) was added to the solution. The solvent was evaporated wih stirring, and the resulting analyte coated support was packed into a glass tube using glass wool as plugs. The tube was connected to the inlet end of a five-port manifold and clean nitrogen gas allowed to flow through the tube at a flow rate between 6 and 20 mL/min to obtain PNA saturated gas. Four adsorbing cartridges and one stainless steel piece of tubing were attached to the five outlet ports of the manifold. The pressure drops across each cartridge and the stainless steel tube were adjusted carefully to the same value. Thus, the same flow rate through each outlet is provided. The stainless steel tube was immersed in liquid nitrogen in order to collect all of the PNAs which pass through the tube after sampling is started. The cartridges were left untouched. After 36 hours, the system was shut down and the cartridges and stainless steel tube were ready for desorption.

The desorption process for the resins is as follows. The resins were removed from each tube taking care to keep the front and back portions separate. A blank resin was also prepared for each resin type

and was used as a control. After removing the sampling resin, it was placed in an appropriate solvent and sonicated for 15 minutes. The resin was allowed to settle for a short time, and then an aliquot was run on the GC/FID system. The tube was desorbed by flowing nitrogen through and into methylene chloride and then warming the tube up to room temperature. The final volume is adjusted and then an aliquot is also analyzed by GC/FID. By comparing the amount found in the resins to the amount found in the tube, a percent recovery can be calculated for the process. Table VII provides some preliminary data obtained with this procedure. Florisol and C_{18} had the lowest background while the Chromosorb 105 and XAD-2 collected vapors of all compounds. This is probably because the resins need to be cleaned before use. We expected to see better results with the Chromosorb LC-9 but the low percent recoveries may be due to the influence of water vapor in the air. Further work is continuing on this procedure. The reproducibility, effect of humidity, and the effect of sampling concentrations will be evaluated. For the desorption study, the effect of sonication time, and choice of solvent need to be determined. Finally, several new resins have come on the market in the last few years and some of these have shown promise for selective adsorption for PNAs. We will add some of these to our list of resins to be evaluated.

Summary of Work to Date

The analytical methods that we are applying to the identification and determination of PNAs at trace levels in oil refining localities appear to be quite effective. These preliminary studies indicate that PNAs are found in and around oil refinery localities using high volume

TABLE VII

Adsorption/Desorption Performances

	Florisil	C_{18}	Chrom 105	XAD-2	LC-9
Naphthlyene	3.6	1.5	24.3	72.6	--
Acenaphthylene	87.0	30.7	63.5	1.2	--
Acenaphthene	91.3	32.2	64.7	7.6	--
Fluorene	85.6	36.1	79.2	6.5	--
Phenanthrene	29.9	13.2	64.2	55.8	--
Anthracene	--	--	--	77.0	--

sampling procedures. However, the concentration level of pollutants found appear to be very low when compared to background samples taken at a Texas Air Control sampling station. Further studies are continuing with particular emphasis on the analysis of vapor phase samples using the adsorbing resins described previously.

References Cited

1. Hatch, T. F.; Gross, P.; Pulmonary Deposition and Retention of Inhaled Aerosols, Academic Press, N.Y. 1964.

2. Natusch, D. F. S.; Tompkins, B. A.; Anal. Chem. 50, 1429 (1978).

3. Chmielowiec, J.; George, A. E.; Anal. Chem. 52, 1154 (1980).

4. Zlatkis, A.; Lichtestein, H. A.; Tishbee, A.; Chromatographia 6, 67 (1973).

5. Lindgren, J. .; Krauss, H. J.; Fox, M. A.; J. Air Pollution Control Association 30, 166 (1980).

Manuscripts Published Since Last Report

1. Ho, C.-N. and Warner, I. M., "Multicomponent Mixture Analysis by Multidimensional Phosphorimetry," Analytical Chemistry, 54, 2486-2491 (1982).

2. Rossi, T., Shelly, D. C. and Warner, I. M., "Optimization of a Multiple Solvent Extraction Flow Injection Analysis System," Analytical Chemistry, 54, 2056-2061 (1982).

3. Wong, M., Oldham, P., Ho, C.-N. and Warner, I. M., "High Speed Parallel Interface for a PAR Multichannel Detector Controller and a HP9845 Minicomputer," Chemical, Biomedical and Environmental Instrumentation, 12, 185-199 (1982).

4. Fogarty, M. P., Ho, C.-N. and Warner, I. M., "Data Handling in Contemporary Fluorescence Spectroscopy," in Optical Radiation Measurement, Volume 3, Edited by K. D. Mielenz, Academic Press, New York, N. Y. pp 249-314 (1982).

5. Karlesky, D., Shelly, D. C. and Warner, I. M., "A Study of Polynuclear Aromatic Hydrocarbons on an Amino Bonded Phase Liquid Chromatographic Column in the Normal and Reversed Phase," J. Liquid Chromatography, 6, 471-495 (1983).

Oral Presentations Since Last Report

1. Warner, I. M., Rossi, T. M. and Ho, C.-N., Invited lecture on "Selected Applications of a Rapid Scanning Fluorometer," Second NBS-ADABSE Analytical Chemistry Workshop, at the National Bureau of Standards, Gaithersburg, October 24-29, 1982.

2. Warner, I. M., Rossi, T. and Ho, C.-N., Invited lecture on "Selected Applications of Rapid Scanning Fluorimetry and Phosphorimetry," 21st Eastern Analytical Symposium, New York, November 17-19, 1982.

3. Warner, I. M., Rossi, T. and Ho, C.-N., Invited lecture on "Recent Studies Using Multiparameter Luminescence Techniques," in Symposium on "Advances in Luminescence Spectroscopy," at the 1983 Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, Atlantic City, New Jersey, March 7-11, 1983.

4. Warner, I. M. and H. C.-N., Invited lecture on "Multiparameter Fluorescence Spectroscopy," 1983 Meeting of the Southeastern Association of Analytical Chemists (SEAAC), Atlanta, Georgia, April 14-16, 1983.

5. Rossi, T. and Warner, I. M., "Image Analysis Techniques for Data Reduction in Two Dimensional Fluorescence Spectroscopy," Thirty-fourth Southeast Regional Meeting, Birmingham, Alabama, November 3-5, 1982.

6. Oldham, P., Wong, M., Ho, C.-N. and Warner, I. M., "A High Speed Parallel Interface for a PAR Multichannel Detector Controller and a HP9845 Minicomputer," 34th Southeast Regional Meeting, Birmingham, Alabama, November 3-5, 1982.

Oral Presentations Since Last Report (Continued)

7. Kennedy, J. R., Somayazulu, G., Ho, C.-N. and Warner, I. M., "A Triatomic Method for Estimation of Gas Chromatographic Retention Indices," 185th ACS National Meeting, Seattle, Washington, March 20-25, 1983.