Determination of polycyclic aromatic hydrocarbons in atmospheric particulate matter of Valencia city

C. Escrivá[1], M. Morales[1], A. La Orden[2], J. Mañes[1], and G. Font[1]

[1] Department of Preventive Medicine and Public Health, Faculty of Pharmacy, University of Valencia, E-46010 Valencia, Spain
[2] Environmental Agency, Conselleria d'Administracio Pública, E-46010 Valencia, Spain

Summary. Polycyclic aromatic hydrocarbons (PAHs) were determined in atmospheric particulate matter in 11 sites of the Valencia area and at several times during the year. Sample analysis was carried out by ultrasonic acetonitrile extraction followed by reverse phase HPLC separation and fluorescence detection. The maximum concentration of total PAH developed in winter and spring. Mean values per sampling site varied from 0.193 to 1.668 $\mu g/m^3$ of filtered air. Environmental noise and temperature were determined at those same 11 sites and correlated with PAH levels.

Introduction

Polycyclic aromatic hydrocarbons (PAHs) and their derivatives are the result of the incomplete combustion of different materials, particularly petroleum fuels. PAHs are found in the atmosphere associated with small particles in suspension [1]. PAHs have been shown to exert a very strong carcinogenic and mutagenic action on animals [2] and the higher degree of atmospheric pollution in urban areas seems to be partly responsible for the higher death rates from lung cancer among individuals living in cities compared with those from rural areas [3]. The determination of individual PAHs in mixtures requires the use of chromatographic methods of analysis, one of them being gas chromatography [4–5]. However reversed-phase high-performance liquid chromatography is the most commonly used technique for PAH analysis. The simplest approach to detect the PAH eluents from HPLC is to use a UV detector set at 254 nm [6–8], although the efficiency of UV detection can be improved by using variable wavelength [9] and diode array UV absorbance detectors [10]. A number of researchers have reported methods for determining PAHs using a fluorescence detector which provides a more sensitive and selective response [11–18].

Available data on atmospheric pollution owing to PAHs in urban areas are very scarce. As part of a program for monitoring pollution, we determined the concentration of several PAHs in the atmosphere of the Valencia area by HPLC with fluorescence detection, correlating them with environmental noise and ambient temperature.

Offprint requests to: J. Mañes

Experimental

Reagents

HPLC grade acetonitrile and distilled water known to be free of fluorescent impurities were used.

Acenaphthene, anthracene, benz(a)anthracene, benzo-(b)fluoranthene, benzofluorene, benzo(a)pyrene, dibenz-(a,h)anthracene, fenanthrene and pyrene were provided in pure form by Aldrich Chemie. Fluoranthene and naphthalene were provided by Scharlau and Jassen Chimica, respectively.

These standards were dissolved in acetonitrile at 500 $\mu g/ml$, though anthracene and benzo(a)pyrene solutions contained toluene (20%) and dibenz(a,h)anthracene chloroform (20%). A stock mixture of PAH standards was made up from the individual solutions in acetonitrile. The concentrations of the individual PAHs in the mixture were: acenaphthene 0.2 $\mu g/ml$, anthracene 0.3 $\mu g/ml$, benz(a)-anthracene 0.01 $\mu g/ml$, benzo(b)fluoranthene 0.1 $\mu g/ml$, benzofluorene 0.035 $\mu g/ml$, benzo(a)pyrene 0.05 $\mu g/ml$, dibenz(a,h)anthracene 0.02 $\mu g/ml$, fenanthrene 0.1 $\mu g/ml$, fluoranthene 4 $\mu g/ml$, naphthalene 3 $\mu g/ml$ and pyrene 0.05 $\mu g/ml$. Portions of this mixture of standards were diluted 1:10, 1:20, 1:30, 1:40 and 1:50 with acetonitrile for use as standards.

Apparatus

PAHs were analyzed using a Shimadzu LC-6A system liquid chromatograph equipped with a Rheodyne 7125 injector (20 μl loop), a Shimadzu RF-535 fluorescence detector and a Shimadzu C-R4A Chromatopac data processor.

A Spherisorb ODS-2 column (25 cm × 4.6 mm i.d.), particle size 3 μm was used at 30°C maintained by a thermostatic oven Shimadzu CTO-6A.

PAH extractions were carried out using a Selecta-P ultrasonic bath.

Ambient sampling collection

Sampling was carried out in low-volume collection bubbler systems, in which a Whatman paper filter No. 1 was installed to determine PAHs in suspended particulate matter.

Total suspended particulate matter samples were collected in Valencia city during the period April 1988 –
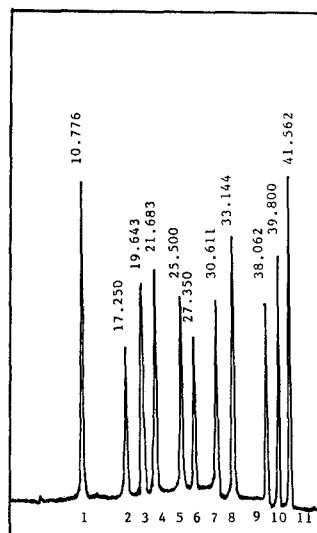
Fig. 1. Chromatogram of 11 PAH standards. *1* naphthalene; *2* acenaphthene; *3* phenanthrene; *4* anthracene; *5* fluoranthene; *6* pyrene; *7* benzofluorene; *8* benzo(a)anthracene; *9* benzo(b)-fluoranthene; *10* benzo(a)pyrene and *11* dibenz(a,h)anthracene

Table 1. Weekly averages of individual PAH values from samples corresponding to the most contaminated site analyzed in the four seasons

	Mean PAH ($\mu g/m^3$)			
	Spring	Summer	Autumn	Winter
Naphthalene	–	–	0.0351	–
Acenaphthene	0.0117	0.0350	0.0091	0.1507
Phenanthrene	0.0027	0.0033	0.0024	0.0087
Anthracene	0.0079	0.0292	0.0233	0.0223
Fluoranthene	0.2901	0.3259	0.3379	0.7611
Pyrene	0.0029	0.0036	0.0034	0.0393
Benzofluorene	–	–	–	0.0020
Benzo(a)anthracene	0.0013	0.0008	0.0013	0.0063
Benzo(b)fluoranthene	0.0132	0.0158	0.0252	0.5195
Benzo(a)pyrene	0.0061	0.0048	0.0040	0.0132
Dibenz(a,h)anthracene	0.0009	0.0007	0.0010	0.0038

Fig.2a, b. Chromatogram obtained from an extract of an atmospheric particulate sample in **a** winter and **b** summer. For peak identification, see Fig. 1

March 1989. Each sample was collected over a period of 24 h and the air volume of each sample was about 2 m³.

Sample extraction

The PAHs were extracted ultrasonically from Whatman paper filters during 30 min with 5 ml acetonitrile in a borosilicate glass-stoppered tube. The extract were then filtered through Millipore FHLP 01300 filter paper. The volume of the extract was then reduced to about 0.3 ml by bubbling a gentle stream of nitrogen gas through the solution at room temperature. The extracts were transferred to a 500 µl volumetric flask and taken up with acetonitrile for direct HPLC analysis.

Procedure

All retention data were obtained under gradient condition, using 60% acetonitrile in water (5 min), 60–70% (5 min linear), 70% (15 min) 70–90% (20 min linear) at a 0.7 ml/min flow rate. The fluorescence excitation and emission wavelengths were 290 and 385 nm, respectively.

Identification and quantitation of peaks

Chromatographic peaks of the environmental samples were identified by three methods. Firstly, tentative identification was made on the basis of the retention times and comparison with standards. Secondly, standards were added to the samples and the mixture was re-chromatographed. A quantitative increase in the peak areas was taken as an additional further characterization. Finally, we identified peaks at two different ($\lambda_{ex}290/\lambda_{em}385$ and $\lambda_{ex}250/\lambda_{em}370$) wavelenght comparing with the ratios obtained for standards. Peak areas were used for quantitation of PAHs in the samples.
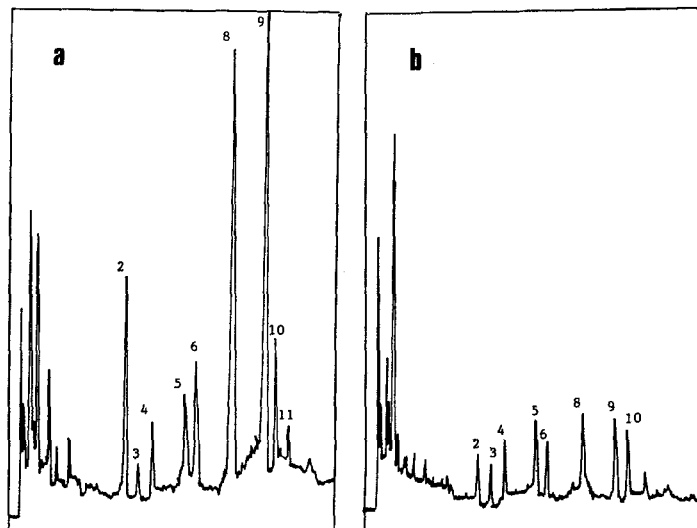
Results and discussion

Figure 1 shows the chromatogram of 11 PAH standards using the solvent program. The detection limits for each PAH calculated assuming a detectable minimum twice the signal to noise level were in the range of 0.01 to 2.88 pg.

Linearity between fluorescence response and concentration was verified for these PAHs with dilutions ranging from 1:10 to 1:50 of the stock mixture of PAH standards. The regression coefficients were between 0.9982 and 0.9992. For quantitative analysis, these calibrations required frequent rechecking. Peak area precision within days ranged from 4 to 9%, relative to standard deviation.

Recovery studies were conducted on spiked filters. In most cases, recoveries were greater than 90%, indicating that spikes were being recovered. For naphthalene and acenaphthene greater variability of recoveries occurred, probably because of the volatility of these PAHs.

This analytical method has been applied to the study of PAHs in atmospheric particulate matter of Valencia city, corresponding to samples supplied by the Agència del Medi Ambient-Generalitat Valenciana (Environmental Agency)

Table 2. Mean values of total PAHs per sampling site and season

	Total PAHs				
	Spring	Summer	Autumn	Winter	Mean
Site 1	0.8019	0.4946	0.4236	0.2778	0.4995
Site 2	0.5819	0.4626	0.4515	1.0604	0.6391
Site 3	0.6719	0.3581	0.3130	0.6587	0.5004
Site 4	0.5448	0.3493	0.1935	1.0158	0.5259
Site 5	0.2962	0.6184	0.3758	0.5611	0.4629
Site 6	0.6127	0.4454	0.3620	0.5755	0.4989
Site 7	0.8036	0.3991	0.4461	0.6808	0.5824
Site 8	0.3367	0.4102	0.4428	1.6686	0.7146
Site 9	0.2977	—	0.3269	0.3535	0.3260
Site 10	0.4020	0.2960	0.3767	0.6861	0.4402
Site 11	0.6145	0.3052	0.2220	0.3062	0.3620
Mean	0.5422	0.4139	0.3576	0.7131	
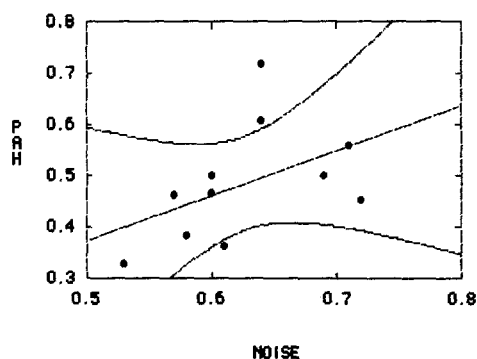
Fig. 3. PAH concentration distribution and noise level (dBA) corresponding to the sampling sites, and regression equation. PAH = −0.068 + 0.882 · NOISE
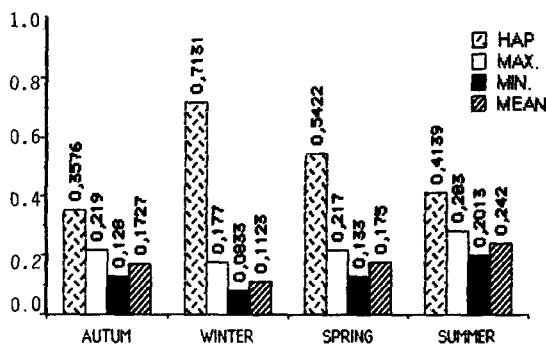
Fig. 4. Temperatures (in °C/100) and PAH concentrations during the different yearly seasons

and from 11 sites in the city. The analytical results of total PAHs were the average of 1 week collection in spring, summer, autumn and winter. The main variations were seasonal, and the higher concentrations of PAH were in winter and spring. Figure 2 shows two examples of PAH patterns from different seasons. Table 1 gives the weekly

average of PAH individual values obtained from samples corresponding to the most contaminated site analyzed in the four seasons. The most abundant PAH was fluoranthene, followed by benzo(b)fluoranthene, both important carcinogens. The mean values per sampling site are shown in Table 2, and varied from 0.193 to 1.668 µg/m³.

With respect to noise (Fig. 3), a polynomial regression equation is described which shows PAH concentration tendency during the year. Figure 4 shows PAH concentration related to temperature during the different yearly seasons. The correlation study shows a significant association ($p < 0.05$) between PAH concentration and the other two variables studied.

The variability of PAH concentrations from different sites was partly due to variations in the emission levels, but also to climatic and chemical phenomena, convection of air masses, changes in the boundary layer and photochemical degradation of the PAHs. Valencia is a heavily contaminated city, but the low concentrations of PAHs in summer were probably caused by a decrease in vehicle traffic during the holiday months, while the low values found in autumn are probably associated with the significant increase in rainfall.

References

1. Nikolaou K, Masclet P, Mouvier G (1984) Sci Total Environ 32:103−132
2. Mckee R-H, Daughtrey W-C, Freeman J-J, Federici J-J, Phillips R-D, Plutnick R-T (1989) J Appl Toxicol 9:265−270
3. Khesina A, Makhover M-S, Khitrovo I-A (1989) Ekssp-Onkol 11:3−8
4. Yamasaki H, Kuwata K, Miyamoto (1982) Environ Sci Technol 16:189−194
5. Karlesky D-L, Rollie M-E, Warner I-M (1988) Anal Chem 58:1187−1192
6. Romanowski T, Funcke W, Balfanz E (1982) Anal Chem 54:1285−1287
7. Wise S-A, May W-E (1983) Anal Chem 55:1479−1485
8. Espigares M, Pérez J-A, Mariscal A, Fernandez M, Gálvez R (1987) J Appl Toxicol 7:143−146
9. Das B-S (1983) Liquid Chromatography in Environmental Analysis. Humana, Clifton, New Jersey
10. Dong M-W, Greenberg A (1988) J Liq Chromatogr 11:1887−1905
11. Su S-Y, Lai E-P-C, Winefordner J-D (1982) Anal Lett 15:439−450
12. Xu X-B, Jin Z-L (1984) J Chromatogr 317:545−555
13. May W-E, Wise S-A (1984) Anal Chem 56:225−232
14. Muel B, Saguen S (1985) Int J Environ Anal Chem 19:111−131
15. Tanaka K, Saito M (1988) Analyst 113:509−510
16. Masclet P, Pistikopoulos P, Beyne S, Mouvier G (1988) Atmos Environ 22:639−650
17. Maher W, Pellegrino F, Furlonger J (1989) Microchem J 39:160−165
18. Miguel A-H, de Andrade J-B (1989) Int J Anal Chem 35:35−41