

Sampling and Analysis of Polynuclear Aromatic Hydrocarbons in Working Environment

Nam Won Paik

Clayton Environmental Consultants, Inc.
Southfield, Michigan, U.S.A.

공기중 Polynuclear Aromatic Hydrocarbons의 측정법에 관한 연구

백 남 원

미국 미시간주 싸우스필드
클레이튼 환경연구소

요 약

공기 중에는 benzo(a)pyrene 을 위시한 여러 가지 polynuclear aromatic hydrocarbons (FNAs)가 존재하고 있으며, 그 측정방법이 매우 복잡하여 아직 통일된 적절한 방법이 없다.

본 연구는 공기 중의 PNAs를 측정하기 위한 적절한 방법을 개발하기 위하여 여러 가지 실험을 실시하였고 또 실제로 근로자들을 대상으로 공기를 채취하여 분석한 결과는 다음과 같다.

(1) 공기 중 PNAs의 채취방법으로는 Teflon filter와 Polyurethane foam 또는 XAD-2를 연결하여 사용 하는 것이 가장 좋은 효과를 보였다.

(2) 검체에서 PNAs를 추출하는 방법으로는 methylene chloride를 이용한 초음속진동법(ultra sonication)이 효과적이었다. benzene과 cyclohexane은 추출효과가 methylene chloride보다 적었으며, 초음속진동시간은 15분이 가장 적절하였다.

(3) 분석법으로는 high pressure liquid chromatograph(HPLC)가 적절하였다.

INTRODUCTION

Polynuclear aromatic hydrocarbons (PNAs) are difficult to monitor and quantify. However, the specific identity of PNAs is often necessary to accurately determine the hazard since the toxicity of various PNAs are believed to vary

greatly, especially in their confirmed carcinogenic potential.¹⁻³⁾ The Occupational Safety and Health Administration (OSHA) has, through its coal tar pitch volatiles standard, presumed similar PNAs profiles for operations as diverse as coke oven procedures, charcoal production, asphalt production, and petroleum coking operations.⁴⁾

This study was designed to evaluate and laboratory-test various sampling and analytical methods for monitoring PNAs in the work environment and, following the laboratory testing, to conduct field surveys using these methods in select petroleum coking operations. At the present time, three PNAs sampling procedures are being used in field tests: (1) a Teflon filter followed by polyurethane foam packed tubes, (2) a Teflon filter followed by an XAD-2 resin tube, and (3) the traditional glass fiber filter/silver membrane filter combination.⁵⁾

METHODS

Laboratory testing was conducted to evaluate the proficiency of various sampling and analytical procedures. Testing to date has centered primarily on the selection of suitable collection media, and optimization of sample preparation and extraction procedures by the evaluation of various extraction solvent techniques and comparing Soxhlet with ultrasonic extraction.

Final analysis and PNAs scans were performed on a Waters Associates dual pump gradient high pressure liquid chromatograph (HPLC) under the following conditions:

Column:	Waters Radial Compression Module
Injection Size:	5 microliters
Flow rate:	3 milliliters/minute
Detectors:	a) Waters 440UV at 254 nm b) Waters 420 fluorescence, 360 excitation, 425 emission.

To determine the most suitable solvent for extraction of PNAs materials, various petroleum

coke fractions were Soxhlet-extracted in triplicate with benzene, cyclohexane, and methylene chloride for up to 72 hours. At various intervals, the solvent was removed and replaced with fresh solvent.

Soxhlet and ultrasonic extractions were compared by depositing known amounts of coke on glass fiber filters and either extracting in the Soxhlet apparatus for 6 hours using methylene chloride or ultrasonically for 15 minutes and 60 minutes, also using methylene chloride.

A variety of filtration and solid sorbent media were evaluated. Ground coke was deposited on glass fiber filters, glass fiber/silver membrane filters, and Teflon filters. The filters were ultrasonically extracted in methylene chloride and analyzed by the HPLC procedure described above.

Other researchers have indicated that it is highly desirable to provide a back-up solid sorbent to improve collection of the volatile PNAs.⁶⁻⁹⁾ Therefore, various backup sorbents were tested. Solid sorbents which were tested included Tenax GC, XAD-2 resin, polyurethane foam (PUF) plugs, Chromosorb 102, and 1% SP-2250. These media, preceded by a glass fiber filter, were exposed to a petroleum coke dust environment and analyzed for PNAs. These solid sorbents were also tested in desorption efficiency studies being spiked with known amounts of naphthalene, anthracene, chrysene, benzo(a) pyrene, and 1,2,4,5-dibenzopyrene. The tubes were desorbed in an appropriate solvent and analyzed using HPLC.¹⁰⁾

The coke used in these studies was obtained from a Mid-western refinery in the United States. The coke was ground in a ball mill to

obtain 90 to 94% of the particles at less than 5 μm . The coke was stored in the dark at 5 to 10°C.

RESULTS

Solvent selection

Extraction efficiencies for cyclohexane, benzene, and methylene chloride are listed in Table 1. Measured as total PNAs, based on six indicator materials—anthracene, benzo(a) pyrene, fluoranthene, chrysene, perylene, and benzo (g,h,i) perylene—methylene chloride was the most efficient of the three solvents. The data over the 72-hour extraction is presented in Figure 1. After 12 hours, each solvent extracted the major portion of the six PNAs.

Soxhlet versus ultrasonic extraction

Six-hour Soxhlet extraction and 15-minute sonication were shown to provide a good extraction of PNAs as measured using nine PNAs as indicators. The data are presented in Table 2. Sonication for 60 minutes produced a lower extraction percentage, possibly indicating a breakdown of some of the PNAs used as indicators.

Table 2. Extraction by Soxhlet versus Ultrasonication

Extraction Procedure	Total Extracted PNAs* (μg)	Total Particulate Weight (mg)	% PNAs**
6-hr. Soxhlet Extraction	84.4	32.0	0.26
15-min. Sonication	54.3	21.8	0.25
60-min. Sonication	43.0	25.0	0.22

* As indicated by analysis of naphthalene, anthracene, pyrene, benzo (a) anthracene, chrysene, benzo (a) pyrene, dibenz (a,h) anthracene, benzo (g,h,i) perylene, 1,2,4,5-dibenzopyrene.

** Percentage PNAs extracted from total particulate.

Table 1. Extraction Efficiencies for PNAs by Soxhlet Procedure Using Three Solvents

Extraction Time (Hours)	Total PNAs Extracted by Solvents, μg		
	cyclohexane	benzene	methylene chloride
4	183	1340	2990
6	243	1470	3200
12	345	1530	3320
24	463	1660	3440
48	482	1700	3470
72	590	1800	3650

Evaluation of sampling media

The stability of PNAs on various filter media was tested by drawing humid and dry air through glass fiber/silver membrane, silver membrane, or Teflon filters upon which petroleum coke had been deposited. Data for the glass fiber/silver membrane and Teflon filters are shown in Table 3. (The silver membrane filter alone did not retain the petroleum coke.) The Teflon filters exhibited better retention of PNAs as shown by a comparison between the initial deposition and extractables following exposure to 7 hours of dry or humid air.

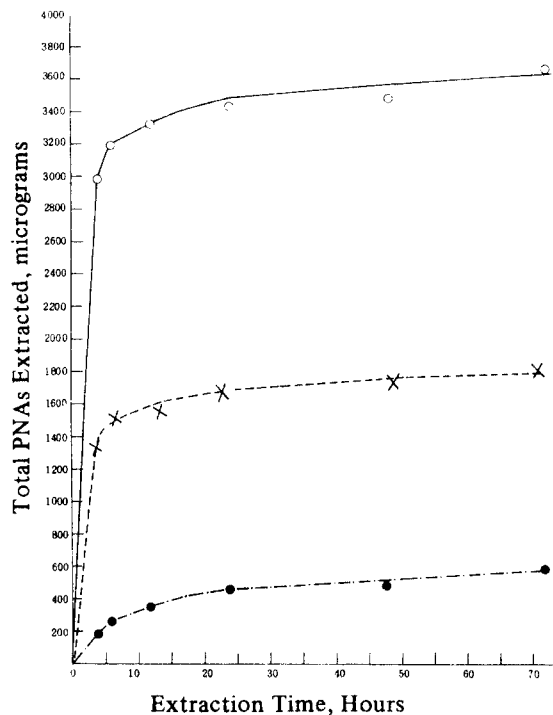


Figure 1. Total PNAs Extracted by Soxhlet Methods using Three Solvents, Cyclohexane (●), Benzene (x), and Methylene chloride (○).

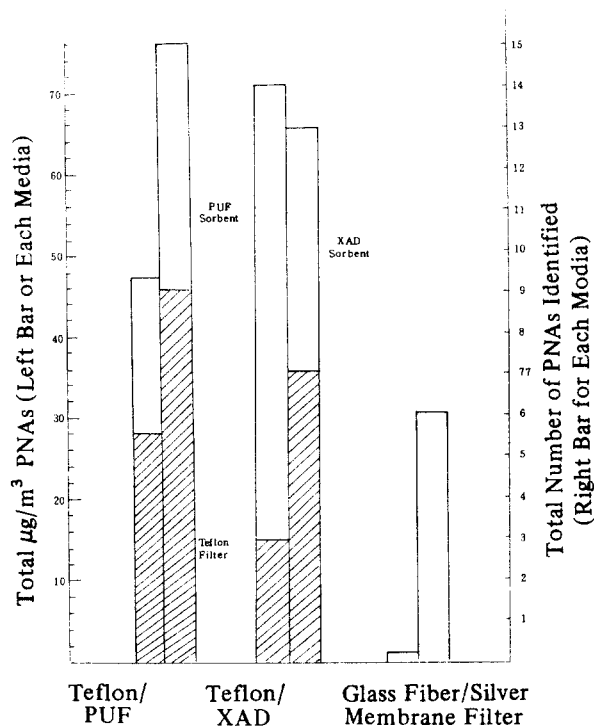


Figure 2. Comparison of Collection for Three Sampling Media.

Table 4. Summary Percentage Recoveries

Solid Sorbent	Percent Recovery			
	Test 1	Test 2	Test 3	Average
Chromosorb 102	68.9	81.3	77.5	75.9
Polyurethane Foam	101.0	101.6	63.2	88.6
XAD-2 Resin	102.1	58.9	97.0	86.0
Tenax GC	59.0	66.3	70.7	65.3

Solid sorbent tubes were evaluated through a procedure similar to that described for filters: coke was deposited on a glass fiber filter and air was drawn through the filter and a solid sorbent-volatile PNAs were presumed to collect on the sorbent. This procedure showed varied and extremely low PNAs values.

Solid sorbents were further tested in desorption studies. Results are presented in Table 4. The PUF tubes and XAD-2 resin tubes were similar in recoveries and showed significant improvement over that seen with Chromosorb 102 and Tenax GC.

Table 3. PNAs Recovered from Coke Dust Deposited on Glass Fiber/Silver Membrane and Teflon Filters

Filter	Total PNAs Extracted (μg)	% PNAs Lost Following Dry or Humid Air
<u>Teflon Filter</u>		
Extraction from initial deposition	2800	—
Extraction following 7 hours dry air*	2500	11
Extraction following 7 hours humid air**	2300	18
<u>Glass Fiber/Silver Membrane Filter</u>		
Extraction from initial deposition	730	—
Extraction following 7 hours dry air	610	16
Extraction following 7 hours humid air	570	22

* Following initial deposition, dry air at 2 liters/minute was drawn through the filter.

** Following initial deposition, humid air at 2 liters/minute was drawn through the filter.

Field test data

Based on our own limited laboratory test data and the experience of others reported in the literature, sampling trains consisting of a Teflon filter followed by either a PUF plug in a tube or an XAD-2 resin tube were chosen for field testing. To date, a variety of personal and area samples have been collected. Preliminary personal sampling results are listed in Table 5. The two procedures are shown to be comparable in the number of PNAs identified and in the amount and number of PNAs which were quantifiable.

The two test procedures were used to collect area samples simultaneously with the NIOSH

glass fiber/silver membrane filters.¹¹⁾ As shown in Figure 2, the number of PNAs identified (right side of each column), and the amount of PNAs quantified (left side of each column) were significantly greater using the Teflon filter with either the XAD-2 or PUF tube than that found with the glass fiber/silver membrane filter. It is interesting to note that a distinct breakoff was observed, with PNAs up to chry-sene (in size and molecular weight) being collected on the sorbent while the larger PNAs were collected on the filter media.

DISCUSSION

A variety of sampling and analytical proce-

Table 5. Preliminary Personal Sampling Results*

PNAs	Amount of PNAs determined, $\mu\text{g}/\text{m}^3$					
	TE/XAD			TE/PUF		
	1	2	3	1	2	3
Naphthalene	--	--	--	--	--	--
Acenaphthalene	--	--	--	--	--	--
Fluorene	--	--	--	<10	--	--
Phenanthrene	< 5	<2	2	15	<2	5
Anthracene	< 5	--	<2	< 5	--	--
Fluoranthene	--	--	--	--	--	--
Pyrene	--	--	--	--	--	--
Benzo (a) anthracene	--	--	--	--	--	--
Chrysene	<10	<5	--	--	--	<5
Benzo (b) fluoranthene	0.5	<2	<2	< 5	<2	<2
Benzo (k) fluoranthene	--	--	--	--	--	--
Benzo (a) pyrene	< 0.5	0.5	<0.2	<0.5	0.5	<0.2
Dibenzo (a,b) anthracene	--	--	--	--	--	--
Benzo (g,h,i) perylene	<10	<5	--	--	--	--
Indeno (1,2,3,c,d) pyrene	--	--	--	--	--	--

* No entry (--) implies non-detected; compounds with less than symbol (<) were identified but at too low an amount to be quantified.

dures have been proposed and tested in order to better distinguish and characterize polynuclear aromatic hydrocarbons in the environment.⁵⁻¹¹) An appropriate sampling procedure should allow identification of PNAs in the worker's breathing zone without significant deterioration of the analyte and with a maximum of precision and accuracy.

Results of laboratory testing suggested that the Teflon filter was superior to the traditional glass fiber in retaining PNAs found in petroleum coke dust. In addition, there was no significant effect due to humid air.

PNAs are soluble in many organic solvents and various organic solvents, such as acetone,

benzene, cyclohexane, chloroform, methanol and other alcohols, acetic acid, methylene chloride, and tetrahydrofuran, have been recommended for the Soxhlet extraction.⁵⁾

Pierce and Katz¹²⁾ have determined extraction curves for PNAs from glass fiber filters; extraction with benzene was essentially complete after 6 hours.

This study indicated that methylene chloride was the solvent of choice although the use of methylene chloride resulted in the extraction of additional aliphatic hydrocarbons as well as improved extraction of particular PNAs.

An interesting alternative to the Soxhlet extraction of atmospheric dust is the use of

ultrasonic vibration at room temperature and this method was adopted by the National Institute for Occupational Safety and Health (NIOSH).^{11,13)}

This study indicated that ultrasonication was similar to the Soxhlet procedure in extraction efficiency where the same solvent was used.

Field testing of the Teflon filter with either a PUF or XAD-2 sorbent back-up tube was conducted; the results showed either procedure to be superior to the glass fiber/silver membrane filter procedure. It is interesting to note that a distinct breakoff was observed, with PNAs up to chrysene (in size and molecular weight) being collected on the sorbent while the larger PNAs were collected on the filter media.

It has been reported that very fine particles associated with PNAs in air might be collected on PUF or XAD-2 tubes and particles of $0.3\mu\text{m}$ or larger in diameter might be collected on filters.^{6,8)}

The analysis of PNAs from this procedure has been conducted through the use of automated HPLC using a programmed gradient mixture. Fifteen PNAs are routinely screened which allows a detailed comparison among sampling and analytical procedures. Harvath¹⁰⁾ reported a detailed laboratory experimental method.

CONCLUSIONS

Laboratory experiments and field studies were conducted to evaluate and develop a method for sampling and analysis of PNAs in the working environment. The following conclusions were obtained from this study:

- (1) Among benzene, cyclohexane, and methylene chloride, methylene chloride was the best solvent for extracting PNAs.
- (2) Extraction by ultrasonication for 15 minutes showed a good result.
- (3) For sampling PNAs, Teflon filter was superior to the NIOSH-recommended glass fiber/silver membrane filters.
- (4) Among four sorbents tested for PNAs sampling, PUF and XAD-2 showed efficient results.

REFERENCES

1. National Academy of Sciences: Biological Effects of Atmospheric Pollutants. Particulate Polycyclic Organic Matter. National Academy of Sciences, Washington, D.C. 1972.
2. Searle, C.E.: Chemical Carcinogens. ACS Monograph 173, American Chemical Society, Washington, D.C. 1976.
3. National Institute for Occupational Safety and Health: Criteria for a Recommended Standard. Occupational Exposure to Coal Tar Products. U.S. DHEW, DHEW(NIOSH) Publication No. 78-107, 1977
4. Occupational Safety and Health Administration: OSHA Safety and Health Standards, 29 CFR 1910, Subpart 8. OSHA 2206, 1978.
5. Lee, M.L., M.V. Novotny, and K.D. Bartle: Analytical Chemistry of Polycyclic Aromatic Compounds. p. 78-87. Academic Press, New York, 1981.
6. Krstulovic, A.M., D.M. Rosie, and P.R. Brown: Selective Monitoring of Polynu-

- clear Aromatic Hydrocarbons by High Pressure Liquid Chromatography with a Variable Wavelength Detector. *Anal. Chem.* 48: 1383-1386, 1976.
7. Bertsch, W., R.C. Chang, and A. Zlatkis: The Determination of Organic Volatiles in Air Pollution Studies: Characterization of Profiles. *J. Chromatogr. Sci.* 12: 175-182, 1974.
 8. Cautreels, W. and K. Van Cauwenberghe: Experiments on the Distribution of Organic Pollutants between Airborne Particulates Matter and the Corresponding Gas Phase. *Atmos. Environ.* 12: 1133-1141, 1978.
 9. Lee, F.S-C., T.J. Prater and F. Ferris: PAH Emission from a Stratified-Charge Vehicle with and without Oxidation Catalyst: Sampling and Analysis Evaluation. In "Polynuclear Aromatic Hydrocarbons," 83-110, edited by P.W. Jones and P. Leber, Ann Arbor Science Publishers, Inc., Ann Arbor, Michigan, 1979.
 10. Harvath, P.V.: Quantitative Analysis of multiple PAH's in the Coal Conversion Atmosphere. *Am. Ind. Hyg. Assoc. J.* 44: 739-745, 1983.
 11. National Institute for Occupational Safety and Health: Analytical Method: Benzene-Soluble Compounds in Air. P & CAM 217, NIOSH Manual of Analytical Methods DHEW Publication (NIOSH) 77-157, 1977.
 12. Pierce, R.C. and M. Katz: Determination of Atmospheric Isomeric Polycyclic Arenes by Thin-Layer Chromatograph and Fluorescence Spectrophotometry. *Anal. Chem.* 47: 1743-1748, 1975.
 13. Griest, W.H., L.B. Yeatts, Jr. and J.E. Caton: Recovery of Polycyclic Aromatic Hydrocarbons Sorbed on Fly Ash for Quantitative Determination. *Anal. Chem.* 52: 199-201, 1980.