

Analysis of Ground and Surface Water Samples from some Area of Dhaka City for Polycyclic Aromatic Hydrocarbons (PAHs)

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I. Introduction

Polycyclic aromatic hydrocarbons (PAHs) constitute a large group of organic compounds with molecular structures containing two or more fused aromatic rings. They are widely distributed in the environment as a result of incomplete combustion of organic materials, from both natural (e.g. forest fires, and volcanic eruption) and anthropogenic sources (e.g. motor vehicles, industrial processes, domestic heating, waste incineration, and tobacco smoke)¹⁻³. The spillage of fossil fuel as well as leaching from pipes, coating, lining, and joint adhesives during water distribution (supply) could be the significant sources of contamination of surface and ground water¹⁻⁵.

PAHs can be absorbed by skin, ingestion or inhalation, being quickly distributed into the organism due to their lipophilic character. US EPA selected sixteen PAHs as priority pollutants due to their mutagenicity and carcinogenicity⁵. With increased industrialization the emission of PAHs has increased several times compared to pre-industrial period throughout the world including Bangladesh⁶. Hence, monitoring of these compounds in water from tap, ponds, lakes and rivers is an important step for the exposure control.

II. Experimental

Sampling and Extraction

Thirty water samples; tap (n=10), pond (n=10) and lake (n=10) were collected from Dhaka city area following standard sampling guidelines for water sampling. The samples were extracted by solid phase extraction (SPE) method using C₁₈ cartridge for pre-concentration as well as for clean up⁷⁻⁸. The C₁₈ cartridge was conditioned by successively passing 10.0 mL of deionized water, methanol, and again deionized water. Water samples (500 mL) were passed through the pre-conditioned C₁₈ cartridge using a suction pump and PAHs were eluted by passing acetonitrile (30 mL). The effluents were evaporated to dryness and were reconstituted in a mixture (1 mL) of n-hexane and acetone (1:1), and analyzed using GC-FID and GC-MS.

GC-FID analysis conditions

For gas chromatographic analyses, a Shimadzu 2025 GC fitted with flame ionization detector (FID) and quartz capillary column (HP-5; 30 m × 0.25 mm × 0.25 μm) were used. The injector and detector temperatures were set at 275°C and 300°C, respectively, and nitrogen was used as the carrier gas. Separations were performed in split mode (split ratio: 1:50) with an oven temperature programmed from

50°C (2 min hold) to 180°C at 20°C/min rise and then to 270°C (2 min hold) at 10°C/min rise.

GC-MS analysis conditions

An Agilent 6890N GC, an Agilent 7683B automatic liquid sampler along with an Agilent 5975B inert XL EI/CI MSD system were used. Separations were performed in splitless mode in a quartz capillary column (Agilent HP-5 MS; 30 m × 0.25 mm × 0.25 μm) at 70 °C (1 min. hold), then 10 °C/min. to 310°C (3 min. hold). The injector and detector temperatures were set at 250°C and 325°C, respectively, and helium was used as the carrier gas.

III. Method Validation Studies

Linearity

The study of linearity for GC-FID method included the analysis of eight standard solutions containing a mixture of naphthalene, anthracene, and phenanthrene at different concentration (0.005 to 5.12 ppm).

The Limit of detection (LOD) and quantitation (LOQ)

The limit of detection (LOD) and limit of quantitation (LOQ) in GC-FID for naphthalene, anthracene, and phenanthrene were determined by considering the peak height of each compound about three and ten times higher than the base line noise, respectively.

Recovery

A known amount of each standard solution in the middle of the calibration range was spiked in 500 mL deionized water, and kept overnight at room temperature after shaking manually for about 20 minutes. These samples were analyzed following the same procedure in order to carry out recovery experiments.

Method and Instrument repeatability

Method repeatability was determined by analysing six identical test samples which were prepared by spiking deionized water (500 mL) with the standard solution of naphthalene, anthracene, and phenanthrene in the middle of the calibration range. Samples were extracted following the same extraction procedure, and analyzed by the same instrument (GC-FID) under same analysis conditions by the same operator. Instrument repeatability was determined by injecting same sample six times in the GC-FID under the same analysis conditions.

IV. Results and Discussion

A reported extraction method was used for the analyses with some minor modifications⁷⁻⁸. Changes were made in the initial

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column temperature (50°C), and injected sample volume (1.0 µL). The method was optimized and validated in terms of linearity, method detection limit, recovery, and method and instrument repeatability. Naphthalene, anthracene, and phenanthrene were symmetrically eluted and their retention times were 7.36, 12.49 and 13.88 min, respectively, with retention factors (*k'*) 3.05, 5.87 and 6.63, respectively. The repeatability (RSD %) of the retention time and peak area were found to be less than 1 % for six replicate injections.

The LOD values for naphthalene, anthracene and phenanthrene were 0.025, 0.01 and 0.012 ppm, respectively, and LOQ were found to be 0.075, 0.030, and 0.035 ppm, respectively. The modified method showed a little higher value of LOD and LOQ than EPA method 8100, because samples were analyzed in split mode rather than split/splitless mode. Split gas liner of GC vaporization chamber is large and in that case there is always loss of compound due to continuous split. In split/splitless gas liner vaporized sample directly go to the column and loss of compound is rather less. A linear calibration curve was produced for each standard naphthalene, anthracene, and phenanthrene in the range of 0.005-5.12 ppm with the correlation coefficient, (*r*²) 0.999 for each compound. The value of the correlation coefficient obtained for each calibration curve showed that the correlation between peak area and concentration was excellent.

Replicate (n=6) recovery experiments for naphthalene, anthracene and phenanthrene were done by spiking the control matrix (deionized water) with known concentration of standards in the middle of the calibration range. The average percent recovery of naphthalene, anthracene and phenanthrene were found to be 76.67, 79.76 and 89.68, respectively, and the method repeatability (RSD %) were 4.21, 2.84 and 4.81%, respectively.

Analysis of collected water samples

Analysis of collected ground (tap, n=10) and surface water (lake and pond, n=10 each) samples collected from the Dhaka city showed that four tap water samples contained anthracene in the range of 0.037-0.054 ppm and three of them contained phenanthrene in the range of 0.036-0.045 ppm. Other two tap water samples were also found to contain trace amount of anthracene which were not possible to quantify as they were below the quantification limit (BQL).

Three pond water samples contained only trace amount of anthracene and phenanthrene, whereas three lake water samples were found to contain anthracene and phenanthrene in the range of 0.032-0.048 and 0.038-0.041 ppm, respectively. One lake water sample was also found to contain trace amount of anthracene. This was in agreement with the results obtained by M. A. Mottaleb *et al*⁹ who found anthracene in the range of 0.005-0.074 ppm in the water samples from Buriganga river. None of the water samples was found to contain naphthalene, which can be explained by its volatile nature and might have evaporated during the analytical procedure.

All the water samples were also analyzed by GC-MS. The Results showed that naphthalene was absent in all water samples. The presence of anthracene and phenanthrene in water samples were confirmed by its mass fragmentation pattern, as molecular ion peak C₁₄H₁₀⁺ (m/z = 178), tropylium cation C₇H₇⁺(m/z = 91), phenyl cation C₆H₅⁺ (m/z = 77) at distinct retention times.

V. Conclusion

In the present study a GC-FID analytical method coupled with solid phase extraction (SPE) was optimized and validated to study the presence of low molecular weight polycyclic aromatic hydrocarbons in ground and surface water samples of the Dhaka city area. Results showed that both ground and surface water contained residual amount of anthracene and phenanthrene. However, relatively low values of the limit of detection (LOD), and quantitation (LOQ) suggests that GC-FID is suitable for routine analysis (screening) of PAHs in water.

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