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Vapor and Particle Phase Determination of Polycyclic Aromatic Hydrocarbons in Urban Air

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Polycyclic aromatic hydrocarbons (PAHs) are a group of toxic compounds that are mostly formed as a result of incomplete combustion of organic material (Vo-dinh 1989; Wagrowski and Hites 1997). Polycyclic aromatic hydrocarbons are widely distributed into the environment from both natural and anthropogenic sources, but these pollutants are released into the atmosphere mainly from anthropogenic sources. PAHs have recently attracted interests because several of these compounds have shown strong carcinogenic and mutagenic activities (Baek et al 1991).

Many different reports concerning the determination of PAHs in urban atmospheres are available in literature. In most studies the concentrations of PAHs associated with airborne particulate matter have been determined after collection on glass fiber filters by high-volume air sampler (Miguel et al 1998; Allen et al 1997). Those PAHs with a vapor pressure above 10^{-8} KP may be substantially distributed between the gas phase and particle phase in the atmosphere. As a result, the determination of the concentrations of PAHs associated with airborne particulate matter is not sufficient to evaluate the hazards of these pollutants. The determination of concentrations of PAHs in vapor phase and particle phase individually has gained a considerable attention during the last decade (Yamasaki et al 1982).

So far, several methods have been developed for the collection of vapor phase PAHs from the atmosphere using a high-volume air sampler supplemented by an adsorbent such as PUF (Poly Urethane Foam), tenax, or a combination of them located downstream of the filter (Krieger and Hites 1992; Baek et al 1992). This type of sampling is not a reliable method for classification of vapor and particle phase PAHs. Because of the pressure across the filter during the sampling, components adsorbed on the particulate matter collected on the filter may volatilize from the particles and be trapped on the adsorbent located downstream of the filter.

The distribution of PAHs between vapor and particle phases depends on the ambient temperature and those with vapor pressures above 10^{-8}Kpa will greatly tend to vaporize from particles collected on the filter. The phenomenon is more

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important in middle-east region where the ambient temperature is high enough to increase this vaporization especially in hot seasons of the year.

MATERIALS AND METHODS

Samples were collected from the atmosphere of the city of Isfahan. The city is located in the central part of Iran and beside a large desert. Two samplers were simultaneously used for collection and classification of vapor and particle phase PAHs from the atmosphere The samplers were equipped with a 10μm size inlet for removing the coarse particles. Inside the first sampler, air was passed through a micro-fiber glass filter to remove the particle phase PAHs. Vapor phase PAHs were collected on the PUF-tenax-PUF sandwich located in a stainless steel tube placed downstream of the filter. The second sampler was an annular diffusion denuder equipped with tenax-coated multi-tubes installed in front of the micro-fiber glass filter. As a result of passing air through the sampler, the vapor phase PAHs were then adsorbed in the multi-tube system and before reaching the filter. Figure 1 shows a schematic diagram of air samplers used in this work.

Polycyclic aromatic hydrocarbons collected on the filters and PUF-tenax-PUF sandwiches in the two samplers were extracted by supercritical carbon dioxide 10% methanol as modifier. The extracts were analyzed by gas chromatographic technique. The extract from the first sampler contained the total atmospheric PAHs, while the extract from the second sampler showed the particle phase concentrations of PAHs.

The extractions were performed by an Isco dual pump system. The Isco 260 D pump supplied CO_2 and Isco 100 D pump supplied methanol as a modifier. The PUF-tenax-PUF was placed into the extraction cell and extracted with supercritical CO_2 and 10% methanol under 400 atm pressure for 40 min. The filters were extracted under the same condition as for PUF-tenax-PUF but for 60 min. The extracts were collected in dichloromethane by a steel restrictor. The extracts were then blown down with nitrogen stream to remove the dichloromethane and remainder methanol. The residue was extracted in n-hexane and used for determination by gas chromatography.

The determination of PAHs concentrations was carried out on a Varian, Model CP-3800 gas chromatograph. The instrument was equipped with a CP-8400 autosampler and FID detector. A BP5 capillary fused silica column (25m x 0.25 mm, i.d., SEG) was used for separation of PAHs. The following temperature programming was used for the better separation; 5 min at 90 °C, 10 °C/min to 150 °C and 5 °C/min to 320 °C. The injection and detector temperatures were 220 °C and 280 °C respectively.

RESULTS AND DISCUSSION

The concentrations of vapor phase PAHs were obtained by subtracting the amount of PAHs collected on the filter and adsorbed in downstream trap in the second

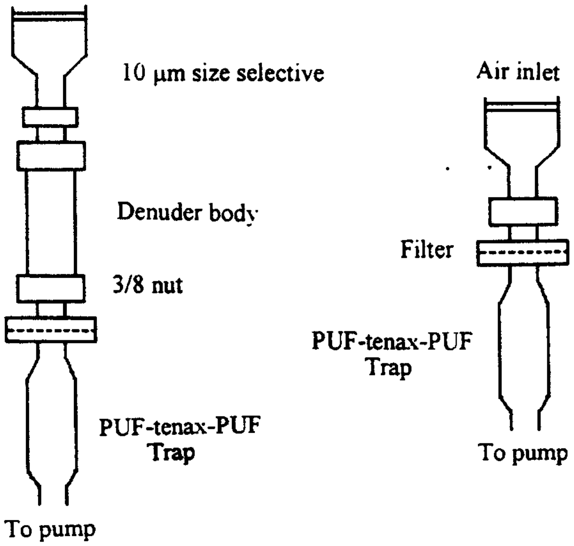

Figure 1. Schematic diagram of air samplers.

sampler from those collected in the first sampler. The concentrations of Polycyclic aromatic hydrocarbons in vapor and particle phases were determined in the atmosphere of the city of Isfahan. Table 1 summarizes the results obtained from this investigation and showed that considerable amounts of atmospheric PAHs and especially the lighter ones exist in the vapor phase.

Table 1. Concentrations of vapor and particle phase PAHs in the atmosphere of the city of Isfahan (ngm^{-3})

Compound	Vapor phase	Particle phase
Fluorene	5.8	1.2
Fluoranthene	3.7	3.4
Phenanthrene	7.2	2.4
Anthracene	3.1	0.9
Benzo (a) anthrasene	4.9	4.7
Chrysene	3.6	3.5
Benzo (a) pyrene	ND	4.1
Benzo (ghi) perylene	ND	2.7

The determination of atmospheric concentrations of vapor and particle phase PAHs were also performed in an area with very low traffic level compared with the city of Isfahan. The area was located about 150 Km far from Isfahan in the east and considered as a rural area. Table 2 shows atmospheric concentrations of PAHs in this area.

Table 2. Atmospheric concentrations of PAHs (ngm^{-3})

Compound	Vapor phase	Particle phase
Fluorene	2.3	ND
Fluoranthene	2.1	ND
Phenanthrene	2.5	2.3
Anthracene	1.2	ND
Benzo (a) anthrasene	3.2	3.1
Chrysene	2.0	ND
Benzo (a) pyrene	ND	2.1
Benzo (ghi) perylene	ND	ND

Although the concentrations of PAHs in rural area were lower than those in the urban atmosphere, finding such compounds in remote area was surprising. However, the meteorological studies had shown that in the city of Isfahan, that direction of a majority of winds in different seasons of the year is from west to east. The wind ia able to transfer the atmospheric PAHs to the remote areas. The concentrations of vapor and particle phase PAHs were investigated in winter and summer seasons. Table 3 summarizes the concentrations of PAHs in the cold and hot seasons in the city of Isfahan.

The total concentrations of PAHs in winter season were higher compared with those in the summer time, despite, the concentrations of lighter PAHs in vapor phase were the major part of the total concentration of PAHs in summer time.

Table 3: Atmospheric concentrations of Gas and particle phase concentrations of PAHs (ngm^{-3})

	Winter		Summer	
Compound	Particle	Gas	Particle	Gas
Fluorene	2.9	6.1	1.3	4.7
Fluoranthene	2.9	3.9	1.8	4.3
Phenanthrene	3.2	7.8	2.1	6.4
Anthracene	2.1	3.4	1.0	3.6
Benzo (a) anthrasene	5.9	3.4	3.6	3.9
Chrysene	3.3.	3.0	2.7	3.2
Benzo (a) pyrene	4.7	ND	3.7	ND
Benzo (ghi) perylene	3.2	ND	2.3	ND

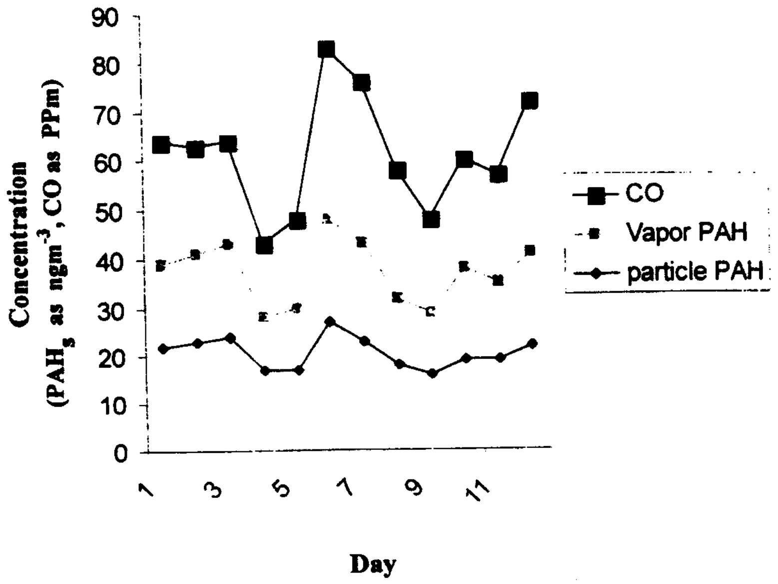

Figure 2: Variation in the concentration of PAHs and CO
(concentrations of CO are 10 x actual concentrations)

The variations in total concentrations of vapor and particle phase polycyclic aromatic hydrocarbons were compared with those for CO in the atmosphere of the city of Isfahan and an excellent similarity was found between them. Pearson correlation coefficient between the concentrations of total PAHs and CO was also investigated and showed that the atmospheric concentrations of these two air pollutants were highly correlated (r=0.94). It was already reported that more than 90% of CO gets into the atmosphere of the city of Isfahan from mobile sources (Department of Environment Isfahan 2000). It can be concluded that these pollutants are realizing into the atmosphere from the same sources, and mobile sources are mostly responsible for emission of PAHs into the city atmosphere. Figure 2 shows the similar variation in concentrations of gas and particulate phase PAHs and CO.

However, the hazard of PAHs in urban atmosphere is very serious. Due to the results obtained in this work, considerable amounts of PAHs exist in vapor phase. and they can easily be inhaled and cause serious adverse health effects. The hazard of atmospheric PAHs is much more than that can be expected from the concentrations of PAHs associated with airborne particulate matter. PAHs can be transferred to remote areas. Concerning to the size of population at risk and continuous nature of exposure, reduction in fossil fuel consumption and also designing a suitable public transporting system should be noticed for the city of Isfahan.

REFERENCES

Allen IO, Dookerman NM, Taghizadeh K, Lafleur AL, Smith KA, Sarofim AF (1997) Measurement of oxygenated polycyclic aromatic hydrocarbons associated with a size-segregated urban aerosol. Environ Sci Technol 31: 2064-2070.

Baek SO, Goldstone ME, Kirk PWW, Lester JN Perry R (1991) Phase distribution and particle dependancy of polycyclic aromatic hydrocarbons in the urban atmosphere. Chemosphere 22: 503-520.

Baek SO, Goldstone ME, Kirk PWW, Lester JN, Perry R (1992) Concentrations of particulate and gaseous polycyclic aromatic hydrocarbons in London air following a reduction in the lead content of Petrol in the United Kingdom. Sci Total Environ 111: 169-199.

Department of Environment (2000) Air pollution report 4. Isfahan. Iran

Krieger MS, Hites RA (1992) Diffusion denuder for collection of semivolatile organic compounds. Environ Sci Technol 26: 1551-1555.

Miguel AH, Kirchstetter TW, Harely RA (1998) On-road emission of particulate polycyclic aromatic hydrocarbons and black carbon from gasoline and diesel vehicles. Environ Sci Technol 32 : 450-455.

Vo-Dinh T (1989) Chemical analysis of polycyclic aromatic compounds. John Wiley & Sons, New York, Chapter 1.

Wagrowski DM Hites R (1997) Polycyclic aromatic hydrocarbons accumulation In urban, suburban and rural vegetation. Environ Sci Technol 31: 279-282.

Yamasaki H, Kuwaia K, Mlyamoto H (1982) Effects of ambient temperature on aspects of airborne polycyclic aromatic hydrocarbons. Environ Sci Technol 16: 189-194.