

# DETERMINATION OF POLYCYCLIC AROMATIC HYDROCARBONS IN AMBIENT URBAN AIR

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**ABSTRACT:** Polycyclic aromatic hydrocarbons (PAH<sub>s</sub>) have been determined in the atmosphere of Isfahan, Iran. Airborne particulate matter was sampled using a high-volume air sampler at roof-top level (~6m). Extraction of PAH<sub>s</sub> from airborne particulate matter has been performed using SFE system and the relationship between the extraction temperature and the recovery of PAH<sub>s</sub> from airborne particulates is investigated. Determination of 16 PAH<sub>s</sub> has been carried out by GC-MS technique. Variation in concentration of PAH<sub>s</sub> has been compared to those for organic carbon and total suspended particles (TSP). A good agreement was found between the variation in concentration of PAH<sub>s</sub> and that for organic carbon, but weak correlation ( $p=0.06$ ,  $r^2=0.42$ ) was found to exist between the PAH<sub>s</sub> and TSP.

**KEY WORDS:** Air pollution, Polycyclic aromatic hydrocarbons, Airborne particulate matter, Extraction of PAH<sub>s</sub> by SFE.

## INTRODUCTION

Polycyclic aromatic hydrocarbons (PAH<sub>s</sub>) are products of incomplete combustion or pyrolysis of carbonaceous material at high temperature. They are ubiquitous in the environment and are generated from a variety of sources including; vehicles industrial processes, waste incineration, and using fossil fuels for residential heating [1,2]. The occurrence of PAH<sub>s</sub> in urban air has recently gained importance because of the continuous exposure, the sized of population at risk, and that a number of these compounds are known carcinogens [3,4]. Polycyclic aromatic hydrocarbons in the atmosphere are known to

be predominantly associated with particulate matter, being incorporated onto the particles by condensation and adsorption during the cooling of an exhaust emission [5].

The extraction of PAH<sub>s</sub> from airborne particulate matter has traditionally been performed by soxhlet system [6,7] which is tedious, time-consuming, and uses environmentally unfriendly solvents.

## EXPERIMENTAL

### *Sampling*

Airborne particulate matter from the atmosphere

of the city of Isfahan was collected on ultra-pure quartz fiber filter (Whatman QM-A) using a high-volume air sampler (Fig. 1) with an average flow rate of  $1 \text{ m}^3 \text{ min}^{-1}$ . Sampling was performed at two sites and close to the commercial areas of the city. Sampling period was 24 hours and samples were collected from roof-top level ( $\sim 6 \text{ m}$ ), where the air is approximately well mixed.

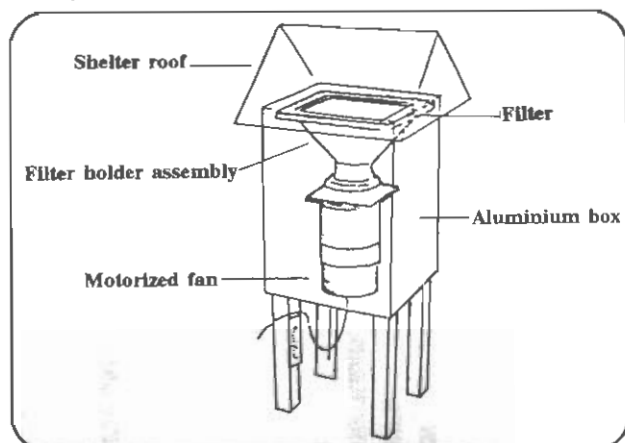


Fig. 1: Schematic diagram of high-volume air sampler

### Reagents and standards

Dichloromethane, methanol and toluene were HPLC grade (Aldrich Chemical Co.). The individual PAH standards and a standard solution of mixed PAH<sub>s</sub> were obtained from Supelco Inc. The standard mix included acenaphthene, fluoranthene, naphthalene, benzo(a) anthracene, benzo(a)pyrene, benzo(b) fluoranthene, benzo(k)fluoranthene, chrysene, acenaphthylene, anthracene, benzo(ghi)perylene, fluorene, phenanthrene, dibenzo(a,h)anthracene, indeno(123-cd) pyrene and pyrene in methanol: methylene dichloride (50:50). The standard solutions were stored in a refrigerator at 5°C.

### Extraction of PAH<sub>s</sub> from airborne particulate matter

Extraction of PAH<sub>s</sub> from air particulates was performed using an Isco dual pump SFE system. The Isco 260 D pump supplied pure CO<sub>2</sub> and the Isco 100 D pump supplied methanol as modifier. An exposed filter was folded and placed into a 10 mL volume stainless steel extraction vessel and extracted with supercritical liquid CO<sub>2</sub> under 400 atm. pressure, 90°C temperature and with 10% methanol for 60

minutes. The extracts were collected in dichloromethane by a steel restrictor.

### Analysis

Filter extracts were blown down to dryness under nitrogen current and sample volume was then increased to 1 mL with high purity toluene and analyzed using GCQTM quadrupole ion trap mass spectrometer (Finnigan MAT, San Jose, Ca, USA). 1  $\mu\text{L}$  of samples were injected onto a BPX-5 GC column (25 m, 0.25 mm i.d., SEG) by an A200S Finnigan MAT autosampler via a splitless injector at 250°C. Temperature programming was used for GC separation. Temperature started from 90°C with a 5 minutes hold time, then to 150°C at 10°C per minute, following by a 5°C per minute to 320°C. The GC-MS transfer line was kept at 250°C.

## RESULTS AND DISCUSSION

Supercritical fluid extraction is a well known technique for extraction of organic compounds and especially polycyclic aromatic hydrocarbons from environmental samples [6,7]. The effects of pressure, extraction time, and modifier on the extraction efficiency of PAH<sub>s</sub> by SFE have already been reported [8,9], but less was known about the influence of extraction temperature on the recovery of these compounds from airborne particulate matter.

In this study, the effect of temperature on the recovery of PAH<sub>s</sub> from air particulate was studied. Several filters were exactly cut into the two equal halves by a pizza cutter. They were then extracted under the same condition of pressure (400 atm.), extraction time (60 min.), and modifier (10% methanol), but at two different temperatures. One half of a filter was extracted at 80°C and the other one at 150°C. The extracts were then analyzed for phenanthrene, anthracene, fluoranthene, pyrene, benzo(a) anthracene, chrysene, and benzo(a)pyrene. The results are represented in Fig. 2 and indicate that increasing in extraction temperature have a positive effect on the recovery of PAH<sub>s</sub> from airborne particulate matter. However the effect of temperature on the extraction efficiency of PAH<sub>s</sub> from air particulate was studied using standard (SRM-1648) and the positive role of temperature on the extraction efficiency was confirmed.

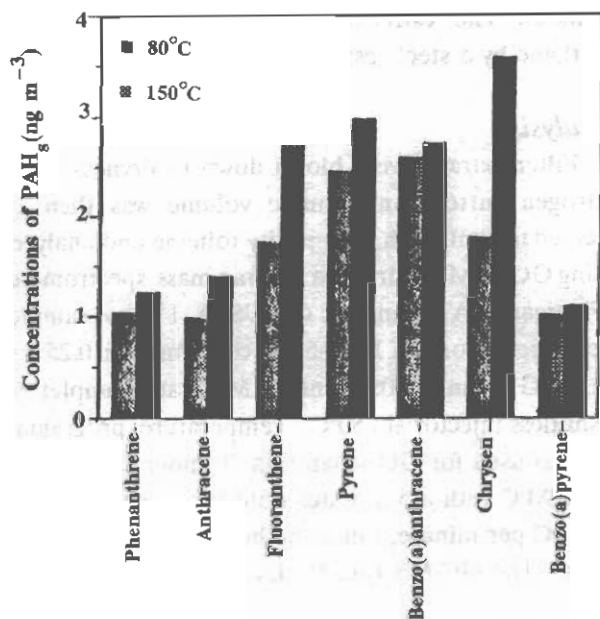


Fig. 2: Graphical representation of the effect of temperature on the recovery of PAH<sub>s</sub> by SFE system

Duplicate sampling was carried out from the atmosphere of the city of Isfahan over 24 hours period during the winter 1995 and chemical analysis took place for sixteen priority PAH<sub>s</sub>. Table 1 lists the PAH<sub>s</sub> detected by GC-MS system in ambient air of Isfahan. Sampling station 2 was located in an area with higher traffic density and the samples collected from this station contain higher concentrations for PAH<sub>s</sub> compared to those collected from the station 1.

A continuous sampling and analysis of airborne particulates was performed to investigate the variation in concentrations of PAH<sub>s</sub> in the atmosphere. The results showed that the concentrations of PAH<sub>s</sub>

varies day to day but always the minimum concentrations were obtained on Friday which is the weekend holiday in the city. A typical weekly variation in concentrations of ΣPAH is shown in Fig. 3. In a series of samples the concentration of ΣPAH<sub>s</sub> was compared to those for TSP and organic carbon. A good agreement was obtained between the ΣPAH and organic carbon ( $r^2 = 0.83, p = 0.0002$ ), but there was found no correlation between ΣPAH and TSP ( $r^2 = 0.40, p = 0.06$ ), the reasons for that are the complication of airborne particulate matrix, and that in cities such as Isfahan which are located beside the desert a considerable part of TSP could be released into the atmosphere as a result of resuspension process which takes place by traffic.

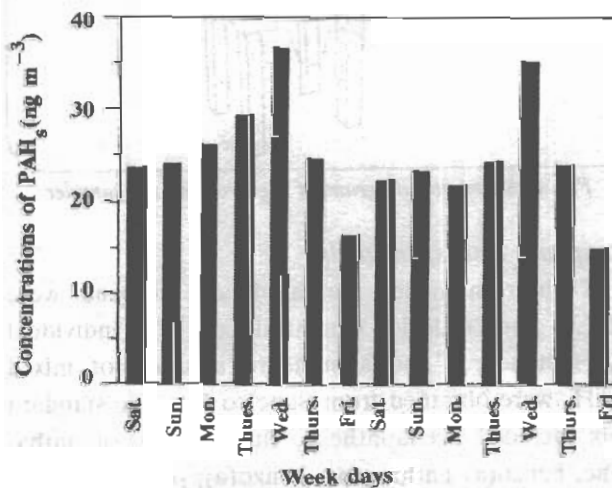


Fig. 3: Typical variation in the concentrations of PAH<sub>s</sub> in the atmosphere during the period of study.

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Table 1: The mean concentrations of PAH<sub>s</sub> in the atmosphere as ng m<sup>-3</sup> (n=10).

Compound	station 1	station 2	compound	station 1	station 2
Naphthalene	0.25	0.30	Benzo(a)anthracene	2.7	2.75
Acenaphthene	1.24	1.45	Chrysene	2.05	2.60
Fluorene	1.50	1.95	Benzo(b)fluoranthene	2.20	2.50
Phenanthrene	1.95	2.20	Benzo(k)fluoranthene	1.20	1.67
Anthracene	0.72	1.20	Benzo(a)pyrene	1.22	1.48
Acenaphthylene	0.80	0.88	Indino(123-cd)pyrene	1.20	1.80
Fluoranthene	2.12	2.19	Dibenzo(a,h)anthracene	1.80	2.05
Pyrene	2.75	3.02	Benzo(ghi)perylene	2.00	2.45

## REFERENCES

- [1] Roussel, R., Allaire, M. and Friare, S., *J. Air, Waste, Manage. Assoc.*, **42**, 1609(1992).
- [2] Lee, M. L. Novotny, V. and Bartle, K. D., "Analytical Chemistry of Polycyclic Aromatic Hydrocarbons", Academic Press Inc., New York, pp. 50-73 (1981).
- [3] Freudenthal, R. F. and Jones, P. W., "Polycyclic Aromatic Hydrocarbons, Chemistry, Metabolism and Carcinogenesis", Raven Press, New York (1976).
- [4] Baek, S. O., Goldstone, M. E., Kirk, P. W. W., Lester, J. N. and Perry, R., *Chemosphere*, **22**, 503 (1991).
- [5] Van Vaeck, L. and Van Cauwenberghe, K. A., *Atmos. Environ.*, **18**, 417(1984).
- [6] Kothandarman, S., Ahlert, R. C., Venkataramani, E. S. and Andrews, A. T., *Environ. Prog.*, **11**, 220 (1992).
- [7] Hawthorne, S. and Miller, D., *Anal. Chem.*, **59**, 38 (1987).
- [8] Lopez-Avila, V. and Dodhiwala, N. S., *J. Chrom. Sci.*, **28**, 468(1990).
- [9] Ho, J. S. and Tong, P. H., *J. Chrom. Sci.*, **30**, 344 (1992).