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POLYAROMATIC HYDROCARBONS (PAHs) AS TOXIC AIR CONTAMINANTS: A FLUORESCENCE STUDY

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ABSTRACT

Polyaromatic hydrocarbons are ubiquitous pollutants formed by incomplete combustion of organic material using in part from natural combustion, such as forest fire and volcanic eruption for most part. However; human activities such as industrial production, smoking, transportation and waste incineration generates significant levels of PAHs. PAHs forms important carcinogenic constituents of the cigarette smoke and vehicular exhaust. Heavy transportation using hydrocarbon fuels leads to environmental pollution resulting in health hazards and ecological imbalances. One key observation was that the mixture of these substances that had carcinogenic activities was fluorescent and had similar fluorescence spectrum to polycyclic compounds by spectroscopy. Work has been done on the vehicular exhaust and tobacco smoke and a number of PAHs were purified and their fluorescence spectra were examined. A simple and precise analytical method for the estimation of alcohol contents in blended petrol has also been developed. As an immediate measure, to meet the present day automobile fuel scarcity and exhaust pollution problems, ethanol can be blended into existing gasoline. The use of alternative fuel can considerably reduce level of pollutants in air.

Key words: Polyaromatic hydrocarbons, Fluorescence spectra, Vehicular exhaust, Tobacco smoke, Blended petrol.

INTRODUCTION

In India, air pollution is wide spread in urban areas where vehicles are the major contributors and in a few other areas, with a high concentration of industries and thermal power plants. Vehicular emissions are of particular concern since these are ground level sources and thus, have the maximum impact on the general population. The PAHs are ubiquitous pollutants formed by incomplete combustion of organic material using in part

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from natural combustion such as forest fires and volcanic eruptions. Sixteen PAHs are included in the priority pollutant list of European Community (EC) and Environmental Protection Agency (EPA), due to their mutagenic and carcinogenic properties. Among these benzo(a)pyrene and dibenz(a, h) anthracene were reported to be most carcinogenic[1,2].

The major causes of air pollution in Jodhpur and Jaipur are the exponential increase in number of petrol and diesel fulled vehicles coupled with narrow road space, innumerable small factories in and around the city producing various toxic compounds. Vehicular exhaust is considered to contain various substances, which are hazardous to human health. Rebecca et al.[3] reported that automobile exhausts remain a major source of pollution and the pollutants cause local changes in the air quality, which affect the human health adversely. The organic compounds of diesel exhaust particles (DEP) were reported to be strong mutagens and carcinogens[4]. Polycyclic aromatic hydrocarbons in diesel exhaust particles (DEP) cause cardiovascular and respiratory diseases and cancer in humans[5]. PAHs in their condensed form are associated with fine particles, which can infiltrate deep into the lungs and deposit there; thus, particulate matter acts as a carrier for PAHs[6]. The reproductive outcome in the wives of traffic policemen exposed to automobile exhausts was studied. Ezoe et al.[7] studied the PAH concentration in air-borne particles in urban air over past twenty years. Heavy transportation using hydrocarbon fuel leads to environmental pollution, resulting in health hazards and ecological imbalance. In addition, fossil fuels are becoming increasingly expensive. Hence, there is a need to search for an alternative fuel that enhances quality of life and protect environment[8] Alternative fuels such as methanol and ethanol have attracted considerable attention as alternative automobile fuels. This is due to their versatility as liquid fuels and clean burning properties. Khatri[9] studied ethanol as an automotive fuel.

Recent advances in instrumentation and availability of commercial automatic recording spectrofluorometers have made possible the more extensive use of fluorescence spectroscopy for analytical purposes. It has served as a valuable tool in laboratory for the identification of PAHs. A number of PAHs were purified and their fluorescence spectra were examined. A report prepared by Centre for Science and Environment 2001 (CSE 2001)[10] shows that in cities facing severe air problems, the use of heavy-duty natural gas engine, in place of diesel, offers numerous environmental benefits. After the implementation of compressed natural gas (CNG) since April 2001, Goyal and Sidhartha[11] reported the trends of CO, SO_2, NO_X and SPM concentration till the end of 2001. Although during this period, only a small fraction of public transport was converted to CNG.

EXPERIMENTAL

A representative number of samples were collected from Ratanada site in Jodhpur, using high volume sampler from December to May 2006. Air was drawn through 20 x 25 cm. glass fiber filter (GFF) sheet at flow rate of 0.8 - 1.2 m^3min^{-1}. After this, the filter samples were separately wrapped in aluminum foil and stored in a freezer at –20^0C until they were processed. For PAHs determinations, the filtered samples were extracted using pressurized liquid extraction (Dionex Titan Way, California, USA) for the fast extraction of PAHs with minimum solvent consumption[12,13]. The extracts were concentrated in a Turbo-Vap 500 (Zymark, Hopkinton, MA, USA) concentrator. The solvent was replaced to 1 mL acetonitrile prior to their analysis for the separation and detection of PAHs compound by HPLC in combination with fluorescence detection. We have also studied the fluorescence of tobacco smoke. A lighted cigarette was held within a few cm of the apparatus and the side stream smoke drifted into the sample region. Then the residue was placed from the smoke at the top of the glass column packed with aluminum powder and solvent was poured over it. As the solvent washed down the alumina, the chemical compounds in the smoke residue separated, and benzo(a)pyrene and four other PAHs – naphthalene, anthracene, pyrene and flouranthene were found.

The detected and quantified PAHs were anthracene, benzo(a)pyrene, pyrene-di-benzo(a, h),anthracene and benzo(g, h, i)perylene. The HPLC system consisted of a liquid chromatography system (Waters, Milford, MA, USA] and a fluorescence detector (Perkin-Elmer fluorescence spectrophotometer). Separation of PAHs was accomplished using a Vydac 201 TP column (250 mm x 4.6 mm) with a gradient elution ranging from a 50/50 acetonitrile-water mix to 100% acetonitrile in 20 minutes. The fluorescence of PAHs was monitored with automatic adjustment of the wavelength for each compound according to their retention time on the HPLC column. A simple and precise analytical method has been developed for the estimation of alcohol content in blended petrol. Ethanol used in the measurement was of Analytical Reagent grade. Petrol was obtained from a local petrol station. Density measurements were carried out on A P Paar DMA 48 Density Meter, Austria. The temperature of the measurement was maintained at 15^0C by an in-built temperature controlled system. Samples of blended petrol were prepared by mixing ethanol in different ratios (Table 1). Samples were shaken thoroughly to get homogeneous mixtures. The samples were injected to the system and their respective densities were measured. Before analyzing the blends, standard ethanol and pure petrol densities were also measured.

RESULTS AND DISCUSSION

Generally, polycyclic aromatic compounds emit in the higher energy range and with increase in the number of benzene rings, the emission maxima of the aromatic compounds are shifted towards the longer wavelengths. Two-rings aromatic hydrocarbons such as, naphthalene exhibits fluorescence maxima at low emission and excitation wavelengths, while five-rings compounds such as, perylene have maxima at high emission and excitation wavelengths[14,15]. Three and four-ring compounds exhibits intermediate fluorescence characteristics. The concentrations of PAHs are generally observed to be higher during winter than in the other seasons. Figure 1 shows the daily variation in fluorescence intensity of benzo(a)pyrene at Ratanada, Jodhpur during 2007. The maximum concentration of PAHs at Ratanada was noticed between 10 pm to 6 am, which is most likely due to the entry of heavy vehicles like truck, trolley, vans etc. through this important traffic intersection at Jodhpur. This type of traffic increases in the late evening hours (after 10 pm) due to restricted entry of heavy vehicles into the city at day time. Figure 2 shows the fluorescence spectra of benzo(a)pyrene, which is purified from tobacco smoke from different quantities of cigarettes. Densities were measured for blended petrol samples (prepared). It is observed from Table 1 that the densities of the blended samples increased linearly with the ethanol content. A calibration graph (Figure 3) plotted for densities against ethanol concentration was found to be linear in the experimental range studied (1 to 20 %). The density obtained from the density meter is in good agreement with the density obtained from the calibration graph. Using the calibration graph, it is very easy to calculate unknown quality of ethanol in ethanol blended petrol.

Table 1: Densities of blended petrol

Ethanol added (%/v)	Density of blended petrol (g/ml at 15^0C)	Recovered ethanol (%/v)
1	0.7364	1.02
2	0.7368	2.04
3	0.7375	2.95
4	0.7380	3.96
5	0.7388	5.00
7.5	0.7402	7.56
10	0.7418	10.15
12.5	0.7434	12.73
15	0.7445	15.02
20	0.7475	19.88

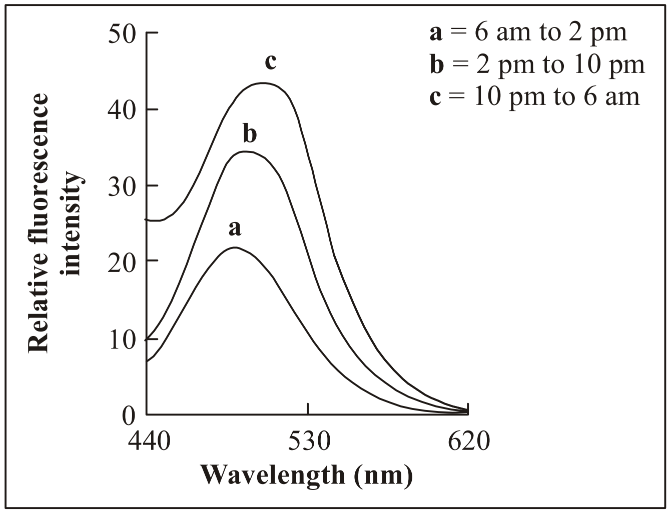

Fig. 1: Daily variation in fluorescence intensity of benzo(a)pyrene at Ratanada, Jodhpur

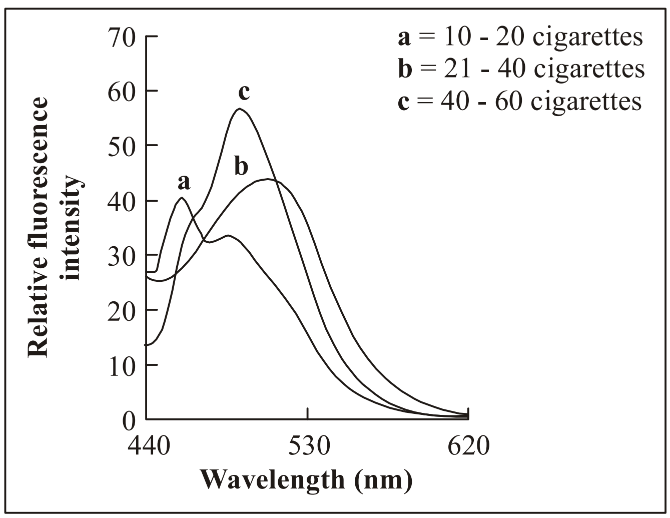

Fig. 2: Fluorescence spectra of benzo(a)pyrene purified from tobacco smoke

CONCLUSION

Haphazard urbanization and unprecedented vehicular growth, that exacerbate air quality, are prevalent features in India. The Jodhpur city due to its climatic conditions and industrial development is experiencing an exponential growth in the vehicular usage and fuel consumption.

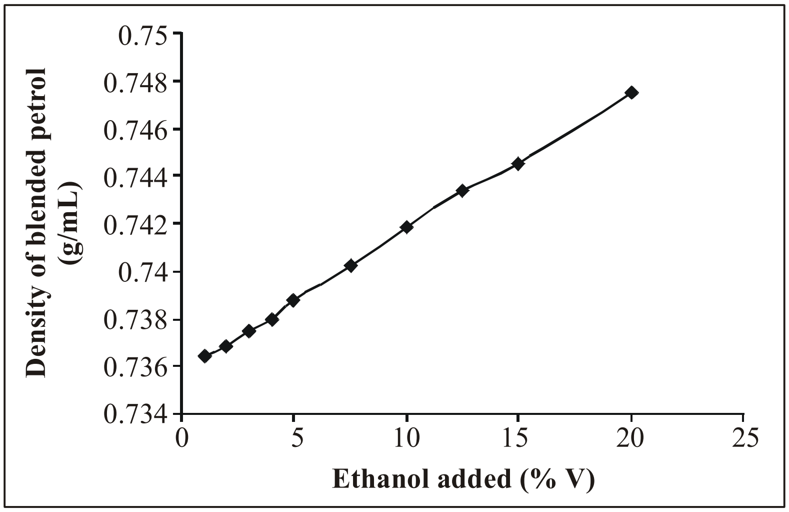

Fig. 3: Densities of blended petrol (g/mL at 15^{0}C) vs ethanol added (%/v)

The spatial pattern of PAHs concentration shows comparatively high concentration during late night and early morning hours and it may be related with the late night movement of heavy vehicles from nearby city through Jodhpur. The exhaust from liquid fuels is deteriorating the quality of air day by day. The increasing respiratory diseases and hospitalization demands to find some alternative to improve the urban quality of life. Hence, there is a need to search for an alternative fuel, which enhances quality of life and also protect the environment.

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