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Average Daily Respiratory Intake of Polycyclic Aromatic Hydrocarbons in Ambient Air Determined by Capillary Gas Chromatography

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High-performance liquid chromatography (HPLC) is well used for the quantitative analysis of polycyclic aromatic hydrocarbons (PAH) in environmental samples (Ogan et al. 1979; Matsushita et al. 1981; Obana et al. 1981) with high sensitivity. However, it has a lower separation efficiency in comparison with capillary gas chromatography (GC). This GC has played an important role in the isolation and identification of various organic compounds, e.g., PAH (Lee et al. 1980, 1982). This method is good for monitoring environmental samples because some of the unknowns are suggested by retention indices of PAH (Lee et al. 1979). Bjørseth (1977) reported on the methodology of determination of PAH by glass capillary GC with good reproducibility. We also examined it by using splitless injection technique and plural internal standards, i.e., several internal standards were added to the PAH reference compounds and samples, and a successful result was obtained (Matsumoto et al. 1983). This paper describes the comparison of the GC method with the HPLC method by measuring the PAH in air particulate matter; and average daily respiratory intake (ADI) of them in ambient air by man is presented here.

MATERIALS AND METHODS

Airborne particulate samples were collected on glass fiber filters (Toyoroshi, GB-100R) at the rooftop of our institute (Osaka, Japan). The sampling period was 24 or 48 h. Samples were collected in November, 1981; January, March and August, 1982; which corresponded to 26000, 11900, 22500 and 36700 m^3 of air, respectively. Organic compounds were extracted from these filters with benzene-methanol (4:1) in Soxhlet extractors for 8 h. Each of the benzene-methanol extract was concentrated to tar with a rotary evaporater (below 40 °C) under reduced pressure. The tar was separated into 3 fractions by a liquid-liquid fractionation, i.e., acidic, neutral and basic fraction, and a PAH containing fraction was prepared from the neutral one by a column chromatography loaded with Wakogel C-100 (Wako pure chemicals industries, Osaka, Japan) by the method of Morita et al. (1981). This fraction was concentrated and 4 internal standards were added . Palmitic acid methyl ester was used as an internal standard for fluorene, phenanthrene and anthracene; stearic acid methyl ester for

fluoranthene, pyrene and benzo[*b*]fluorene; arachidic acid methyl ester for benz[*a*]anthracene and triphenylene (and chrysene); n-triacontane for benzo[*b* and *k*]fluoranthene, benzo[*e* and *a*]-pyrene, perylene, 3-methylcholanthrene, indeno[*1,2,3-cd*]pyrene, dibenz[*a,h*]anthracene and benzo[*ghi*]perylene; respectively.

The gas chromatographic analyses were made on a Hewlett Packard 5710A GC equipped with a fused silica capillary column (0.31 mm i.d. x 25 m) coated with SE-54. After the column temperature was held for 2 min at 150 °C, it was programmed from 150 °C to 300 °C at the rate of 4 °C/min and then held at 300 °C for 8 min. Injector and detector temperature were set at 300 °C. Helium was used as the carrier gas at the column flow rate of 1.0 ml/min. Two µl of each sample solution was injected by the splitless injection technique. The chromatographic peaks on a recorder were quantified by comparing the peak heights with those of corresponding internal standards and the quantification was corrected for relative response factors. The peaks were identified by comparing retention times with those of standards and GC-MS anlysis by using JOEL JMA DX-300 operated in the electron impact (EI) mode at an ionization voltage of 70 eV. The HPLC equipment comprised a fluorescence detector and 6 mm i.d. x 15 cm column packed with ODS of 5 µm particle size (Obana et al. 1981). The mobile phase was acetonitrile-water (7:3). The flow rate was 2.0 ml/min.

RESULTS AND DISCUSSION

Gas chromatograms of the reference PAH and the sample (Aug., 1981) fortified with internal standards were illustrated in Fig. 1. The relative standard deviation of each PAH was less than 8 % in all cases when a solution containing standard mixtures and internal standards was injected repeatedly (11 times) and each PAH had a good linearity from 1 to 6 ng; so that the precision of the method was thought to be excellent (Matsumoto et al. 1983). Detection limit of this GC method was 0.05 ng of each PAH/m^3 of air and therefore PAH contents of a daily sample could be measured. Moreover, the GC method had advantages that simultaneous analysis of many PAH was able to be made; the rise and fall of not only identified organic pollutants but also the unknowns were obiviously investigated; whereas the HPLC method was not good to find out the latter. Assuming that the retention indices by SE-54 capillary column were the same as those by SE-52, peak a in the chromatogram B in Fig. 1 was supposed to be benzo[*ghi*]fluorene because m/z of EI parent peak was 226 and PAH index was 389.0 (Lee et al. 1979). Similarly, since peak b had a EI parent peak of 306 and PAH index of 492.0 it was supposed to be m-quaterphenyl. Peak c was identified as coronene by comparing retention time with that of standard and GC-MS analysis.

Table 1 showed PAH contents in ambient air measured by GC and HPLC analyses. The concentrations of benzo[*b*]fluoranthene and benzo-[*ghi*]perylene by GC were well in accord with those by HPLC. And therefore, average contents of them by GC were equal to those by HPLC, respectively. However, PAH contents of pyrene, benzo[*k*]-

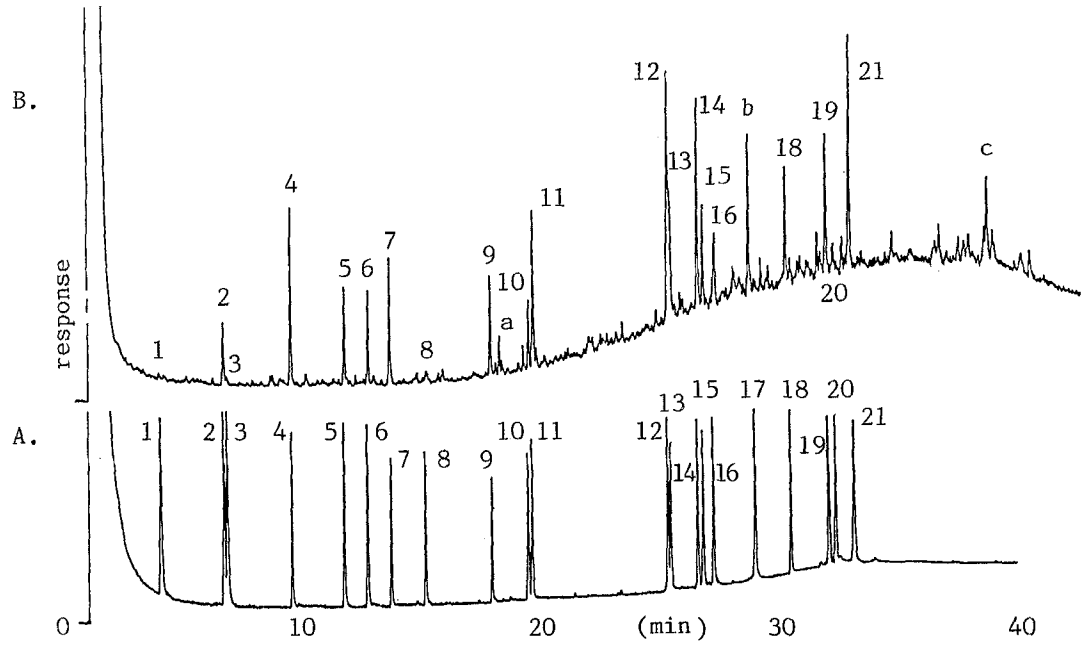

Figure 1. Capillary column gas chromatograms of standard PAH (A) and sample (B; Aug.,1981) fortified with internal standard. 1: Fluorene, 2: Phenanthrene, 3: Anthracene, 4: Palmitic acid methyl ester, 5: Fluoranthene, 6: Pyrene, 7: Stearic acid methyl ester, 8: Benzo[*b*]fluorene, 9: Arachidic acid methyl ester, 10: Benz[*a*]anthracene, 11: Triphenylene + Chrysene, 12: Benzo[*b*]-fluoranthene, 13: Benzo[*k*]fluoranthene, 14: Benzo[*e*]pyrene, 15: Benzo[*a*]pyrene, 16: Perylene, 17: 3-Methylcholanthrene, 18: n-Triacontane, 19: Indeno[*1,2,3-cd*]pyrene, 20: Dibenz[*a,h*]anthracene, 21: Benzo[*ghi*]perylene.

Table 1. PAH contents in ambient air

PAH	PAH contents (ng/m^3 of air)				
	Nov.	Jan.	Mar.	Aug.	average
Fluorene	0.15	0.14	0.10	0.08	0.12
Phenanthrene	1.79	2.64	1.29	0.79	1.63
Anthracene	0.26	0.57	0.17	0.27	0.32
Fluoranthene	3.94	8.33	2.19	1.50	3.99
Pyrene	4.13(3.38)	8.96(6.57)	2.02(1.50)	1.52(1.02)	4.16(3.12)
Benzo[*b*]fluorene	0.51	0.94	0.19	0.46	0.53
Benz[*a*]anthracene	3.31(4.43)	6.95(4.78)	1.49(1.64)	0.99(0.67)	3.19(2.88)
Triphenylene + Chrysene	5.16	9.03	2.04	1.54	4.44
Benzo[*b*]fluoranthene	8.76(9.15)	12.44(12.61)	4.72(4.72)	3.12(3.54)	7.26(7.51)
Benzo[*k*]fluoranthene	3.24(3.00)	7.65(5.39)	2.70(1.87)	1.80(1.26)	3.85(2.88)
Benzo[*e*]pyrene	6.67(5.39)	8.96(6.78)	3.41(2.52)	2.66(2.18)	5.43(4.22)
Benzo[*a*]pyrene	5.20(4.18)	8.41(7.31)	2.14(1.77)	1.60(1.28)	4.34(3.64)
Perylene	0.84	1.15	0.53	0.51	0.76
3-Methylcholanthrene	nd	nd	nd	nd	nd
Indeno[*1,2,3-cd*]pyrene	6.56	11.77	3.36	2.64	6.08
Dibenz[*a,h*]anthracene	1.15(0.55)	1.19(0.96)	0.46(0.24)	1.06(0.33)	0.97(0.52)
Benzo[*ghi*]perylene	8.43(9.04)	12.11(12.18)	3.59(4.50)	3.24(2.68)	6.84(7.10)

PAH contents measured by HPLC are indicated in parentheses.
nd: not detected (<0.05 ng/m^3 of air)

Table 2. Average daily respiratory intake of PAH in ambient air

PAH	average daily intake (ng/day/man)
Fluorene	0.5
Phenanthrene	7
Anthracene	1
Fluoranthene	16
Pyrene	17 (12)
Benzo[*b*]fluorene	2
Benz[*a*]anthracene	13 (12)
Triphenylene + Chrysene	18
Benzo[*b*]fluoranthene	29 (30)
Benzo[*k*]fluoranthene	15 (12)
Benzo[*e*]pyrene	22 (17)
Benzo[*a*]pyrene	17 (15)
Perylene	3
3-Methylcholanthrene	<0.2
Indeno[*1,2,3-cd*]pyrene	24
Dibenz[*a,h*]anthracene	4 (2)
Benzo[*ghi*]perylene	27 (28)

The average daily respiratory intake can be set at 4C ng, where C is the total concentration of the pollutant (Van Cauwenberghe et al. 1983), which measured by GC; those by HPLC are indicated in parentheses.

fluoranthene, benzo[*e*]pyrene, benzo[*a*]pyrene and dibenz[*a,h*]-anthracene by GC were slightly higher than those by HPLC in all samples. Especially, in the case of dibenz[*a,h*]anthracene (peak No. 20 in Fig. 1B), other compounds, e.g., dibenz[*a,c*]anthracene, were considered to be contaminated in its peak due to imperfect separation, so the ratio of GC value to HPLC one of the PAH became from 1.2 to 3.2 on the average of 2.1. Moreover, because the separation efficiency between benzofluoranthenes (peak No. 12 and 13 in Fig. 1B) was not better, it was supposed that the concentration of the shoulder peak benzo[*k*]fluoranthene (peak No. 13 in Fig. 1B) by GC became higher than that by HPLC.

Matsushita (1980) reviewed the seasonal variation on benzo[*a*]-pyrene concentration in urban air (Winter>Autumn>Spring>Summer). Our data showed that it appeared with not only benzo[*a*]pyrene but also other PAH in Osaka. Goto et al. (1982) reported that PAH contents of benzo[*a*]pyrene, benzo[*k*]fluoranthene, benzo[*ghi*]-perylene and perylene in urban Tokyo air in January were 3.9, 1.7, 4.1 and 0.8 ng/m^3 of air (arithmetrical means) respectively, which were determined by thin-layer chromatography and spectrofluorometry. In ambient air of Kyoto, the annual concentration of benzo[*a*]pyrene was 2.84 ng/m^3 of air (Ohe. 1982). The values of PAH in urban Osaka air were much higher than those in Tokyo and Kyoto. Ambient benzo[*a*]pyrene concentration in Oslo (Norway) determined by capillary GC (Møller et al. 1980) was roughly similar to our results, but that of the residental area in an

industrial city (GFR) was much higher than ours (Grimmer. 1981). PAH contents in ambient air have a great influence on daily intake of them. The daily intake of an organic aerosol component can be roughly expressed as propotional to its atmospheric concentration (Van Cauwenberghe et al. 1983): 20/100 x 20 m^3 x C ng/m^3 = 4C ng, where C = the total concentration of the pollutant, and 20 m^3 = the air volume sampled by man over 24 h. Table 2 indicates the ADI calculated from PAH contents by GC and HPLC. The ADI measured by GC of benzo[*b*]fluoranthene, benzo[*k*]fluoranthene, benzo[*e*]pyrene, benzo[*a*]pyrene and benzo[*ghi*]perylene are 29, 15, 22, 17 and 27 ng/day/man, and these values are equal to those calculated by HPLC. However, since the recovery rate about fluorene and anthracene from the glass fiber filters was low (Matsumoto et al. 1982) and the PAH less than 4 rings, which have relatively high vapor pressures, were not sufficiently trapped on glass fiber filters (Yamasaki et al. 1982), the ADI of them must be much higher than those calculated. The ADI value of benzo[*a*]-pyrene is about one third as much as a value of dietary daily intake of it, 60 ng/day/man (Obana et al. 1984). That values of other PAH were also similarly about one third as much as those of them, respectively.

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