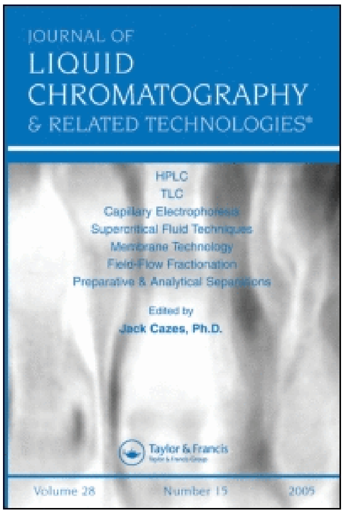

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MONITORING OF PERSISTENT ORGANIC POLLUTANTS (POPs) IN AEROSOLS USING HPLC

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ABSTRACT

Isocratic reversed phase high performance liquid chromatography (HPLC) with ultra violet (UV) detection was optimized for separation and quantification of polycyclic aromatic hydrocarbons (PAHs). Acetonitrile-water mixture (70 : 30 v/v) was used as mobile phase at a flow rate of 1.5 mL per minute. The volume of the sample loop was 0.1 mL. The UV detection was carried out at 254 nm. A method for the simultaneous determination of PAHs in aerosols is described. The recoveries of the compounds are in the range of 89–99% for the extraction. The detection limits typically are at the low to sub-ng/m^3. Concentrations of PAHs in aerosol samples collected at five different locations in Mumbai, India were measured. In addition to PAHs

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in ambient aerosols, concentrations of PAHs in indoor aerosol samples, where kerosene is used as cooking fuel, were also measured.

INTRODUCTION

The development of high performance liquid chromatography has contributed significantly to the determination of toxic organic contaminants in the environment and in foods. In addition, conventional column and thin layer chromatography (TLC) methods are powerful techniques for cleanup processes of environmental samples. Chromatography, thus, has the advantage of accommodating both the clean up and the separation of pollutant of interest.[1] Organic pollutants are emitted into the environment from a variety of natural and anthropogenic sources. With the rapid advancement of industrial and agricultural technology, the problem of environmental pollution by chemical carcinogens has escalated, many of them organic in nature. Some of the organic pollutants are highly resistant to photolytic, chemical, and biological degradation, and remain in the environment for quite a long time. These pollutants are termed as persistent organic pollutants (POPs) and they can be found in well-measurable amounts in air, water, and food.

Polycyclic aromatic hydrocarbons (PAHs) belong to the group of persistent organic pollutants (POPs) of known chemical carcinogens. PAHs are released into the atmospheric air through incomplete combustion of fossil fuels. The urban sources are coal-fired power plants, organic flares in petrochemical industries, and automobile exhausts. Organic refuse incineration is also a potential source. Releases from domestic cooking stoves and cigarette smoke are two indoor sources of these compounds. Study on the concentrations of the PAHs in atmospheric air is important, since many of the PAHs and their nitro derivatives are found to be carcinogenic and mutagenic.[2] PAHs in atmospheric air are associated with small size particles (0.08–0.2 μm). These aerosols penetrate into the pulmonary region of the lung where the clearance mechanisms are slower and, hence, there is a greater risk due to prolonged exposure.[3]

Reversed phase high performance liquid chromatography (HPLC) with ultra violet detection was optimized for separation and quantification of polycyclic aromatic hydrocarbons (PAHs) in aerosols. The technique was applied in Mumbai city of India to monitor PAH concentration in ambient aerosol samples, as well as in indoor aerosol samples where kerosene is used as cooking fuel. The main objective of this study is to develop a simple and sensitive method for determination of carcinogenic PAHs. The relative proportions of individual PAH in aerosols can be used for characterization of the number and nature of sources.

EXPERIMENTAL

Chemicals and Materials

Benzene (analytical grade, Merck) and acetonitrile (HPLC grade, Sisco, Mumbai); portable air sampling pumps (model No. DBA-P189-FD by GAST Co, USA) with a suction rate of about 30 litres per minute for the collection of particulate matter; glass fiber filters (7.6 cm dia) supplied by Whatman International in plastic filter holders; soxhlet extraction apparatus of 30 mL capacity; Standard Reference Material (SRM) 1649 Urban Reference Dust, supplied by the U.S. National Institute for Standards and Technology). Standard PAH compounds, supplied by Supelco Inc. (1000 μg/mL). Stock solutions of all the PAHs in the concentration ranges of 0 to 80 ng/mL in acetonitrile were used for calibration. Structures of some of the PAH compounds are presented in Figure 1.

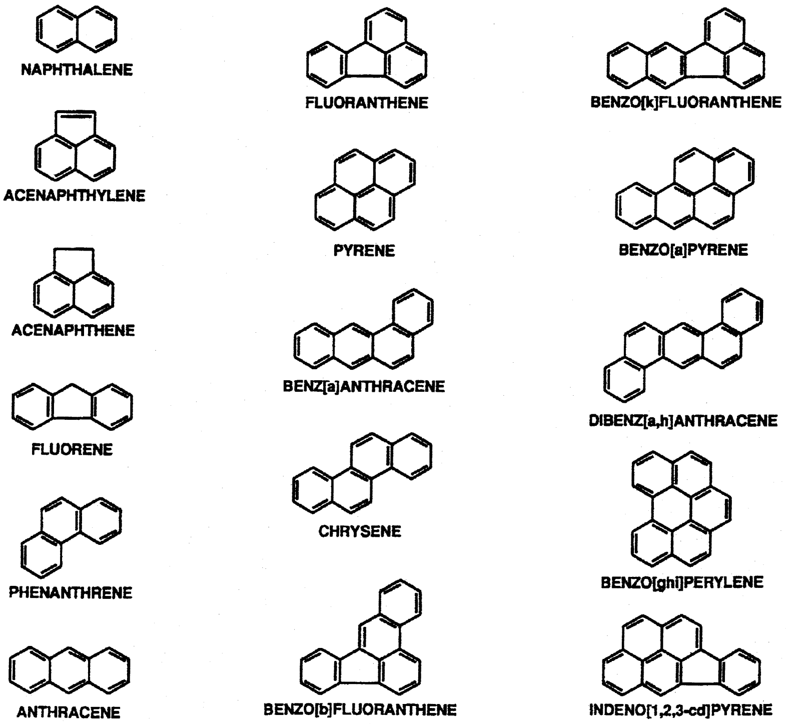

Figure 1. Structure of 16 PAH compounds identified as priority pollutants by U.S. EPA.

Instruments

The system used for determination of PAHs was a high pressure liquid chromatograph (HPLC) of Shimadzu model LC-10 AD with ultra violet detector of model Shimadzu Spectrophotometric detector (SPD-10A). Separation was performed on C-18 micro Bondapak column (250 mm × 4.6 mm i.d.with 10 mm × 4.6 mm i.d. guard column) with porous silica particles of size 5 μm.

Sample Collection for PAHs

Air samples were collected for 24 hours from Trombay, Khar, Maravali, TTC Area, and Borivli, five different locations in Mumbai City of India, at a height of 6 m, using a high volume sampler. Pre-weighed glass fiber filter papers (Whatman EPM2000) with polyurethane foam (PUF) plugs as backup filter were used to collect suspended particulate matter. Air was pulled at approximately 1.1 m^3/min. The size of the filters was 20.3 × 25.4 cm and they were prewashed in hexane and dried at 500°C for 8 hrs before use. After sampling, the filter papers and PUF plugs were dried in a desiccator using anhydrous calcium chloride. They were weighed before and after the sample collection to determine the dust load. The filters and plugs were sealed in polythene covers and stored in a deep freeze at -25°C, prior to soxhlet extraction.

In addition to ambient aerosols, indoor aerosol samples were also collected at the Trombay site where kerosene is used as fuel. The outdoor samples at the Trombay site were collected in an open area 5–6 m away from the house, while the indoor samples represent the cooking environment. For indoor samples also, pre-weighed glass fiber filter papers with PUF plugs as backup filter were used. The filter holder was positioned at a height of 1.5 m from the ground and at an angle of 45 degrees to the ground. This resembles the position of the nose of a man with average height, ensuring representative sample collection for exposure assessment. Sampling was conducted only during the cooking period in the house. Each integrated sample was collected covering all four sessions of cooking in a day, viz., early in the morning, mid afternoon, early evening, and late evening, representing the cooking during the preparation of breakfast, lunch, evening tea, and dinner, respectively. The filter assembly was kept covered with light tight envelopes during the non-cooking periods. The total time period of integrated sample collection varied between 6 and 7 hours.

Sample Extraction

The glass fiber filters and PUF plugs were soxhlet extracted with 50 mL of benzene for 8 h (at 12 cycles/h). The extract was filtered using a sintered glass disc to eliminate other particulate impurities and were transferred into a 50 mL conical flask. The extract was dried by a flow of dry nitrogen. The residue obtained was redissolved in 1 mL of acetonitrile for analysis by HPLC. The recovery efficiencies were determined by spiking filter paper samples and PUF plugs (n = 6) with PAH standard mixture. The mean recovery varied from 80 to 97%.

Analysis of Samples for PAHs Using Reversed-Phase HPLC

Acetonitrile-water mixture (70 : 30 v/v) was used as mobile phase at a flow rate of 1.5 mL per minute. The volume of the sample loop was 0.1 mL. The UV detection was carried out at 254 nm. The chromatographs were processed with a CR7A Chromatopac data processor. Linear calibration graphs were obtained for all the PAH in the concentration ranges of 0 to 80 ng/mL. Using this method, PAH concentrations of sub-nanogram in the sample could be quantified.

Quality Control and Assurance

A strict regime of quality control and assurance was operated in every stage. To offset the possibility of semi-volatile organic compound blow-off losses or adsorption gains to the particles on the filter during sampling,[4,5] PUF plugs were used as backup filters. Blanks were run with each sample batch. Efficacy of the method was verified using the standard reference material (CRM) 1649 Urban Reference Dust (supplied by the U.S. National Institute for Standards and Technology). The resulting values were in agreement with the certified values given for this material as shown in Table 1.

Table 1. Mean Concentration of PAHs Analysed in Six Batches of NBS 1649 Urban Reference Dust

Compound	Certified (μg/g)	Observed (μg/g)
Phenanthrene	4.2–4.8	5.05 ± 0.85
Fluoranthene	6.5–7.5	8.25 ± 0.65
Pyrene	5.9–6.7	6.56 ± 0.43
Benzo(a)anthracene	2.4–2.8	2.30 ± 0.31
Chrysene	3.4–3.8	3.59 ± 0.25
Benzo(k)fluoranthene	1.9–2.1	2.05 ± 0.29
Benzo(a)pyrene	2.3–3.0	2.91 ± 0.43

RESULTS AND DISCUSSION

An isocratic HPLC system with UV detector was found to be a very simple and sensitive method for separation and characterization of different polycyclic aromatic hydrocarbons in atmospheric aerosols. The retention data for the PAHs and the limit of detection for various compounds are given in Table 2. A typical chromatogram of standard PAHs and PAHs in atmospheric aerosols, collected at Trombay, are shown in Figure 2.

Figure 3 shows levels of PAHs at different locations in Mumbai. Eight PAH compounds are characterized in the air samples. Total PAH concentration varied from 4.1 ng/m^3 at Borivili to 44.1 ng/m^3 at Thane Belapur Industrial Area. The Borivili site, which is a suburban area, shows the least levels of concentration of total PAHs as compared to other sites, whereas the TTC area, which is surrounded by several industries, shows the highest levels of total PAHs. Table 3 represents the PAH profiles developed by normalizing each PAH concentration to that of the total PAH concentration present in the ambient aerosols. Though the profile patterns of PAH obtained do not provide explicit information about the source because of multi-source contribution of PAHs at the study areas, a qualitative source apportionment can be worked out.

Different PAH markers, identified by earlier workers[6–8] have been used for the qualitative source apportionment in the present study. Total PAH at the Trombay site was dominated by relatively more volatile compounds such as anthracene, fluoranthene, and pyrene, which can be attributed to coal combustion, coke production, and refineries. Total PAH in the Khar area was found to be mostly dominated by benzo(a)anthracene/chrysene, benzo(k)fluoranthene, and benzo(a)pyrene, indicating vehicular emission being the primary source, and this is consistent with the sampling sites being very close to roads having high traffic

Table 2. Retention Data and Detection Limit for Some of the PAH Compounds Using the HPLC-UV System

Compounds	Retention Time (minutes)	Detection Limit (ng/m^3)
Phenanthrene	9.4	0.01
Anthracene	10.4	0.01
Fluoranthene	12.7	0.02
Pyrene	14.4	0.02
Chrysene	18.5	0.01
Benzo(a)anthracene	19.7	0.01
Benzo(k)fluoranthene	31.5	0.01
Benzo(a)pyrene	35.3	0.01

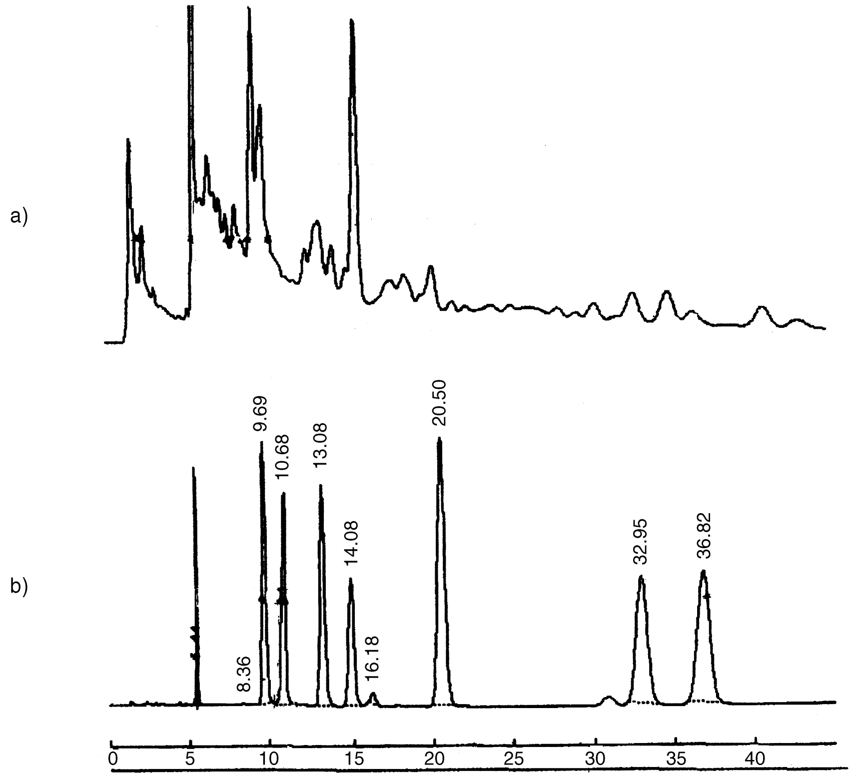

Figure 2. Typical chromatograms of a) PAH standard and b) PAH in ambient aerosols.

density. The Maravali site, which is close to oil refineries and fertilizer plants, accounted for higher concentrations of fluoranthene, followed by benzo(a)anthracene/chrysene and benzo(k)fluoranthene. This indicates the presence of multiple sources like oil refineries, fertilizer plants, and vehicular emission. Site Borilvili, which is a suburban area, shows the lowest concentration of PAHs. But, the relative abundance of ambient PAHs indicates long-term transport from coal combustion and oil burning industries. Trans-Thane Industrial (TTC) area showed the maximum concentration of ambient PAHs, which can be attributed more to the industrial emission than vehicular emission. This data on PAH concentration at different sites of Mumbai will be used for source characterization and to evaluate the exposure levels to the public residing in these regions.

The concentration ranges of individual PAH compounds, along with their mean concentration observed for indoor and outdoor locations, are given in

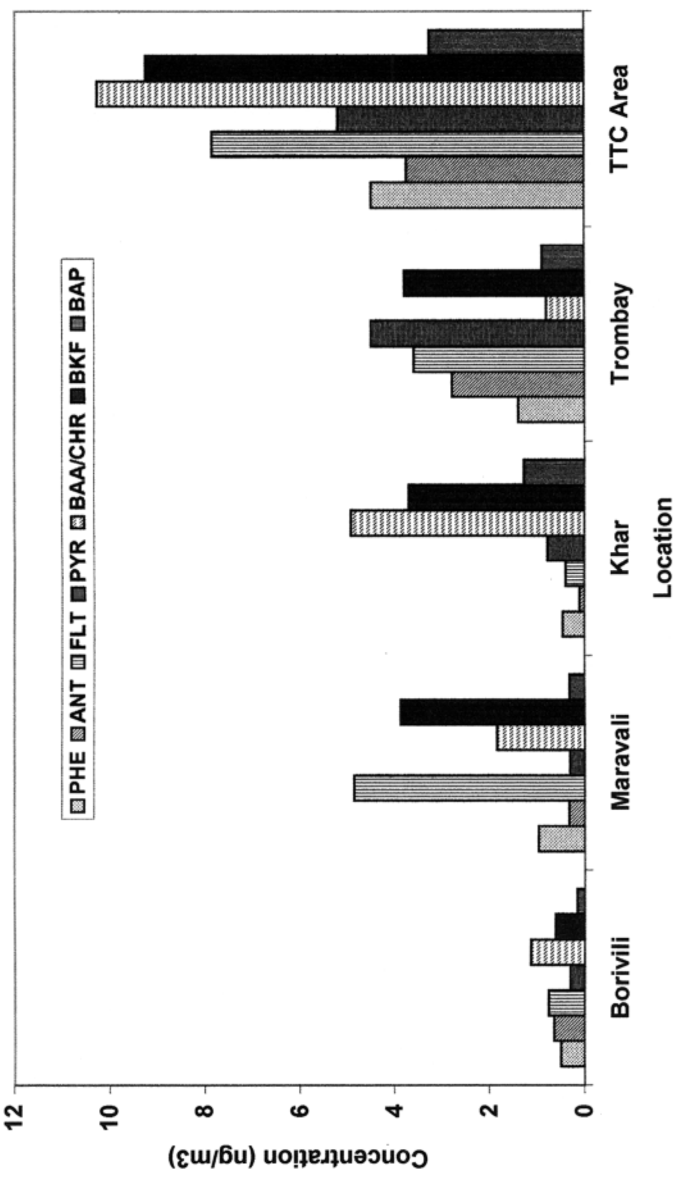

Figure 3. Mean concentration of individual PAHs at different locations in Mumbai.

Table 3. Concentration of Individual PAH Compounds (ng/m^3) at Different Places in Mumbai

Location	PHE	ANT	FLT	PYR	BAA + CHR	BKF	BAP	∑PAH
Borivili	0.50	0.64	0.75	0.30	1.14	0.61	0.16	4.10
Maravali	0.98	0.33	4.86	0.31	1.85	3.88	0.32	12.53
Khar	0.46	0.10	0.40	0.78	4.93	3.71	1.28	11.46
Trombay	1.40	2.80	3.60	4.50	0.80	3.80	0.90	17.80
TTC Area	4.50	3.75	7.85	5.20	10.27	9.24	3.27	44.08

Figure 4. The concentration of total PAHs in an indoor environment varied from 23.2 to 164.5 ng/m^3. The concentration of the carcinogenic benzo(a)pyrene in indoor and outdoor environments varied from 0.2–17.6 ng/m^3 and 0.2–2.0 ng/m^3, respectively. Details regarding exposure to indoor PAH concentration have been discussed elsewhere.[9,10]

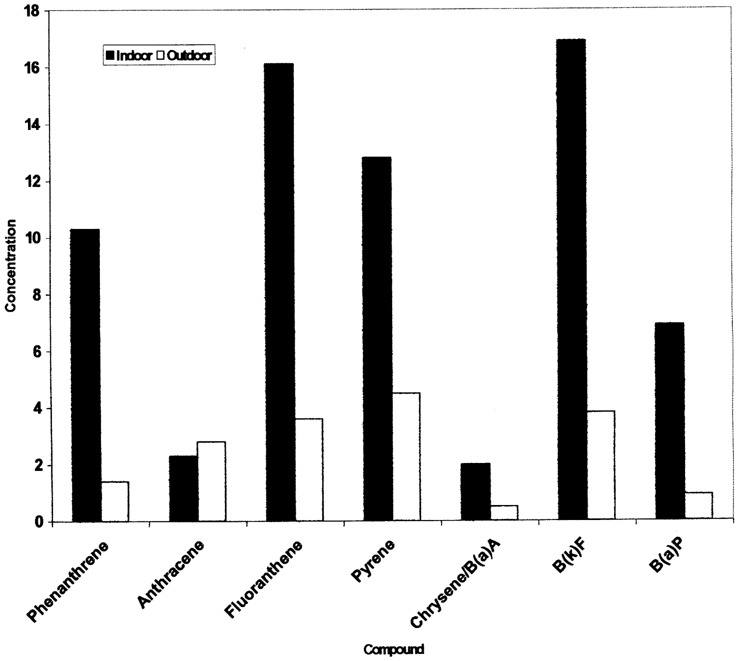

Figure 4. Mean concentration of PAH compounds in indoor and outdoor samples (ng/m^3).

CONCLUSIONS

The isocratic high pressure liquid chromatography system with ultra violet detector was found to be a very simple and sensitive method for separation and characterization of different polycyclic aromatic hydrocarbons in atmospheric aerosols. Concentration of total PAHs at the Trans-Thane Industrial area is found to be much higher than the other four locations. The qualitative source apportionment presented here, indicates that industrial emissions and vehicular emission are the likely primary contributors to PAHs in Mumbai. The mean concentrations of some individual PAH compounds are higher by about an order of magnitude in indoor cooking environments than outdoors. This study will be very useful in evaluation of carcinogenic risk from PAH exposure.

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