Identification of polycyclic aromatic hydrocarbons (PAHs) in air particulate samples using synchronus fluorescence spectroscopic technique.

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Abstract

We have designed a simple, rapid, and inexpensive method for identifying polycyclic aromatic hydrocarbons (PAHs) including benz(a)anthracene [B(a)A], benzo(a)pyrene [B(a)P], benzo(k)fluoranthene [B(k)F], pyrene [Pyr], and benz(ghi)perylene [B(ghi)P] in suspended particulate matter (SPM) in the urban environment of Delhi. Samples of urban suspended particulate matter were collected in 2018 at two locations (Okhla, Daryaganj) on glass fibre filter papers and extracted using dichloromethane (DCM) and hexane with ultrasonication. Comparison of the emission spectra with standards enabled the identification of PAHs. The degree of condensation of aromatic compounds was determined, and individual compounds were identified. The use of Δλ (delta lambda) parameter values enhanced the identification efficiency. This technique offers a valuable tool for monitoring PAHs in urban environments, supporting air quality management and health risk assessment.

Introduction

Polycyclic aromatic hydrocarbons (PAHs) are organic contaminants of great importance because many of them are known mutagens and carcinogens. They can be emitted from various combustion sources, such as wood-burning heaters, forest fires, agricultural waste burning, diesel and gasoline engine exhaust, tobacco smoke, waste incineration facilities, and asphalt roads [1]. The highest concentration of atmospheric PAHs is generally found in the urban environment due to increasing vehicular traffic and dispersion of the atmospheric pollutants due to the high density of population in the cities the risk associated with human exposure to atmospheric PAHs is the highest.

The aim of the present investigation is for the identification of polycyclic aromatic hydrocarbons (PAHs) in Delhi's urban environment, which is a significant area of research because of the carcinogenic and mutagenic properties of these hydrocarbons. The study is expected to provide valuable information about the environmental levels of these harmful substances in metropolitan cities in India.

Design/Other information

Sampling Site Characteristics

Two sampling sites were strategically selected in Delhi, India, based on diverse anthropogenic activities, including vehicular traffic density, and industrial, and commercial activities. The chosen locations were:

1. Daryaganj, a site with high vehicular traffic and densely populated residential area.

2. Okhla, a site with industrial activities commercial activities, and nearby by residential area.

These sites were selected to represent varying environmental conditions and pollutant sources, enabling a comprehensive understanding of PAH distributions in the city.

Conclusions

It is seen that simultaneous analysis of multi-component mixtures can be done by taking a limited number of spectral data points that are responsible for the identification of individual compounds. Notably, the synchronous fluorescence spectroscopy technique successfully identified all five polycyclic aromatic hydrocarbons (PAHs) in the suspended particulate matter (SPM) mixture. By employing five distinct Δλ values, 5 PAHs were identified. This technique offers a tremendous potential as a rapid, cost-effective, and simple straightforward technique for identifying PAHs in a complex mixture, making it a valuable tool in various fields.

Set up

Instrument Used

Spectrofluorimeter

All spectra were measured using a Clay Eclipse spectrofluorimeter (Instrument Serial Number: EL-01035456, Varian India Pvt. Ltd.). A standard 1 cm × 1 cm quartz cell was used for fluorescence measurements of liquid samples. The synchronous fluorescence spectra of n-hexane solutions were acquired at a rate of 600 nm/min.

Reagents

The PAHs used in this study, namely benz(a)anthracene [B(a)A], benzo(a)pyrene [B(a)P], benzo(k)fluoranthene [B(k)F], pyrene [Pyr], and benz(ghi)perylene [B(ghi)P], were purchased from Sigma-Aldrich and employed as standards. The solvents used, including methanol, hexane, n-hexane, dichloromethane, and acetone were procured from Merck. The chemicals were used as received, without further purification.

Analytical Procedures :

The suspended Particulate Matter (SPM) sampling was conducted using a high-volume sampler (Model: Envirotech APM-411, Envirotech Instruments Pvt. Ltd., New Delhi) which was placed on a rooftop at a height of 10-14 meters above ground level. The sampler operated at a laminar flow rate of 1.5 liters per minute, collecting airborne particles. The particles were collected on glass fiber filter papers (size: 8" x 10") for 24 hours. Before sampling, filter papers were pre-conditioned in a vacuum desiccator for 24 hours to remove any moisture content. After sampling, the filter papers were again put in the vacuum desiccator for 24 hours to demoisturise them and then wrapped individually in aluminum foil and stored in a refrigerator at approximately 4°C until analysis. The experimental procedure for measurements of polycyclic aromatic hydrocarbons (PAHs) is described in [2].

Results

Table 1

Wavelength intervals (Δλ) selected for each polycyclic aromatic hydrocarbons (PAHs) and maximum excitation wavelength (λexc) used for their identification.

Polycyclic Aromatic Hydrocarbons (PAHs)	Optimized wavelength intervals (Δλ)	Excitation (nm) λexc	Refs. [3-6] Δλ	Refs. [3-6] λexc
B(a)A	95	290	95	290
B(a)P	15	387	15	387.2
B(a)F	95	308	95	307.1
Pyr	50	334	50	334
B(ghi)P	115	301	115	301

benzo(a)anthracene [B(a)A]

Fig. 1

benzo(a)pyrene [B(a)P]

Fig. 2

benzo(k)fluoranthene [B(k)F]
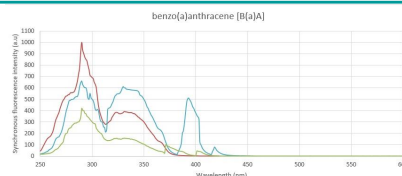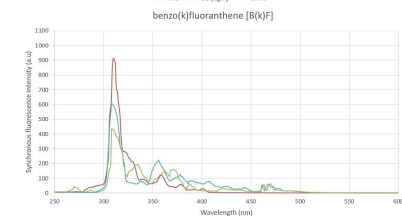
Fig. 3

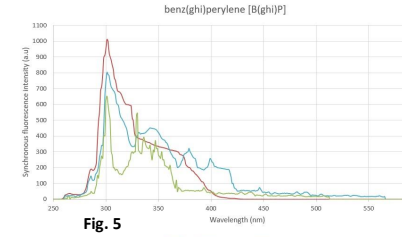Pyrene [Pyr]

Fig. 4

benz(ghi)perylene [B(ghi)P]
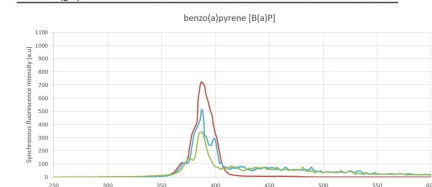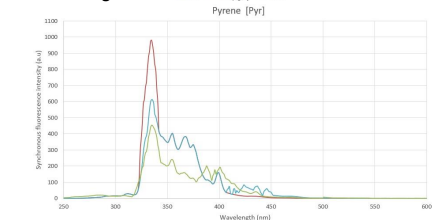
Fig. 5

The selection of the experimental conditions is crucial for the identification of the different PAHs in a mixture. The synchronous fluorescence spectroscopy technique can achieve some sort of spectral confinement or spectral separation into individual components without requiring a physical separation process. The use of optimized Δλ value eliminates the need for prior knowledge of the components in a mixture, with exceptions requiring the general matching rule of the 0-0 bands are those situations where the compounds exhibit no overlapping or weak emission and absorption bands. Optimized synchronous parameters for selected PAHs in the synchronous excitation wavelength range 250-600 nm were found by changing Δλ in the range 5-200 nm in an interval of 10 nm. The Δλ which gave the highest synchronous fluorescence intensity for a particular species was chosen as optimized Δλ for that species and the corresponding peaks as the optimized peak.

Synchronous optimized parameters (Δλ and λexc) of different selected PAHs are given in Table 1, and corresponding synchronous fluorescence spectra are shown in Figs 1-5. In these figures, the intensity of emission peaks is given in an arbitrary scale of 0-1100. The optimized Δλ values and maximum excitation wavelength (λexc) of each compound were used as the individual identification peak for each compound in their unknown mixture.

The figures display three different spectra: the fluorescence of standard compound (STD) and samples collected from the Daryaganj and Okhla sampling sites. Notably, the total individual PAH concentrations at the Daryaganj site were generally higher than those at the Okhla site.

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