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Evaluation of Sampling and Analytical Methods for the Determination of Polycyclic Aromatic Hydrocarbons in the Ambient Atmosphere

Sung-Ok Baek

Dept. of Environmental Engineering, Yeungnam University
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Abstract

In this study, sampling and analytical procedures were evaluated for the determination of ambient levels of atmospheric PAH, both in gaseous and particulate phases. The method involves low-volume sampling and Soxhlet extraction of the filters and Tenax absorbent, followed by a clean-up stage using a silica column prior to analysis by reversed-phase HPLC with wavelength programmable fluorescence and UV detection. A total of 18 PAH were identified and quantified, all of which have been of environmental concern. In order to validate the methodology and to ensure compatibility of the results, the analytical method used for the determination of PAH was evaluated with respect to the efficiencies of extraction and clean-up procedure, HPLC separation, and lower limits of detection. In addition, substrate dependency of PAH recovery was investigated for the two types of filters, i.e. glass fiber and PTFE filters.

1. INTRODUCTION

In recent years, there has been a considerable concern regarding possible adverse effects on human health of polyclic aromatic hydrocarbons (PAH) in the atmospheric environment. The environmental concern for these compounds is well justified since not only have many of them proven carcinogenic and/or mutagenic properties (U.S. NAS, 1983 ; IARC, 1983), but they are also known to be ubiquitous in ambient air, both indoors and outdoors, to which the general public is exposed (U.S. NAS, 1981). It is generally believed that long-term chronic exposure to environmental carcinogens is of greater significance than short-term acute exposure (Lioy and Daisey, 1986). Due to their carcinogenicity, it is accepted that there will always be some risk, however small, to a population exposed to these compounds on a continuous basis (WHO, 1987). Although human exposure to PAH can occur through various pathways, the occurrence of PAH in urban ambient air has caused a particular concern because of the continuous nature of the exposure and the magnitude of the population at risk.

A number of PAH compounds have been measured in ambient air over the last three decades, but the most extensive data available are on benzo(a)pyrene (BaP) (Faoro, 1975 ; Harkov and Greenberg, 1985 ; Santodonato et al., 1981). Although BaP is one of the principal carcinogenic PAH, it represents only a small fraction of the total PAH in most circumstances (Baek, 1988). There are many limitations to use this 'BaP surrogate' method for estimating risks posed by a mixture of PAH compounds since the proportion of carcinogenic activity attributable to BaP in products of incomplete combustion is known to vary among source categories and sometimes within a source category (Grimmer, 1983).

The determination of PAH in ambient air is, for several reasons, a difficult task, as concentrations of these compounds are in general very low and many of them are unstable and volatile (Van Vaeck et al., 1984). As a result, a large air sample

is necessary in order to collect sufficient amounts of PAH to be above the detection limits of an analytical method and to enhance the accuracy of the measurements. On the other hand, shorter sampling duration is generally recommended not only to minimize the evaporative losses of collected samples but also to avoid the formation of chemical artifacts during sampling.

Of great concern in data collection for PAH or POM (Polycyclic Organic Matter) is a general lack of standardized methods of sampling and analysis (Karcher, 1983). In order to permit a consistent assessment of the health impacts of an environmental pollutant with wide ranging distributions such as PAH, and to ensure reliable analytical control, the harmonization and/or standardization of sampling and analytical procedures is highly desirable. In PAH/POM analysis, however, the harmonization and/or standardization efforts have been complicated by a large variety of emissions and matrices containing a broad and variable spectrum of PAH and their heterocyclic compounds (Daisey et al., 1986). This frequently requires the development and application of specific sampling and analytical techniques for a particular monitoring situation, which consequently makes intercomparison of data difficult.

In this study, a comprehensive sampling and analytical regime, using filters and Tenax-TA adsorbent, is outlined which enables the collection of 18 PAH in ambient air, both from the particulate and gaseous phases. A simple sample preparation process is described, which prepares the sample for reversed-phase high performance liquid chromatography (HPLC) by transferring the analyte to acetonitrile. Optimal chromatographic conditions for the HPLC was also examined for the quantitation of 18 PAH. In addition, a number of tests on the overall methodology were carried out to varify that the procedure provides a sensitive and effective method for assessing ambient levels of various PAH in the atmosphere.

2. MATERIALS AND METHODS

2.1 Collection of Environmental Samples

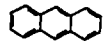
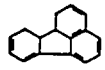
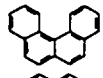
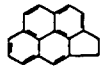
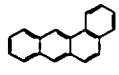
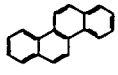
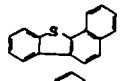
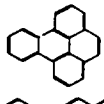
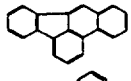
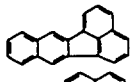
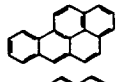
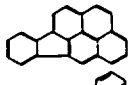
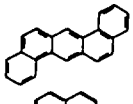
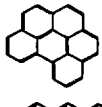
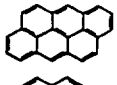
The sampling methods selected for this study were low-volume ambient air sampling using specific substrates to collect gaseous and particulate PAH. The sampling was carried out on the roof of 4 stories building at an urban site close to a busy road, where automotive emission is one of the main source of air polltion.

Particulate Samples: Sampling for the particulate PAH was performed with a low-vol sampler operated at a flow rate of approximately 30 l/min. Particulate matter was collected using PTFE (Polytetrafluoroethylene) filters (Millipore FH) and glass fiber filters (Gelman Spectro Grade), placed in a stainless steel open filter holder (Sartorius, 47 mm). The glass fiber filters were used after pre-extraction with dichloromethane. The filter holder was mounted with the filter facing downwards in a weather shelter. For each sample, an average volume of 40 m^3 of air was drawn over 24 hours sampling. The exposed filters were placed in air sealed plastic envelopes and then stored in the dark at $-20℃$.

Gaseous Samples: Samples for gas phase PAH were trapped for a week by the passage of filtered air through a glass tube containing about 1 g of Tenax-TA (35/60, Chrompak). The ambient air was drawn by a pump through PTFE connection tube, and a 47 mm filter holder with a 0.45 μm pore size cellulose filter. The prefilter was replaced and discarded every 12 hour in order to avoid the contribution of particulate 'blow off'. The amount of Tenax was determined by considering sampling parameters, such as flow rate, temperature and breakthrough volumes reported in the literatures (Van Vaeck et al., 1984 ; Pellizarri et al., 1975). The average flow rate through the Tenax cartridge was 5.5 l/min. The breakthrough volume was checked experimentally by pulling approximately twice the normal sampling volume over two identical Tenax cartridges connected in series, and analyzing both cartridges separately. The glass cartridge was wrapped in an aluminum foil to cut out direct sunlight during sampling. The Tenax polymer was purified before use by Soxhlet extraction with 100 ml of cyclohexane for 16 hours. The glass tube was soaked in 10% chromic

acid and then rinsed in distilled water while the glass wool was also extracted with dichloromethane. The packed Tenax cartridge was preconditioned at 250℃ under a Helium stream for

Table 1. Nomenclatures, abbreviations and structural formulae of 18 PAH analysed in this study.

Nomenclature (IUPAC)	Abbreviation	Structure	Formula (M.W)
1. Phenanthrene	PHEN		$C_{14}H_{10}$ (178)
2. Anthracene	ANTHR		$C_{14}H_{10}$ (178)
3. Fluoranthene	FLUR		$C_{16}H_{10}$ (202)
4. Pyrene	PYR		$C_{16}H_{10}$ (202)
5. Benzo(c)phenanthrene	BcPH		$C_{18}H_{12}$ (228)
6. Cyclopenta(c,d)pyrene	CcdP		$C_{18}H_{10}$ (226)
7. Benz(a)anthracene	BaA		$C_{18}H_{12}$ (228)
8. Chrysene	CHRY		$C_{18}H_{12}$ (228)
9. Benzo(b)naphtho(2,1-d)-thiophene	BNTH		$C_{16}H_{10}S$ (234)
10. Benzo(e)pyrene	BeP		$C_{20}H_{12}$ (252)
11. Benzo(b)fluoranthene	BbF		$C_{20}H_{12}$ (252)
12. Benzo(k)fluoranthene	BkF		$C_{20}H_{12}$ (252)
13. Benzo(a)pyrene	BaP		$C_{20}H_{12}$ (252)
14. Dibenz(a,h)anthracene	DahA		$C_{22}H_{14}$ (278)
15. Benzo(ghi)perylene	BghiP		$C_{22}H_{12}$ (276)
16. Indeno(1,2,3-cd)pyrene	I123P		$C_{22}H_{12}$ (276)
17. Anthanthrene	ANTHN		$C_{22}H_{12}$ (276)
18. Coronene	COR		$C_{24}H_{12}$ (300)

about 5 hours.

2.2 Analytical Method

An analytical procedure, largely based on the method of May and Wise (1984), was adapted in this study for the determination of individual PAH in samples. The nomenclatures, structures, and formulae of the 18 PAH analyzed in this study are listed in Table 1, together with their abbreviations.

Reagents and Glassware: All solvents used in extraction, fractionation, clean-up, and HPLC analysis were HPLC grade. Acetonitrile and water utilized as the mobile phase in HPLC analysis were pre-filtered, and then trapped air bubbles were removed by ultrasonication. All glassware was of borosilicate, which was precleaned by soaking in 10% Decon 90, rinsing with distilled water, and then soaking in 10% chromic acid for a day, and finally rinsing again in distilled water.

PAH Standards: PAH standards were obtained from the following suppliers and were used without purification: PHEN, BeP, DahA, BghiP and COR from Aldrich Co.; BkF and I123P from Phase Separation Ltd.; ANTHR, FLUR, PYR, BaA, CHRY and BaP from Ralph N. Emmanuel Ltd.; BcPH, CcdP, BNTH, BbF and ANTHN from the Community Bureau of Reference of the Commission of the European Communities in Brussels, Belgium. The concentrations of PAH in stock solutions and in the mixture of standards were chosen empirically to give comparable fluorescence and UV response with selected chromatographic conditions and wavelength programmes.

Extraction: Filters containing the crude particulates were extracted for 16 hours with 120 ml of dichloromethane in a Soxhlet apparatus. Cycle time was approximately 10 min. For the Tenax adsorbent, a 16 hour Soxhlet extraction was carried out with 100 ml of cyclohexane instead of dichloromethane since the degradation of the Tenax polymer by dichloromethane was observed. The filters and Tenax adsorbent were placed in pre-extracted Whatman glass fiber thimbles (19 × 90 mm). The extracts were subsequently concentrated to about 3 ml using a rotary evaporator at 40℃, and finally evaporated to near dryness with a stream of oxygen free nitrogen. The residue was then redissolved in 3 ml of hexane. Analyses for blank/spiked samples were run through the same procedures.

Clean-Up: The fractionation and clean-up of extracted samples were performed using Waters SEP-PAK silica cartridges. The SEP-PAK cartridge, a radially compressed mini column, was used as an alternative to a conventional purification method such as TLC clean-up or a silica gel open column. Prior to use, each cartridge was rinsed with 10~15 ml of hexane, a non-polar solvent. The concentrated extract was then loaded onto the cartridge, and the flask containing the residue was rinsed twice with 2 ml of hexane. These rinsings were also loaded onto the cartridge. After discarding the hexane eluent, the cartridge was eluted with 5 to 6 ml of 15% dichloromethane in hexane, a more polar solvent, and the eluent was collected in a 10 ml test tube. Subsequently, the cartridge eluent was evaporated slowly to near dryness under a stream of oxygen free nitrogen, and redissolved in 1 ml of acetonitrile.

HPLC Analysis: The chromatographic analysis was carried out by reversed phase HPLC using a gradient elution. The HPLC system consisted of two solvent delivery pumps (Waters 6000 LC Pump and M45 LC Pump), an automatic gradient controller (Waters Model 680), an injector (Waters U6K) with a 2 ml sample loop, an analytical column (Waters PAH Analysis Radial-PAK, 5 mm × 10 cm, 10 μm particle size C_{18} packing) with a guard column (Waters Guard-PAK with C_{18} inserts) and two detectors (Perkin Elmer LS-4 Programmable Fluorescence and Waters 480 UV Spectrophotometers). Two different sets of chromatographic conditions, as shown in Table 2, were employed: one for the particulate and the other for the gaseous samples. The flow rate of the mobile phase was 2 ml/min for both conditions.

Detection: The spectra of fluorescence emission and UV absorption from the eluting fractions were monitored by fluorescence and UV detectors, which were connected to the analytical column in series. The fluorescence detector was programmed into 4 pairs of wavelength conditions in order to

Table 2. Chromatographic conditions used for the HPLC analysis.

		Solvent Program (A)	Solvent Program (B)
Application	:	Particulate samples	Gaseous samples
Mobile Phase	:	Acetonitrile in water	Acetonitrile in water
Gradient Elution	:	35% to 92% for 42 mins	30% to 85% for 40 mins
		(Non-linear Gradient)*	(Linear Gradient)
		92% to 92% for 6 mins	85% to 85% for 10 mins
Equilibration	:	100% to 100% for 5 mins	100% to 100% for 10 mins
		35% to 35% for 7 mins	30% to 30% for 7 mins
Flow rate	:	2 ml/min	
Temperature	:	Room temperature (Approximately 15℃ to 20℃)	

*Program No. 5 on the Waters Automated Gradient Controller.

give a good response to each PAH of interest as it eluted, while the UV detector was set at 290 nm. The fluorescence and UV spectral characteristics for the analyzed PAH were obtained either from experiments using a stop-flow and rapid scanning technique (May and Wise, 1984 ; Ogan et al., 1979) or from the literature (Wise, 1983). The specific excitation and emission wavelength conditions used for the fluorescence detection of each PAH are shown in Table 3, where the PAH are listed in their order of elution.

Identification and Quantitation: The chromatographic peaks of the sample were identified by two methods. Firstly, each PAH was tentatively identified on the basis of their retention times by refering to those of standards. Secondly, the ratios between fluorescence and UV responses were used to confirm the identification by comparison with corresponding standards. The quantitation was also made by comparing the measured peak heights with those of the standards of known concentrations.

Table 3. Fluorescence wavelength conditions used for the detection of selected PAH in four groups.

Wavelength (nm)		PAH of interest	
Excitation	Emission	Particulate PAH samples	Gaseous PAH samples
260	430	PHEN, ANTHR, FLUR, PYR	PHEN, ANTHR, FLUR, PYR
285	385	BcPH, CcdP, BaA, CHRY, BNTH, BeP, BbF	BcPH, CcdP, BaA, CHRY, BNTH
295	410	BkF, BaP	BeP, BbF, BkF, BaP
300	455	DahA, BghiP, I123P, ANTHN, COR	DahA, BghiP, I123P, ANTHN, COR

Quality Control of the Analytical Method: A mixture of 18 PAH standards and a blank were routinely injected to check column performance and to optimize operating conditions for each batch of analyses. The characteristics of retention times and selectivities for the 18 PAH on the HPLC analytical column were also examined by calculating retention indices and selectivity factors. In addition, a number of experiments were undertaken to evaluate the analytical method, with respect to precision of the HPLC analysis, detection limits and recovery efficiency.

3. RESULTS AND DISCUSSION

The compounds determined in this study cover a wide range of PAH, from the volatile compounds to those found predominantly in the particulate matter. A total of 18 PAH were identified and quantified, all of which have been of environmental concerns since each of them is included either on the U.S. EPA's list of priority pollutants (U.S. Federal Register, 1980) or on a tentative list for a general report of PAH emissions proposed by the Commission of the European Communities (Karcher, 1983).

3.1 Evaluation of Sampling Protocol

Sampling protocol employed in this study is classified into low-vol air sampling both for particulate and gaseous samples. This technique has often been used in the occupational environments where PAH concentrations are high (Andersson et al., 1983) but has not been frequently used for the ambient PAH sampling because of a constraint to require an extended sampling period for the collection of sufficient samples (Bjorseth et al., 1978; Commins and Hampton, 1976). However, the recent development of more sensitive analytical methods has led to eliminate this factor as a limitation in the PAH sampling strategy (Grosjean, 1983; Davis et al., 1987).

Adsorption by Tenax-GC (now Tenax-TA) has been widely recommended as an enrichment technique for volatile organic compounds (VOC) (Pellizari et al., 1975; Leinster and Evans, 1986). Quantitative trapping (>95%) for most of VOC was observed at flow rates up to 10 l/min.cm^2 by Pellizari et al., (1975). Van Vaeck et al., (1984) estimated a theoretical breakthrough volume for ANTHR, one of the most volatile PAH compounds investigated in this study, to be 5×10^4 m^3/g at 20℃, based on the determination from the retention volume of the compound on GC columns filled with preweighed Tenax-GC. In this study, the collection efficiency of the Tenax-TA was determined experimentally by pulling increased air volumes over two identical Tenax cartridges connected in series. Analysis of the second cartridge would show at which air volume the threshold of appearance of the compound of interest is reached at ambient temperature. For the collection of volatile PAH from 90 m^3 of air, no detectable PAH was found in the second cartridge at an ambient temperature of 18℃, which was the weekly mean temperature during the sampling period. In fact, the nominal flow rate adopted in this study through a cartridge filled with 1 g of Tenax-TA was 5.5 l/min (about 50 m^3 for the weekly sampling), which was considerably lower than the highest flow reported in the literature for the quantitative retention of their test compounds (Van Vaeck et al., 1984).

3.2 Extraction and Clean-Up Procedure

A large number of solvents have been applied for the extraction of PAH from airborne particulates. In this study, the extractable organic matter was recovered from the particulates on filters and Tenax adsorbent by Soxhlet extractions for 16 hours with dichloromethane and cyclohexane, respectively. Dichloromethane was selected for filter samples since it is easy to replace with a non-polar solvent (hexane), a necessary step prior to prefractionation by adsorption chromatography. Typically, Tenax polymer has been used for sampling volatile analytes for subsequent thermal desorption (Pellizari et al., 1975) rather than for semivolatile analytes, such as PAH, for subsequent solvent extraction (Van Vaeck et al., 1984; Cautreels and Van Cauwenberghe, 1978). Since only high molecular weight compounds (M.W.> 178) were of interest in this study, the extraction was carried out by a solvent to be compatible with the subsequent analytical method. The dichloromethane, however, could not be used for the Tenax samples because of irreversible deterioration of the Tenax polymer by the solvent. Accordingly, cyclohexane was prefered for the Tenax samples to more polar solvents since it tends to discriminate against many of the interfering polar substances while retaining relatively good efficiency of extraction (Lee and Schuetzle, 1983).

A simplified clęan-up procedure was developed to obtain a PAH-enriched fraction that can be subsequently analyzed by HPLC with fluorescence and UV detections. The dichloromethane and cyclohexane extracts were separated into 'non-polar' and 'neutral/polar' fractions using silica columns (Waters SEP-PAK). Further separation of the neutral component from the more polar fraction was carried out by controlling the polarity of an eluting solvent. The choice of a more polar solvent was largely based on a trial and error. The efficiency of the fractionation was evaluated only qualitatively by comparing HPLC chromatograms of each fraction with that of directly injected standard mixture. This clean-up procedure was simple and fast. Since the samples were not saponified, the neutral/polar fractions probably

contain many other classes of compounds other than the aromatic hydrocarbons. For example, fatty acids, alcohols, phenols and nitro-compounds were commonly found in ambient air (Daisey et al., 1986), and some of these interfering compounds would elute together with PAH compounds in the neutral fraction, depending on their polarity.

3.3 HPLC Separation

One of major problems associated with the determination of PAH in complex mixtures in general, and in organic extracts from atmospheric aerosols in particular, is the separation and identification of individual PAH in the presence of numerous other isomers and alkylated PAH. Since the biological properties of many PAH were known to be isomer specific (IARC, 1983; Santodonato et al., 1981), the determination of individual isomers is essential. Thus, both efficient separation procedures and selective detection techniques are highly recommended for the characterization of PAH in complex environmental samples.

For the HPLC analysis used in this study, two different chromatographic conditions were employed: one for the particulate and the other for the gaseous samples. The gradient profiles of the mobile phase for the two conditions were shown in Table 2. Fig. 1 and 2 show chromatograms obtained from the fluorescence and UV detectors for the mixture of the 18 PAH standards analysed with the two solvent programs, while the identification and retention times for each peak are summarized in Table 4.

As shown in Fig. 1 and 2, the 18 PAH in the standard mixture were detected as 17 and 16 peaks by the fluorescence and UV detection, respectively. CcdP was not detected by the fluorescence method at an excitation wavelength of 285 nm and an emission wavelength of 385 nm, while ANTHR and ANTHN were not detected by the UV detector at 290 nm. The separation of individual PAH was generally good, showing in most cases about 1

Table 4. Summary of the HPLC analyses of 18 PAH standards under solvent programmes used for the particulate and gaseous PAH samples.

Peak No.	PAH	M.W.	No. of aromatic carbon	Amount injected (ng)	Response ratio*		Retention time (min)	
					Programme (A)	Programme (B)	Programme (A)	Programme (B)
1.	PHEN**	178	14	10.1	0.3	0.3	9.2	18.5
2.	ANTHR	178	14	13.6	N.A.***	N.A.	10.0	20.2
3.	FLUR	202	16	18.8	1.3	1.3	11.2	22.4
4.	PYR	202	16	60.0	2.0	2.0	12.0	23.8
5.	BcPH	228	18	11.6	2.3	2.2	13.3	25.6
6.	CcdP**	226	18	36.5	0.0	0.0	15.5	27.3
7.	BaA	228	18	7.6	4.8	4.3	16.4	28.1
8.	CHRY	228	18	22.5	3.6	3.6	17.0	28.9
9.	BNTH**	234	16	46.0	0.6	0.6	18.0	30.5
10.	BeP	252	20	6.3	1.5	0.5	19.0	32.0
11.	BbF	252	20	25.0	0.2	2.1	19.5	33.0
12.	BkF	252	20	2.5	40.1	2.1	19.5	33.0
13.	BaP	252	20	10.8	7.4	7.1	22.9	36.5
14.	DahA**	278	22	12.5	0.3	0.3	26.6	39.3
15.	BghiP**	276	22	15.5	0.5	0.5	27.5	40.2
16.	I123P**	276	22	135.0	0.4	0.4	29.2	41.8
17.	ANTHN	276	22	6.8	N.A.	N.A.	34.2	46.0
18.	COR	300	24	30.0	0.9	0.9	38.5	53.0

*Fluorescence to UV ; **Quantitation was based on UV detection ; ***No response by UV detection

min or greater interval between each PAH. BaP was almost completely separated from its isomers such as BkF, BbF and BeP, while only partial separation occurred for BaA/CHRY and DahA/BghiP. Examination of Table 4 reveals the chromatographic behavior of the PAH compounds except BNTH on the Radial-PAK column is generally governed by the number of aromatic rings. In the case of BNTH which contains a sulphur atom, however, its retention time was only in accordance with the order of molecular weights. The response ratios between fluorescence and UV detection, which were used to confirm the identification of peaks with respect to retention times, are not

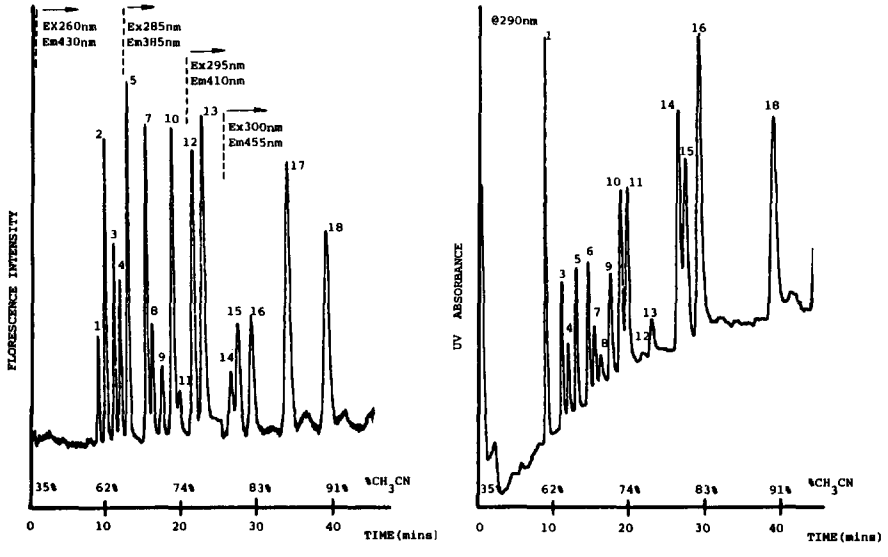


Fig. 1. Chromatograms of 18 PAH standards analysed by the reversed-phase HPLC under the solvent programme (A) shown in Table 2.: fluorescence detection (left) and UV detection (right).

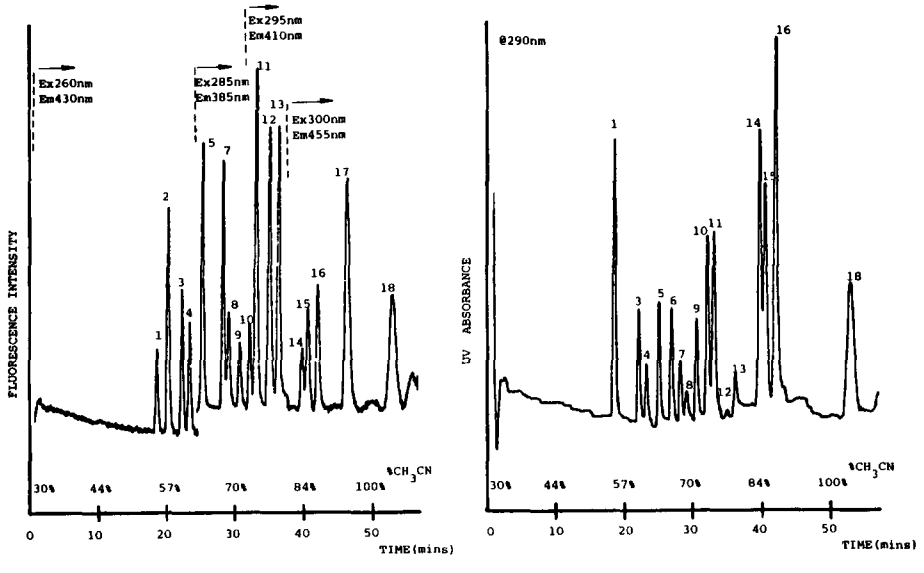


Fig. 2. Chromatograms of 18 PAH standards analysed by the reversed-phase HPLC under the solvent programme (B) shown in Table 2.: fluorescence detection (left) and UV detection (right).

absolute but represent only typical figures obtained by routine gain settings of the two detectors.

The majority of the HPLC separations of PAH reported in the literature have used C_{18} reversed-phase columns. In order to evaluate the selectivity for PAH on the C_{18} column used in this study, retention data for the 18 PAH were calculated as described by Wise et al. (1980) and compared with those reported in the literature. The results are presented in Table 5. Using the retention data, the selectivity factors for several PAH pairs were also

Table 5. Retention indices* for PAH analysed by reversed-phase HPLC, in comparison with previously published data.

PAH	Waters Radial-PAK PAH Analysis column		Other columns** evaluated by Wise *et al.* (1980)							
	Solvent programme (A)[a]	Solvent programme (B)[b]	A[c]	B[c]	C[d]	D[d]	E[c]	F[c]	G[e]	H[c]
PHEN	3.00	3.00	3.00	3.00	3.00	3.00	3.00	3.00	3.00	3.00
ANTHR	3.15	3.19	3.14	3.19	3.12	3.11	3.11	3.11	3.24	3.14
FLUR	3.34	3.44	3.42	3.44	3.43	3.42	3.45	3.43	3.38	3.44
PYR	3.46	3.59	3.62	3.69	3.60	3.59	3.61	3.63	3.56	3.66
BcPH	3.64	3.77	—	—	—	—	—	—	—	—
CcdP	3.91	3.93	—	—	—	—	—	—	—	—
BaA	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00
CHRY	4.07	4.08	4.00	4.04	3.98	3.98	3.96	3.97	4.10	3.99
BNTH	4.18	4.24	—	—	—	—	—	—	—	—
BeP	4.30	4.38	4.40	4.43	4.50	4.50	4.48	4.48	4.25	4.48
BbF	4.35	4.46	4.40	4.41	4.47	4.47	4.47	4.46	4.30	4.45
BkF	4.54	4.67	4.48	4.49	4.48	4.52	4.53	4.47	4.45	4.52
BaP	4.67	4.76	4.63	4.66	4.65	4.64	4.64	4.66	4.52	4.68
DahA	4.96	4.96	4.78	4.74	4.89	4.90	4.92	4.88	4.69	4.85
BbCHRY	5.00***	5.00***	5.00	5.00	5.00	5.00	5.00	5.00	5.00	5.00
BghiP	5.09	5.09	5.05	5.05	5.18	5.17	5.14	5.10	4.71	5.16
I123P	5.28	5.25	5.03	5.04	5.14	5.09	5.13	5.10	4.83	5.13
ANTHN	5.86	5.64	—	—	—	—	—	—	—	—
COR	6.35	6.31	—	—	—	—	—	—	—	—

*Retention reported as logarithm of the retention index (Log I), which was calculated using the following formula: $\text{Log } I_x = \text{Log } I_n + (\text{Log } R_x - \text{Log } R_n)/(\text{Log } R_{n+1} - \text{Log } R_n)$, where x represents the solute, n and n+1 represent the lower and higher standards, and the R values are the corresponding corrected retention volumes. The standards were assigned the following values (Log I): PHEN (3), BaA (4), and benzo(b)chrysene (5). The retention indices greater than benzo(b)chrysene were determined from extrapolation of a plot of Log R vs Log I for the standards.

**A: Lichrosorb RP-18 (Brown Lee, Rheodyne Inc., Berkeley, CA, USA); B: Micro PAK CH-10 (Varian Assoc., Walnut Creek, CA, USA); C: Micro PAK MCH-10 (same as column B); D: Nucleosil 10 C_{18} (Macherey-Nagel, Duren, FRG); E: Partisil 5 ODS (Whatman, Clifton, NJ, USA); F: Radial-PAK A (Waters Assoc., Milford, MA, USA); G: Vydac 201TP reverse phase (The separation Group, Hesperia, CA, USA); H: Zorbax ODS (Du Pont Co., Wilmington, DE. USA).

***Benzo(b)chrysene was not included in this study, but an average value of the corrected retention volumes of DahA and BghiP was taken for the comparison with other columns.

a) Non-linear gradient elution from 35% CH_3CN in water to 92% CH_3CN in water.

b) Linear gradient elution from 30% CH_3CN in water to 85% CH_3CN in water.

c-d) Isocratic elutions at 80%, 70% and 90% CH_3CN in water, respectively.

Table 6. Column selectivities* for reversed-phase HPLC separation of PAH, in comparison with previously published data.

PAH	Waters Radial-PAK PAH Analysis column		Other columns** evaluated by Wise *et al.* (1980)							
	Solvent programme (A)[a]	Solvent programme (B)[b]	A[c]	B[c]	C[d]	D[d]	E[c]	F[c]	G[e]	H[c]
ANTHR/PHEN	1.10	1.08	1.12	1.22	1.10	1.08	1.07	1.08	1.42	1.11
FLUR/ANTHR	1.11	1.11	1.27	1.24	1.29	1.24	1.23	1.28	1.20	1.27
PYR/FLUR	1.08	1.06	1.19	1.27	1.14	1.12	1.11	1.16	1.29	1.18
BcPH/PYR	1.12	1.08	—	—	—	—	—	—	—	—
CcdP/BcPH	1.18	1.07	—	—	—	—	—	—	—	—
BaA/CcdP	1.06	1.03	—	—	—	—	—	—	—	—
CHRY/BaA	1.04	1.03	1.00	1.06	0.99	0.98	0.96	0.97	1.27	0.99
BNTH/CHRY	1.06	1.06	—	—	—	—	—	—	—	—
BeP/BNTH	1.06	1.03	—	—	—	—	—	—	—	—
BbF/BeP	1.03	1.08	—	—	—	—	—	—	—	—
BkF/BbF	1.10	1.08	1.10	1.12	1.01	1.04	1.17	1.29	1.05	1.32
BaP/BeP	1.21	1.15	1.29	1.34	1.14	1.12	1.11	1.15	1.89	1.18
BaP/BkF	1.07	1.03	—	—	—	—	—	—	—	—
DahA/BaP	1.16	1.08	—	—	—	—	—	—	—	—
BghiP/DahA	1.03	1.02	1.32	1.40	1.27	1.24	1.17	1.29	1.40	1.32
I123P/BghiP	1.06	1.04	—	—	—	—	—	—	—	—
ANTHN/I123P	1.17	1.10	—	—	—	—	—	—	—	—
COR/ANTHN	1.13	1.15	—	—	—	—	—	—	—	—

*Selectivity was expressed as the selectivity factor for the two PAH, which was calculated as follows: selectivity factor $= (V_2 - V_0)/(V_1 - V_0)$, where V_1 and V_2 are the elution volumes of the two PAH and V_0 is the unretained volume of the column.

**Refer to the note in Table 5 for the specifications of the columns.

a-e Refer to the note in Table 5 for the chromatographic conditions used for each column.

calculated, being summarized in Table 6.

Examination of data in Table 5 and 6 indicates that the various C_{18} columns exhibit not only varying efficiencies but also different selectivities in the separation of PAH. For nearly complete resolution of two components on these columns, it was suggested by Wise et al. (1980) that the logarithms of the retention indices should differ from each other by more than 0.06 unit. The retention data presented in Table 5 indicate that the Waters Radial-PAK column was successful in resolving all the 18 PAH identified in this study. Three groups of PAH isomers that have traditionally been known to be difficult to separate, i.e. (i) BaA and CHRY, (ii) BkF, BbF, BeP and BaP, (iii) BghiP and I123P, were also chromatographically separated in the study. In addition, the selectivity was generally enhanced by changing the fluorescence excitation and emission wavelengths during the chromatographic separation in order to optimise the detection of each PAH. The excitation and emission spectra of a number of PAH included in this study did not overlap, indicating that a single compromise excitation and emission wavelength pair was not practically possible. The effect of changes in the mobile phase polarity on the relative selectivities for PAH was also demonstrated by the data in Table 5. The selectivities under solvent programme (A) are generally higher than those under programme (B), indicating that a reduced mobile phase strength (i.e. higher % acetonitrile) is necessary to enhance the resolutions, as previously reported (Ogan et al., 1979).

3.4 Precision of HPLC Analysis

The reproducibilities of the retention times and

peak heights for each PAH were estimated in terms of relative standard deviations (RSD) for both within-a-day and day-to-day basis by six replicate injections of a standard mixture. The RSD for within-a-day ranged from 2.8% to 5.2%, while comparison among the results from day-to-day showed only a slight reduction of precision (i. e. 4.8% to 9.8%). The reproducibilities for the retention times appeared to be significantly influenced by the equilibration time prior to injection of the sample.

The linearity between the fluorescence and/or UV responses and the amounts of PAH injected was also verified by analyzing 5 sets of different concentrations of PAH standards. The results showed good linearity of response for each of the 18 PAH over a wide concentration range. The coefficients of correlation for the calibration plots were between 0.998 and 1.000. According to the slope data, which indicate sensitivities for individual PAH by definition, the greatest sensitivity was found for BkF while the lowest for I123P. It should be noted, however, that these sensitivities are not absolute since selectivities for each PAH are highly variable, being largely dependent on the wavelength programming.

3.5 Recovery Tests

A number of recovery test were carried out to estimate the extraction efficiencies of PAH from different collecting substrates and to investigate the possible losses of PAH during the extraction and clean-up procedure. Five replicate subsamples for each of blank glass fiber, PTFE filters and pre-extracted Tenax polymer were spiked with three different concentration levels of stan-

Table 7. Recoveries of 18 PAH from spiked blank filters and Tenax-TA adsorbent.

PAH	Spiked amount, C (ng)	Average % Recovery*											
		Glass fibre filters				PTFE filters				Tenax-TA adsorbent			
		Low (0.1C)	Medium (C)	High (2C)	Total** (n=15)	Low (0.1C)	Medium (C)	High (2C)	Total** (n=15)	Low (0.1C)	Medium (C)	High (2C)	Total** (n=15)
PHEN	10.1	68	74	64	69±4a***	70	71	63	68±5a	58	56	52	55±5b
ANTHR	13.6	67	70	64	67±5c	65	74	65	68±5c	59	58	52	56±5d
FLUR	18.8	87	92	87	89±3e	87	89	84	87±3e	69	64	63	65±7f
PYR	60.0	80	76	85	80±5g	82	87	80	83±5g	68	62	65	65±6h
BcPH	11.6	83	90	89	87±4i	88	91	92	90±3i	73	70	67	70±5j
CcdP	36.5	85	88	83	85±3k	84	90	85	86±4k	75	78	71	75±4l
BaA	7.6	90	92	85	89±3m	88	95	93	92±3m	85	82	72	80±5n
CHRY	23.0	91	90	88	90±4o	86	94	92	91±4o	81	84	79	81±4p
BNTH	46.0	84	91	89	88±3q	91	94	87	91±4q	85	86	79	83±3r
BeP	6.3	95	91	90	92±4s	90	96	96	94±3s	82	87	80	83±5t
BbF	25.0	91	95	90	92±3u	90	95	94	93±4u	85	80	79	81±5v
BkF	2.5	92	95	92	93±4w	90	97	89	92±3w	86	78	80	81±5x
BaP	11.0	78	88	87	84±4y	85	82	89	85±3y	82	79	74	78±5z
DahA	12.5	89	95	93	92±3A	90	96	93	93±3A	83	81	75	80±5B
BghiP	16.0	92	95	85	91±3C	94	95	89	92±2C	85	79	74	79±5D
I123P	135.0	93	95	92	93±2E	95	90	91	92±4E	84	84	79	82±3F
ANTHN	6.8	73	67	58	66±8G	67	73	67	69±6G	64	64	61	63±6G
COR	30.0	95	95	90	93±2H	96	98	90	95±2H	90	83	88	87±3I

*Of five replicate analyses for each of low, medium and high concentration range.

**Expressed as 95% confidence limits for the population mean.

***Means not followed by a common letter for each PAH are significantly different at a significance level of 0.05.

dard mixtures, i.e. low, medium and high concentrations. The results are summarized in Table 7.

Recoveries for the 18 PAH varied widely, ranging from 66% to 95% for the filter materials and from 55% to 88% for the Tenax adsorbent. It was apparent that the recovery generally increases as the molecular weight of the PAH increases. Despite its high molecular weight, however, ANTHN exhibited substantially lower recoveries compared to other PAH with a similar molecular weight. Regardless of the type of substrate, consistently lower recoveries were obtained for PHEN and ANTHR, suggesting that evaporative losses for these compounds during the sample preparation steps may be of more significance than for higher molecular weight PAH due to their higher volatilities. No apparent relationship was found between PAH concentration and PAH recovery.

Recoveries of PAH from Tenax adsorbent appeared to be generally 10% lower than those from filters. An F-test comparing average % recoveries from each sustrate indicated that the Tenax results were significantly different from those for glass fibre and PTFE filters, while no significant differences between the two types of filter were found. The lower recoveries from the Tenax adsorbent might have resulted from the relatively inferior extraction efficiency of cyclohexane compared with dichloromethane and/or from the different nature of the substrate itself.

Recovery tests were also carried out with filters loaded with ambient particulates. Particulate-laden filters were cut into two identical parts and then extracted separately with and without spiking. Comparison of the results with Table 7 did not show any statistically significant differences in average recovery efficiencies and hence apparent differences between sub-samples seem to be generally due to random errors. Recoveries of 3-ring PAH, i.e. PHEN and ANTHR, from ambient particulate matter were also substantially lower than for higher molecular weight PAH as was the case with spiked blank filters, indicating that there is measurable bias with respect to PAH molecular weight in the extraction and/or evaporation procedure, which is often used for the HPLC analyses.

3.6 Lower Limits of Detection

The lower limits of detection for each PAH were calculated from the signal-to-noise of the individual peaks in chromatograms for standards, assuming a minimum detectable signal-to-noise level of 2. These values are included in Table 8, being refered to as instrumental detection limits (IDL). In order to ensure the confidence of low concentration data determined using the IDL as the criteria, method detection limits for each PAH were also calculated and compared with the IDL. The definition of MDL implies that, on average, 99% of the trials measuring the analyte concentration at the MDL must be significantly different from zero analyte concentration. Since the MDL refers to samples processed through all the steps comprising an established analytical procedure, blank filters and pre-extracted Tenax adsorbent were spiked with a mixture of PAH standards, of which concentrations were prepared to correspond to their IDL in the range of 2 to 5 times, and then subjected to the analytical procedure as for actual samples. The estimated MDL data are also given in Table 8.

Comparison of the MDL with the IDL indicates that all the IDL are higher than or very close to the MDL, demonstrating high reliability for the low concentration PAH data. The lower limits of detection was estimated to be about 0.1 ng for BkF and 5.2 ng for I123P, which are the most and the least sensitive compounds among the 18 PAH. These limits are equivalent to approximately 2.5 and 130 pg/m^3 respectively in terms of a quantitation limit, which represents a value arising from a 40 m^3 of air sample and a 0.1 ml HPLC injection, i.e. normal operating conditions employed in this study for daily particulate samples.

3.7 Application to the Environmental Samples

Typical chromatograms of samples extracted from ambient particulate matter collected on a PTFE filter and from volatile PAH trapped by the Tenax adsorbent are shown in Fig. 3 and 4, respectively. The identification of individual PAH was first achieved chromatographically with respect to their retention times and subsequently confirmed

Table 8. Estimated lower limits of detection for PAH analysed by the reversed-phase HPLC coupled with fluorescence and UV detection.

PAH	Spiked amount (ng)	Chromatographic condition (A)[a]						Chromatographic condition (B)[b]					
		No. of samples	Average recovery (ng)	Average recovery (%)	SD[c] (ng)	MDL[d] (ng)	IDL[e] (ng)	No. of samples	Average recovery (ng)	Average recovery (%)	SD (ng)	MDL (ng)	IDL (ng)
PHEN*	1.0	10	0.69	69	0.07	0.20	0.26	5	0.58	58	0.09	0.34	0.36
ANTHN	1.4	10	0.94	67	0.13	0.36	0.64	5	0.83	59	0.15	0.56	0.80
FLUR	1.9	10	1.65	87	0.13	0.36	1.05	5	1.31	69	0.26	0.98	1.41
PYR	6.0	10	4.88	81	0.63	2.82	4.00	5	4.08	68	0.71	3.70	3.90
BcPH	1.2	10	1.02	85	0.10	0.28	0.35	5	0.87	73	0.13	0.48	0.50
CcdP*	3.7	10	3.11	84	0.20	0.56	1.95	5	2.78	75	0.36	1.35	1.99
BaA	0.8	10	0.72	90	0.05	0.14	0.22	5	0.68	85	0.08	0.30	0.30
CHRY	2.3	10	2.05	89	0.22	0.62	1.97	5	1.87	81	0.20	0.75	2.30
BNTH*	4.6	10	4.05	88	0.29	0.82	3.10	5	3.86	84	0.36	1.35	3.07
BeP	0.6	10	0.56	93	0.04	0.11	0.20	5	0.49	82	0.07	0.25	0.72
BbF*	2.5	10	2.28	91	0.25	0.71	1.00	5	2.12	85	0.23	0.85	0.91
BkF	0.3	10	0.27	91	0.02	0.06	0.09	5	0.26	86	0.03	0.11	0.15
BaP	1.1	10	0.92	84	0.07	0.20	0.38	5	0.89	81	0.12	0.45	0.55
DahA*	1.3	10	1.17	90	0.08	0.22	0.38	5	1.08	83	0.15	0.56	0.50
BghiP*	1.6	10	1.49	93	0.10	0.27	0.64	5	1.36	85	0.14	0.53	0.58
I123P	13.5	10	12.56	93	0.63	1.79	5.17	5	11.34	84	0.95	3.54	4.91
ANTHN	0.7	10	0.49	70	0.07	0.20	0.29	5	0.45	64	0.06	0.23	0.28
COR	3.0	10	2.88	96	0.12	0.34	1.64	5	2.67	89	0.15	0.56	2.30

a : Chromatographic condition (A) was used for the analysis of particulate PAH samples.

b : Chromatographic condition (B) was used for the analysis of gaseous PAH samples.

c : Standard deviation.

d : Method detection limits. The MDL was calculated from the equation given below: $MDL = t(n-1, 0.99) \times SD$, where $t(n-1, 0.99)$ is the Student's t value at n-1 degrees of freedom and the 99% confidence level.

e : Instrumental detection limits based on the signal-to-noise level of 2.

* Quantitation was based on UV detection.

by comparison of the ratios between fluorescence and UV responses with those of standards as indicated in Table 4. In some cases, the identification of individual compounds was corroborated by the addition of small amounts of PAH standards to a portion of each extract, resulting in chromatograms with enhanced peaks at the predicted retention times. Since main objective of this study is to evaluate a sampling and anlytical regime for the determination of PAH in both of gaseous and particulate phases, only limited number of the environmental samples were collected for the application purpose. Thus, in order to more precisely evaluate the ambient levels and phase distributions of the PAH, a larger data-base by extended monitoring is highly required.

4. CONCLUSIONS

Reversed-phase HPLC with wavelength programmable fluorescence detection appeared to be a reliable method in terms of both sensitivity and selectivity for the determination of individual PAH in extracts of either suspended particulate matter or volatile organic compounds collected from urban ambient air on Tenax-TA adsorbent.

An evaluation of the losses of PAH during extraction and clean-up procedures demonstrated that there was measurable bias in recoveries of PAH with respect to their molecular weights. In

general, losses of the lower molecular weight PAH appeared to be more significant than those of the higher molecular weight PAH, indicating that such losses were predominantly due to the volatilization of these compounds during solvent concentration steps. In addition, differences in extraction solvents and sample collection substrates (filters and Tenax-TA adsorbent) were also likely to influence the recoveries of PAH during the extraction procedure. However, no apparent relationships were found between PAH concentrations and their recoveries.

In order to investigate the distributions of these compounds between the gaseous and particulate

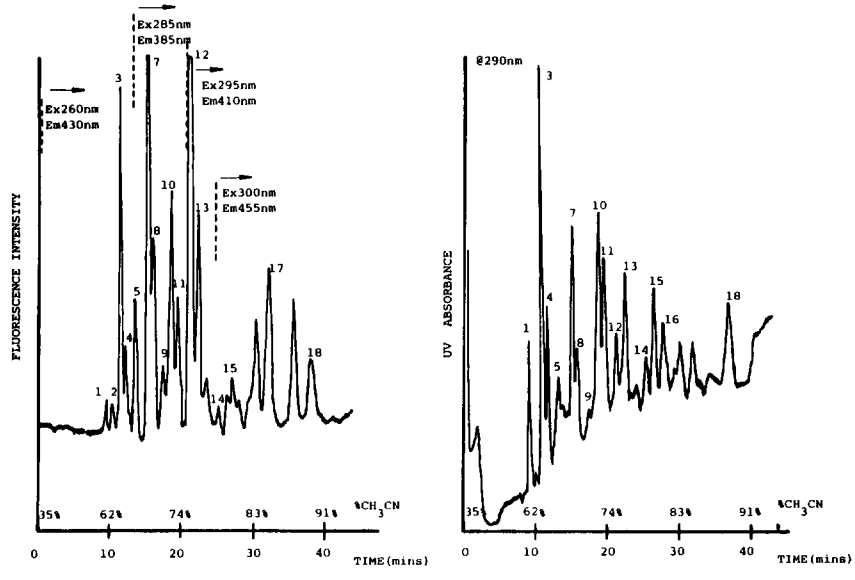


Fig. 3. Typical HPLC chromatograms for PAH extracted from ambient particulate matter.

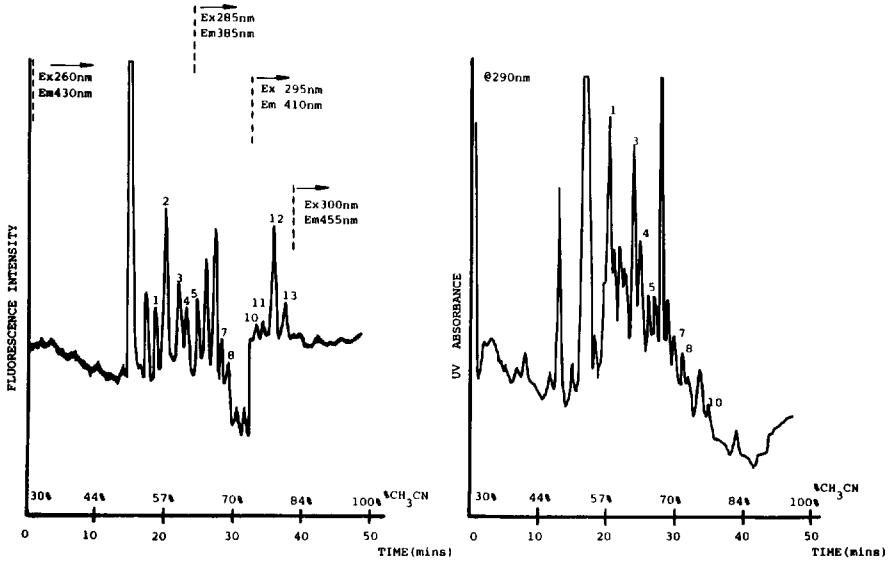


Fig. 4. Typical HPLC chromatograms for PAH extracted from volatile organics trapped by Tenax-TA adsorbent.

phase, the concentrations of the individual PAH should be determined on the filters and the Tenax adsorbent separately. It is, however, important to note that volatilization and reaction losses of the PAH associated with airborne particles collected on the filters would inevitably take place during sampling and hence the results may not be expected to yield an accurate distribution of PAH between the two phases. Most of the literature is ambiguous regarding the significance of these factors on measuring PAH, even though any degree of loss during the collection procedure further reduces the quality of the data. This issue is particularly of importance since these phenomena may not effect all compounds in an equal manner.

5. ACKNOWLEDGMENT

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환경대기중 다환방향족탄화수소의 포집과 분석방법에 관한 연구

백 성 옥

영남대학교 환경공학과

초 록

본 연구에서는 대기중 저농도 수준의 다환방향족탄화수소(PAH) 농도를 측정하기 위하여 이들의 포집과 분석방법을 평가하였다. PAH의 포집매체로서 기체상은 Tenax 흡착제를, 입자상은 PTFE 및 유리섬유필터를 이용하였으며 양자 모두 저유량샘플러에 의해 포집되었다. 필터 및 흡착제에 함유된 유기성분은 Soxhlet 장치로 추출하였으며 신속하고도 간편한 Silica 미니칼럼을 이용허여 PAH 함유성분을 분리하였다. PAH 성분은 역상 HPLC로 분리되어 형광 및 UV 검출기로 검지하였다. 분석은 환경보건학적 중요성을 갖는 18개의 PAH에 대하여 행하여졌다. 분석방법의 타당성을 검토하기 위하여 추출능(시료의 회수율), 시료의 전처리단계, HPLC 분리능과 재현성 및 검출한계치 등이 평가되었으며 아울러 서로 다른 포집매체의 이용에 따른 회수율의 영향도 비교 검토되었다. 본 연구에서 채택된 포집 및 분석방법을 실제 환경시료에 적용하여 가스상 및 입자상 PAH 분석을 위한 실례를 제시하였다.