Determination of Polycyclic Aromatic Hydrocarbons in Wetland and River Waters

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Polycyclic aromatic hydrocarbons are one of the most widespread groups of organic pollutants in the environment. In this work, two different solid-phase extractions, sorbents have been used. C_{18} and XAD-2 resin packed in micro-columns were used for separation, clean up and pre-concentration of polycyclic aromatic hydrocarbons and the recovery of polycyclic aromatic hydrocarbons from XAD-2 resin was studied and then used for pre-concentration of polycyclic aromatic hydrocarbons. The samples were collected from the river Zayandeh-Rud and Ghav-Khooni wetland in the province of Isfahan (Iran) where the heavy industries are located around the stream. The determinations were carried on a gas chromatography coupled to mass spectrometry and internal standard quantification was performed using four deuterated polycyclic aromatic hydrocarbons. For increased sensitivity, quantification was performed in the selected ion monitoring mode. In water samples of the river Zayandeh-Rud, the amounts of total polycyclic aromatic hydrocarbon ranged from west to east and the highest polycyclic aromatic hydrocarbon concentration was found in the Gav-Khooni wetland.

Key Words: Water analysis, Polycyclic aromatic hydrocarbons, XAD-2 resin, GC-MS-SIM.

INTRODUCTION

Polycyclic aromatic hydrocarbons are the products of pyrolysis or incomplete combustion of carbonaceous material at high temperatures and consist of several hundred compounds containing two or more condensed rings[1,2]. The sources of polycyclic aromatic hydrocarbons can be divided into two groups; 1) natural sources such as volcanic activities and forest burning and 2) anthropogenic sources including; iron and steel industries, power plants, waste incineration and combustion of fossil fuels in automobile engines[3].

The anthropogenic sources are known as the major source for introduction of polycyclic aromatic hydrocarbons into the environment. The contamination of the environment by polycyclic aromatic hydrocarbons is becoming a rising environmental concern. They have a widespread distribution in the environment and the carcinogenicity and mutagenicity of several of these compounds have been proven[4,5]. Polycyclic aromatic hydrocarbons are classified as unambiguous priority pollutants by the environmental protection agency[6]. Identification and quantification of this class of contaminants in water resources are necessary for solving several environmental problems arising from their biological activity and the huge number of people at risk. Concerning to the low concentrations of polycyclic aromatic hydrocarbons in water samples, the monitoring of these compounds needs to the effective methods for separation and preconcentration[3].

Several methods have been proposed for the analysis of polycyclic aromatic hydrocarbons, the most common being HPLC-UV-FL detection[7,8] or GC by FID or MS detectors[9]. Analytical methods are described in the US environmental protection agency (EPA) methods (550, 610, 8310 and 525). The environmental protection agency methods for the determination of polycyclic aromatic hydrocarbons, which uses GC-MS in the full scan mode. This method is not capable of achieving low enough detection limits for some applications. Thus the GC-MS can be operated in the selected ion monitoring (SIM) mode. For the extraction of water samples, most environmental protection agency methods use liquid-liquid extraction, solid-phase extraction and solid-phase microextraction[10].

The aim of this work was to investigate the concentrations of polycyclic aromatic hydrocarbons in river waters and the distribution of polycyclic aromatic hydrocarbons in the river Zayandeh-Rud and Ghav-Khooni wetland and present simplified extraction and clean-up methods for analysis of 16 polycyclic aromatic hydrocarbons in water. We used GC-MS (SIM) to ensure unambiguous identification and more realiable quantification of polycyclic aromatic hydrocarbons.

EXPERIMENTAL

All the solvents were HPLC grade (Merck Co.) The individual polycyclic aromatic hydrocarbons and a standard

mixture containing 16 polycyclic aromatic hydrocarbons and internal standard; acenaphthene-d10, phenantherene-d10, perylene-d12, chrysene-d12 were prepared from Supelco Inc.

XAD-2 resin was purchased from Rohm and Hass Company. C_{18} particles (mesh = 40-63) prepared from Sigma Chemical Company. Water used throughout the work was prepared by Milli Q water purifying system.

Sampling: Wetland water samples were collected from Gav-Khooni international wetland located at the east part of Isfahan. River water samples were collected from the river Zayandeh-Rud water. Zayandeh-Rud is the most important river in the central part of Iran that flows through the industrialized area in the city of Isfahan and finally is discharged to Gav-Khooni wetland[11]. The samples from the river were collected from the locations where the industrial activities were developed around the river and the industrial treatment plant effluents were discharged into the river[11]. The samples were collected in 1 L amber coloured bottles from a depth of 50 cm below the water surface. The water was filtered through 0.45 μm filter membrane after sampling.

C_{18} phase was packed in the central part of micro-column 10 cm long and 0.6 cm i.d. it was then conditioned with 1 mL of methanol followed by 10 mL of de-ionized distilled water. The water sample was passed through the micro-column with a flow rate of 20 mL/min by a peristaltic pump. At this flow rate polycyclic aromatic hydrocarbons content of water can be adsorbed on the C_{18} surface. The adsorbed organic materials were eluted by two portions of ethyl acetate, each portion was 3 mL and elution was performed after 30 sec. static time. The extract was transferred on a glass column with 0.6 cm i.d. in length of 30 cm which was packed with 2 g of XAD-2 resin in order to separate the polycyclic aromatic hydrocarbons phase from the other organic compounds. The resin column was eluted with 5 mL of n-pentene followed by 5 mL portions of methanol, 5 mL of *n*-pentene and 15 mL of ethyl acetate respectively. The volume of the extract with ethyl acetate was reduced to 1 mL under the nitrogen current and used for the analysis of polycyclic aromatic hydrocarbons.

Analysis of polycyclic aromatic hydrocarbons was carried out on an Agilent GC Model 6890 coupled to a quadrupole mass spectrometer (5975C). The system was operated in electron impact mode (EI, 70 eV). A HP-5 MS column (30 m × 0.25 mm I.D. 0.25 μm film thickness, Agilent) was used for separation of polycyclic aromatic hydrocarbons. In order to get the proper GC separation a temperature programming was used. Temperature started from 80 ℃ with a 5 min hold time, it was then increased to 150 ℃ at a rate of 10 ℃/min. It was then increased to 300 ℃ at a rate of 5 ℃/min, keeping the final temperature for 5 min.

Injection was performed in the splitless mode. Helium gas was used as a carrier gas at a constant flow rate of 1.5 mL/min. Injector, transfer line temperatures were 250, 280 ℃, respectively. Ions were selected after considering the total ion chromatogram of solution of compounds. The ions were divided into four groups. Peak detection and integration were carried out using Chemstation software and AMDIS (automated mass spectral deconvolution and identification system). The ion mass program used for quantification is given in Table-1.

TABLE-1
ION MASS AND SIM WINDOWS FOR 16 POLYCYCLIC AROMATIC HYDROCARBONS

Time window (min)	Compound	Quantification ion (*m/z*)	Confirmation ions (*m/z*)
4-18	Naphthalene	128	127, 102
	Acenaphtylene	152	151, 76
	Acenaphtene	154	153, 76
	Acenaphthene-d10	164	
	Flourene	166	165, 139
18-28	Phenanterene	178	176, 89
	Phenantherene-d10	188	
	Anthracene	178	176, 89
	Fluoranthene	202	200, 101
	Pyrene	202	200, 101
28-34	Benzo(a)anthracene	228	226, 114
	Chrysene	228	226, 113
	Chrysene-d12	240	
	Benzo(b)fluoranthene	252	250, 126
	Benzo(k)fluoranthene	252	250, 126
	Benzo(a)pyrene	252	250, 126
39-47	Benzo(ghi)perylene	276	277, 138
	Dibenzo(a,h)anthracene	278	276, 139
	Indeno(1,2,3,cd)pyrene	276	277, 138
	Perylene-d12	264	

RESULTS AND DISCUSSION

The recovery of different polycyclic aromatic hydrocarbons in the process of the pre-concentration by blowing down nitrogen gas was investigated by spiking the known amounts of polycyclic aromatic hydrocarbons in MQ water and following the pre-concentration process. The results of this investigation are summarized in Table-2.

TABLE-2
RECOVERY OF PAHS FROM THE PRE-CONCENTRATION PROCESS

Compound	Recovery (%) ± RSD (n = 4)
Phenanthrene	93 ± 7
Flourene	92 ± 5
Pyrene	101 ± 3
Chrysene	103 ± 4
Benzo(a)anthracene	98 ± 3
Benzo(b)fluoranthene	102 ± 5
Benzo(a)pyrene	102 ± 4
Indeno(1,2,3,cd)pyrene	98 ± 5
Benzo(k)fluoranthene	97 ± 6
Dibenzo(a,h)anthracene	107 ± 7
Benzo(ghi)perylene	103 ± 5
Fluoranthene	101 ± 3

The hydrophobic polycyclic aromatic hydrocarbons are difficult to analyze, especially when they are present in water samples. With the use of XAD-2 in order to separate the polycyclic aromatic hydrocarbons phase application has been developed with good recoveries. The average recoveries of selected polycyclic aromatic hydrocarbons from XAD-2 are summarized in Table-3.

The system was proved for the determination of polycyclic aromatic hydrocarbons in spiked water samples. Table-4 shows the results of determination of selected polycyclic aromatic hydrocarbons in a spiked water sample.

TABLE-3
RECOVERY OF POLYCYCLIC AROMATIC HYDROCARBONS
FROM XAD-2 RESIN COLUMN

Compound	Recovery (%) n = 4
Phenanthrene	98 ± 5
Benzo (a) anthracene	100 ± 3
Benzo (b) fluoranthene	100 ± 4
Benzo (a) pyrene	100 ± 4
Pyrene	99 ± 3
Indeno (1,2,3,cd) pyrene	98 ± 6

TABLE-4
DETERMINATION OF SELECTED POLYCYCLIC AROMATIC
HYDROCARBONS IN A SPIKED WATER SAMPLE

Compound	Spiked (ppb)	Found (ppb)	Recovery (%)
Phenanthrene	2.0	1.6	80
Benzo (a) anthracene	2.0	1.7	85
Pyrene	2.0	1.7	85
Benzo (a) pyrene	2.0	1.9	95

The concentrations of polycyclic aromatic hydrocarbons in the river water in two different stations are summarized in Table-5. In Fig. 1 the concentration of total polycyclic aromatic hydrocarbons in different sampling stations are presented.

TABLE-5
CONCENTRATION OF TOTAL POLYCYCLIC AROMATIC
HYDROCARBONS IN THE RIVER WATER IN TWO
DIFFERENT STATIONS (ng/L)

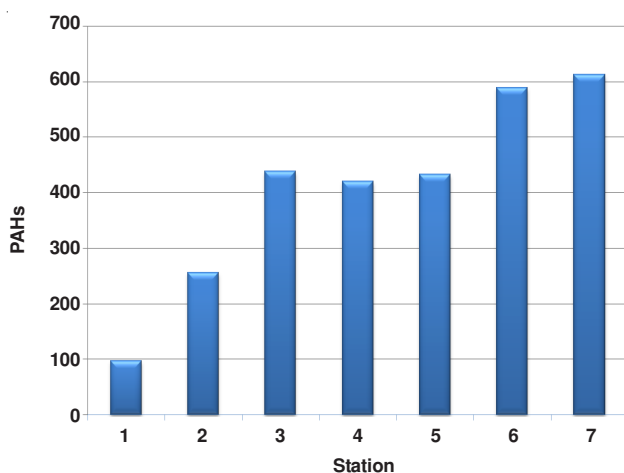| Compound	Station A[a]	Station B[b]
Phenanthrene	101	74
Benzo (a) anthracene	109	71
Benzo (b) fluoranthene	51	39
Benzo (a) pyrene	149	112
Pyrene	47	32
Indeno (1,2,3,cd) pyrene	32	ND
a. Station A= station number 6; b. Station B= station number 5		

Fig. 1.   Concentration of total polycyclic aromatic hydrocarbons in different sampling stations

The analysis of individual polycyclic aromatic hydrocarbons was carried out on several samples prepared from river and wetland waters by GC-MS. Table-6 represents the results obtained from this investigation for river and wetland water. The results obtained from the individual analysis of polycyclic aromatic hydrocarbons showed that the concentrations of polycyclic aromatic hydrocarbons are different in river and wetland water.

TABLE-6
MEAN CONCENTRATION OF INDIVIDUAL PAHS IN
RIVER AND WETLAND WATERS (ng/L)

Compound	Concentration in river	Concentration in wetland
Phenanthrene	12.4	15.9
Flourene	6.6	7.9
Pyrene	5.2	6.9
Chrysene	0.6	4.5
Benzo(a)anthracene	0.6	2.4
Benzo(b)fluoranthene	0.5	1.9
Benzo(a)pyrene	0.5	1.9
Indeno(1,2,3,cd)pyrene	0.4	3.3
Benzo(k)fluoranthene	0.6	1.4
Dibenzo(a,h)anthracene	9.8	10.6
Benzo(ghi)perylene	6	8.9
Fluoranthene	8.7	12.8

Conclusion

In water samples of the river Zayandeh-Rud, the amounts of total polycyclic aromatic hydrocarbon ranged from west to east. Highest polycyclic aromatic hydrocarbon concentration was found in the Gav-Khooni wetland. Where as a gradual increase in total concentration was observed from west to east. The results show, there was significant difference in the pollution level of the eastern and the western side of the river. Therefore we came to the conclusion that the origin of polycyclic aromatic hydrocarbons contamination in the river Zayandeh-Rud and the Gav-Khooni wetland have been an industrial waste effluent.

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