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Research Article

Comparison Study of Polycyclic Aromatic Hydrocarbons (PAHs) in Bangladeshi Compressed Natural Gas (CNG) and Diesel Engine Vehicles by Gas Chromatography-Mass Spectrometry

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Abstract. A more sensitive GC-MS method has been established for the determination of some polycyclic aromatic hydrocarbons (PAHs) in vehicle exhaust fumes and tar samples from compressed natural gas (CNG) and diesel engine vehicles plying the streets of Dhaka, the metropolitan city of Bangladesh, and its impact on the ambient environment. A suitable procedure for the extraction of PAHs from tar samples has been developed. The tar sample was extracted with liquid-liquid extraction using dichloromethane (DMC): n-hexane solvent mixture. A multi-layer clean-up (silica gel/sodium sulphate) column was used, followed by glass fibre filter (GFF) paper to eliminate the interfering organic compounds as well as the lipids. Three PAH compounds (naphthalene, phenanthrene and anthracene) were found where the average concentrations were 1.68 μg/g for napthalene, 2.11μg/g for anthracene and 1.97 for phenanthrane, respectively.

Keywords: vehicle exhaust, pollution, quantification, toxic polycyclic aromatic hydrocarbons, GC-MS, Bangladesh.

Introduction

Polycyclic aromatic hydrocarbons (PAHs) are the products of incomplete combustion and, in the urban and industrial atmosphere, are almost entirely anthropogenic by origin. Most carcinogenic PAHs have been found to associate with particulates, predominately with fine particulate [1]. Some PAHs are strong carcinogens and can cause pulmonary inflammation and allergic asthma in human airway cells [2, 3]. A study of the bioactivity of particulate matter both *in vivo* and *in vitro* indicates that the size of particulate may play a role in the effect on pulmonary inflammation and allergic asthma [4]. Particulates in the low-micrometer range traverse deep into lungs and inflict more damage and death than that of larger particles that are arrested in the upper respiratory tract and removed by the mucociliary action. Thus, it is important to analyze particulate size distributions when assessing the possible influence of PAH on human health.

Motor vehicles have proven to be a significant source of PAH emission [5, 6]. Particulate emissions from motor vehicles are among the major contributors to fine particle concentrations in the urban atmosphere [7, 8, 9]. Furthermore, particulate PAHs, measured in roadway tunnels using dynamometers, have been found in the respirable size range. In order to assess health risk, it is necessary to specify both the size distribution and the chemical composition of particulate emissions as they occur at their source. Size distributions of PAHs emitted from diesel and gasoline vehicles have been studied based on samples collected from the roadway tunnels [10, 11] using a dynamometer [9, 12]. All these studies utilized a cascade impactor as the sampling device. To our knowledge, there are no data available on the particulate and PAH size distribution pertaining to emissions from motor vehicles in the current literature.

Motor vehicles are also one of the most important modes of transportation in many countries around the world. Bangladesh, a South Asian country, also falls into the same category where we have over one million microbuses which account for 17% of all the motor vehicles. The health risk associated with this high number of motor vehicles in these countries is both significant and alarming. PAHs, including the 16 USEPA priority PAHs plus naphthalene, anthracene and phenanthrene, were selected as the target compounds in this study for their carcinogenicity. In this research, the quantification and comparison study of these three major PAHs out of a group of sixteen PAHs in the compressed natural gas (CNG) and diesel engine vehicles run by the highway roads in Dhaka city is described.

Experimental

General experimental procedures

Naphthalene, anthracene and phenanthrane standards were purchased from Sigma-Aldrich Company with purity 99.9%. Dichloromethane (BDH, UK) and acetone (Merck, Germany) were of HPLC grade. Anhydrous sodium sulphate (Merck, Germany) was cleaned by heating at 200^{o}C before use. Silica gel (60-120 mesh, Loba, India) was activated at 400^{o}C for 12 hr. prior to use.

Instrument and operating conditions

GC-MS was carried out using total ion monitoring mode on a Varian 3800 gas chromatograph interfaced to a Varian Saturn ion trap 2200 GC-MS mass spectrometer. The temperatures of transfer line and ion source were 280°C and 275°C respectively. Ions were obtained by electron ionization mode. The VF-5 capillary column (30m length, 0.25mm I.D., 0.25 µm film thickness) was used. A 20% split injection mode was selected with a solvent delay time of 3 min. with injection volume 0.2 µl. The initial column temperature was started at 50°C for 1 min, programmed at 8°C min^{-1} to 200 °C and heated until 280^{o}C at 10^{o}C min^{-1}. Injection port was set at 250°C. Helium was used as carrier gas with a flow-rate of 1.0 ml min^{-1}. Molecular ions were monitored for identification. Mass range: 40-500 m/z.

Preparation of standard

Calibration curves for the samples treated according to the described analytical procedure were made using the SIM mode. Different concentrations of napthalene, anthracene and phenanthrene (0.5 ng/ml, 1ng/ml, 5 ng/ml, 10 ng/ml and 20 ng/ml) were used to establish the calibration curves.

Sample collection

Exhaust deposited tar samples were collected by a spatula from a CNG and a diesel engine microbus at the Atomic Energy Centre, Dhaka, Bangladesh in December 2007. After collection, the sample was kept in a polyethylene bag with aluminum foil protected cover and stored in a refrigerator to avoid any deterioration. Before extraction, the samples were dried at 40^{o}C. On the other hand, the exhaust fume was collected from the exhaust part of the same vehicles at the same station by a series of gas collector systems. The bottom part of the first collector bottle was in dichloromethane-acetone (1:1, 100 ml) and the second collector was also with the same solvent and same proportion (50 ml). The exhaust pipe of the microbuses was connected through to the two fume collectors by a polyethylene tube and the fumes generated from the engines were continuously passed through the solvent for half an hour.

Extraction procedure

The tar sample (0.075 g) was refluxed at 120^{o}C with 20 ml dichloromethane-n-hexane (1:1) for 30 minutes by heating mantel. It was then filtered and the filtrate was evaporated and concentrated to 1 to 2 ml by using Kuderna-Danish concentrator (K-D concentrator). For fumes, the solvent was gathered from the two collectors and combined together to get the two-layer appearance. The layers were separated by the separating funnel and the organic layer was collected. The organic layer was dehydrated by Na_2SO_4 and filtered. Finally the filtrate organic solvent was evaporated until the concentration reached 1- 2 ml by using K-D evaporator.

Clean-up procedure

The cleanup column (ID = 1 cm) was filled with cotton in the bottom. An activated silica gel (17 gm) soaked with solvent was loaded into the cleanup column (5 cm), which was then topped with 1.5 cm of anhydrous sodium sulphate. 5 ml of solvent was added to wash the sodium sulphate and the silica gel. The pre-concentrated dried tar and fume solvent, 1 ml of each sample, were then separately transferred into the column and the vessel was rinsed twice with 2 ml loaded solvent, which was also added to the column. 60 ml of loaded solvent was added to the column and allowed to flow through at a rate of 3–5 ml/min, and the eluent was then collected. The collected eluent from the cleanup procedure was re-concentrated to 1 ml by using K-D concentrator.

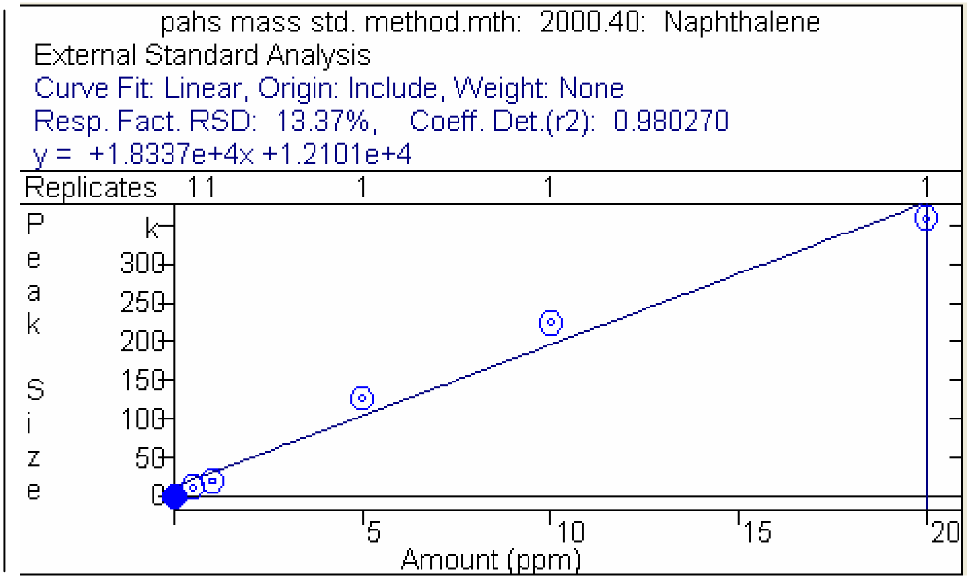
Results and Discussion

In Bangladesh, for example, there are more than one million microbuses, which account for about 17% of all motor vehicles. Most of these vehicles run on diesel and are continuously polluting the environment. The health risk arising from these vehicles is increasingly high. The three polycyclic aromatic hydrocarbons (PAHs), napthalene, anthracene and phenanthrane out of 16 PAHs, were selected as the target compounds in this study for carcinogenicity [6-7].

The objective of this study was to quantify and compare the extent of PAHs in the tar and fume samples from the exhaust part of compressed natural gas (CNG) and diesel engine vehicles in Dhaka city. One CNG and one diesel microbus take off were selected and the tar and fume samples were collected from the exhaust by using a mechanical and special sample collector system.

The tar samples were refluxed with dichloromethane-hexane mixture solvent for 30 min. It was then filtered and the filtrate was evaporated and pre-concentrated using a Kuderna-Danish concentrator. The exhaust fume was also collected from the exhaust from the same vehicles at the same station by a series of collectors. The bottom part of first collector bottle was in dichloromethane-acetone mixture solvent (100 ml) and the second collector was in same solvent (75 ml) and the third and final collector also with the same mixture solvent (50 ml). From the vehicle exhaust through to the three collectors, a connection was made by a polyethylene tube and the exhaust fume which was generated by the engine was passed continuously through the solvent mixtures in the collectors for half an hour. The solvent mixtures from the individual collector were processed and concentrated by the K-D evaporator.

The quantitative determination of naphthalene, anthracene and phenanthrane were done by the external calibration curve method. The calibration curves already prepared with known concentration of naphthalene, anthracene and phenanthrane are detailed below (**Figs. 1-3**).



pahs mass std. method.mth: 2000.40: Naphthalene
External Standard Analysis
Curve Fit: Linear, Origin: Include, Weight: None
Resp. Fact. RSD: 13.37%, Coeff. Det.(r2): 0.980270
$y = +1.8337e+4x +1.2101e+4$

Figure 1. Standard Calibration Curve of Napthalene.

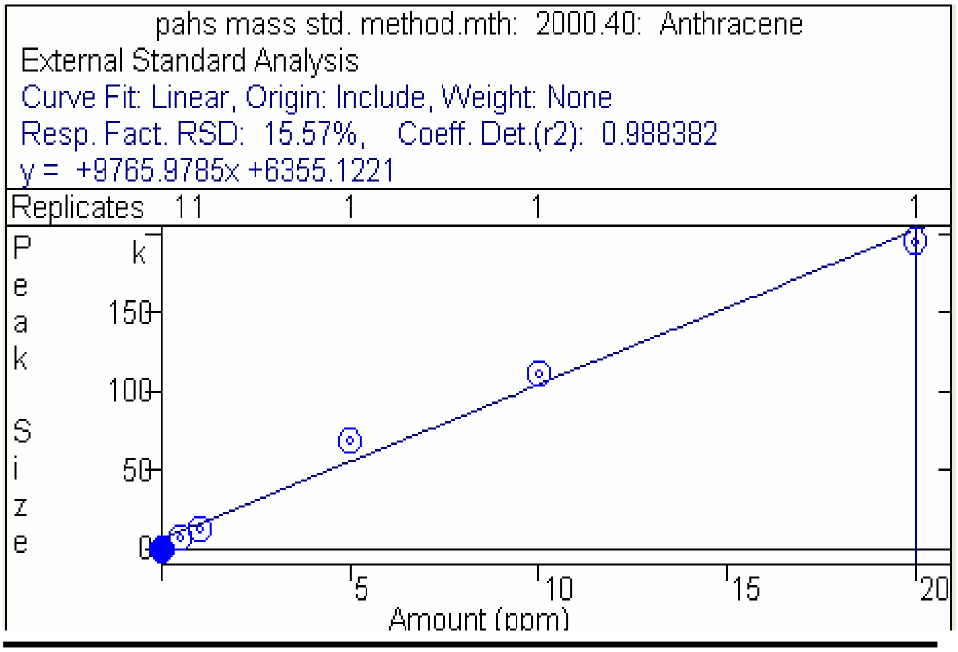


Figure 2. Standard Calibration Curve of Anthracene.

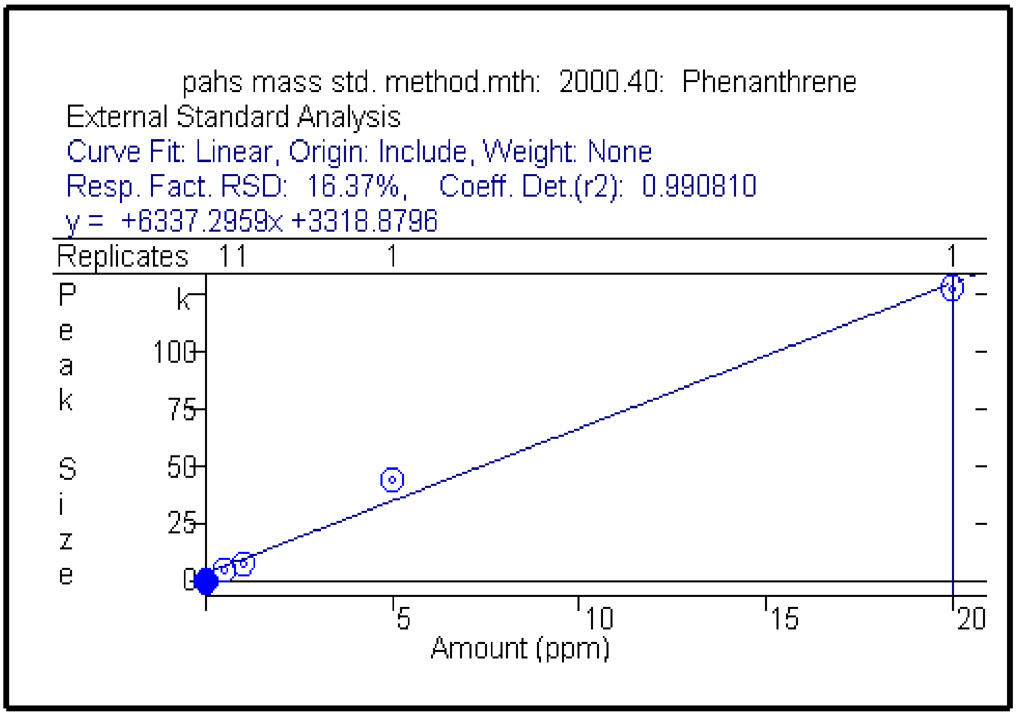


Figure 3. Standard Calibration Curve of Phenanthrane.

The quantitative determination was performed by gas chromatography-mass spectrometer using the calibration curve method. Standard curves for naphthalene, anthracene and phenanthrane generated by plotting the area of five spots vs. the concentration, gave high correlation coefficients. Linear responses were achieved for naphthalene, anthracene and phenanthrane in the concentration range for tar samples in diesel engine with the values 1.68, 2.11 and 2.01µg/g respectively. Over this concentration range, the linear regression analysis of peak areas (y) in function of concentration (x), calculated by least square method, leads to the following equations: $y = +1.8337^{e+4x} +1.2101e^{+4}$ ($r^2 = 0.980270$); $y = +9765.9785x + 6355.1221$ ($r^2 = 0.98838$) and $y = +6347.2959x + 3318.8796$ ($r^2 = 0.990810$) for naphthalene, anthracene and phenanthrane.

The amount of naphthalene, anthracene and phenanthrane in tar and fumes were calculated from the standard curves by gas chromatography-mass chromatography method. The concentrations of naphthalene, anthracene and phenanthrane in exhaust tar and fumes from the CNG and diesel engine with dichloromethane-hexane mixture solvent are given in Table 1.

Table 1. Concentration of naphthalene, anthracene and phenanthrane in tar and fume samples.

Sl. No.	**Solvent system**	**CNG Engine** (µg/g)			**Diesel Engine** (µg/g)		
	Tar Samples	Napthalene	Anthracene	Phenanthrane	Napthalene	Anthracene	Phenanthrane
1	Dichloromethane-hexane (1:1)	0.007	nd	nd	1.68	2.11	1.97
		0.0068	nd	nd	1.57	2.03	2.01
		0.0071	nd	nd	1.61	2.07	1.91
2	Fume Samples						
	Dichloromethane-hexane (1:1)	nd	nd	nd	0.017	0.083	0.032
		nd	nd	nd	0.017	0.083	0.032
		nd	nd	nd	0.017	0.083	0.032

From Table 1, it is seen that among the tar samples collected from the CNG fuelled microbus, only one carcinogenic PAH, naphthalene, was found at a low concentration, but the other two PAHs, anthracene and phenanthrane, were not at a detectable range. Whereas the tar samples collected from the diesel fuelled microbus, the three carcinogenic PAHs, naphthalene, anthracene and phenanthrane, were found at a considerably high rate. On the other hand, as the fume samples were collected directly from the gas outlet of the CNG and diesel engine microbuses with the help of a special device, it was clear that the fumes did not have the three PAHs in the detectable range. Again in case of the diesel engine, the three PAHs were found at moderate concentrations.

Conclusion

From the results it can be concluded that the diesel engine is responsible for the emission of polycyclic aromatic hydrocarbons. The compounds of interest in this case are naphthalene, anthracene, and phenanthrane. The CNG engine seems to be innocuous although a negligible amount of naphthalene has been found in the tar samples. This could be because of the effect of the diesel engine, as both CNG and diesel engines co-exist in the same microbus. Therefore, due to incomplete combustion of fuel, the diesel engine is continuously emitting PAHs as pollutants and thus posing a threat to the environment. Future assessment of the health risk associated with exposure to the PAHs content of environmental air samples is recommended.

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