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Determination of Polycyclic Aromatic Hydrocarbons in Water Samples by Solid Phase Extraction and Gas Chromatography

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Abstract: Eleven polycyclic aromatic hydrocarbons namely; naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo[*b*]fluoranthene, benzo[*a*]pyrene and benzo[*ghi]*perylene were extracted simultaneously by solid phase and analysis by gas chromatograph. The LC-18 solid phase showed good recoveries for extraction of 11 PAHs by using 3 mL of the mixture of (1:1:1) dichloromethane : cyclohexane : hexane as eluent, the percentage recoveries were in the ranges of 87.31-97.38 with the standard deviation of 1.56-4.74. The detection limits for solid phase extraction were in the ranges of 0.05-0.55 mg/l. Application for analysis of water samples were done by this technique. The concentration of PAHs in water samples were found slightly varied from the location. The advantages of solid phase are solvent consumption, reuse in several times and pre-concentration.

Key words: Solid phase extraction · Polycyclic aromatic hydrocarbon · Gas chromatography

INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are hazardous organic chemicals consisting of two or more benzenoid groups[1]. They are ubiquitous pollutants in our environment. The importance of PAHs in the environment are discussed because of their carcinogenicity and mutagenicity [2]. The heavier compounds are rapidly condensed or adsorbed onto particles, when they are deposited directly onto the surface water, the dissolved fraction pollute the water, while the hydrophobic contaminant are embedded in bottom sediments. The 16 PAHs considered as priority by the American Environmental Protection Agency (EPA) are naphthalene, acenaphthylene, acenaphthene., fluorene, anthracene, phenanthrene, fluoranthene, chrysene, benzo[a]anthracene, pyrene, benzo[*k*]fluoranthene, benzo[*b*] fluoranthene, benzo[*a*]pyrene, dibenzo[*a,h*] anthracene, dibenzo[*b,c*]fluoranthene and benzo[*ghi*]perylene [1]. Some of PAHs compounds are low biodegradability low concentration in the environment and difficult to eliminate by general treatment, they may be present in environment samples. The enrichment and clean up procedure are usually required prior determination. There are several reports mention the application of solid phase extraction on the pre-concentration of PAHs from water [3-5] precipitation [6] and aerosol [7]. Solid phase extraction (SPE) is a simple treatment technique which passed a liquid sample through a sorbent. The analyte or interference of samples are retain on a sorbent by difference mechanism. The analytes were eluted in a small volume of solvent, concentrated and also cleaned up the sample. The objective of this research was to extraction of 11 PAHs in water sample by solid phase extraction and analyzed by gas chromatography-flame ionization detector.

MATERIALS AND METHODS

Chemicals: The 11 PAHs: acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo[*b*]fluoranthene, benzo[*a*]pyrene were obtained from BDH, naphthalene and benzo[*ghi*]perylene were obtained from Fluka. The stock solution of PAHs were prepared by dissolving in dichloromethane. All organic solvents were obtained from Labscan.

Instrumentation: Gas chromatography model GC17 (Shimadzu, Japan) with a DB-1 fused silica capillary

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column (30×0.25 mm, 0.25 µm film thickness) was used. The injector temperature was 275°C, flame ionization detector temperature was 300°C and the column temperature program. The temperature program was started from 40°C to 140°C with the rate of 20°C/min. then ramp to 290°C with the rate of 10°C/min and held for 12 min.

The 3 ml solid phase extraction columns were packed with 500 mg of ENVI-18 and 500 mg of LC-18 (Supelco, USA). The solid phase manifold with the vacuum pump (Supelco, USA) was used.

Optimization of Solid Phase Extraction: Prior to extraction, the SPE columns were conditioned with 5 ml methanol under vacuum, following with 5 ml of deionized water. The 10 ml of deionized water was spiked with the standard solution PAHs (0.015 mg of each) and subsequently passed through the column with the flow rate of 1 ml/min. The extraction time was 5 min. After drying the SPE column, the PAHs were eluted with organic solvent. Comparison between the solid phase column LC-18 and ENVI-18 was obtained with various eluents. Determination of percentage recovery by gas chromatography was carried out.

Linearity Ranges and Detection Limits: A 1µl of polyaromatic hydrocarbon solution standard mixture (0-5 mg/l) was injected onto gas chromatograph. The detection limits were taken as the lowest concentration of polyaromatic hydrocarbons that could be extracted and yielding good recoveries. The detection limits were taken as the lowest concentration of PAHs that could be simultaneously extracted with the optimum condition and yielding good recoveries.

Applications: Determination of polycyclic aromatic hydrocarbon in 4 water samples was done. The water samples were collected from the water resources in Mahasarakham University.

RESULTS AND DISCUSSION

Figure 1 shows chromatogram of the 11 PAHs by gas chromatography with DB-1 fused silica capillary column. The linearity ranges for determination of 11 PAHs by gas chromatograph were 0-5 mg/l with the correlation factor ranging from 0.9958-0.9999. The detection limits for solid phase extraction were in the ranges of 0.05-0.55 mg/l with the good recoveries in the ranges of 62.89-98.58%, as summarized in Table 1.

The conditioning step is important for the SPE procedures, to wet the SPE column can open up the groups on the sorbent surface and increase the surface area for interaction. Drying the SPE column after the sample loading, the organic solvent is forced through it by gravity and enables complete elution [7].

The 11 PAHs were simultaneous extracted by solid phase ENVI-18 and solid phase LC-18 with 3 ml of dichloromethane as eluent, as shown in Table 2. The extraction by solid phase LC-18 showed good percentage recovery than ENVI-18, since LC-18 is more non polar than ENVI-18 and the interaction between LC-18 and PAHs are hydrophobic. The 11 PAHs are typical non-

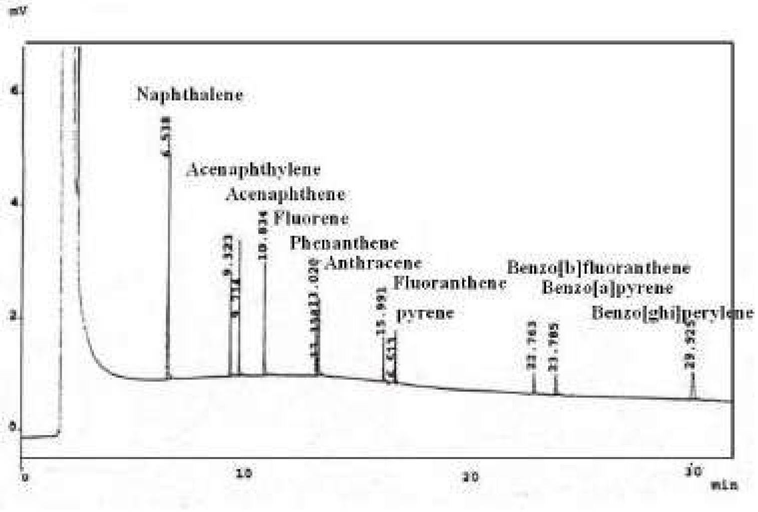

Fig. 1: Chromatogram of 11 PAHs by DB-1 fused silica capillary column, injector temperature 275°C, flame ionization detector temperature 300°C and the column temperature program

Table 1: Linearity range, calibration data of standard solution and detection limit for extraction of PAHs by LC-18 with (1:1:1) dichloromethane:cyclohexane:hexane

PAHs	Linearity range(mg/l)	Linear equation	R^2	Detection limit(mg/l)	% recovery
Naphthalene	0-5	Y=2477x+62	0.9994	0.05	89.38
Acenapthylene	0-5	Y=1033x-84	0.9999	0.18	60.08
Acenapthene	0-5	Y=1882x+32	0.9994	0.06	81.05
Fluorene	0-5	Y=1343x-57	0.9998	0.07	98.58
Phenanthene	0-5	Y=992x-2	0.9969	0.13	63.97
Anthracene	0-5	Y=1359x+54	0.9995	0.06	81.51
Fluoranthene	0-5	Y=668x-95	0.9968	0.15	83.11
Pyrene	0-5	Y=1562x-180	0.9965	0.09	79.09
Benzo[*b*[fluoranthene	0-5	Y=687x-145	0.9958	0.27	87.18
Benzo[*a*]pyrene	0-5	Y=345x-36	0.9979	0.26	62.89
Benzo[*ghi*]perylene	0-5	Y=307x-40	0.9980	0.55	76.19

Table 2: The percentage recoveries of PAHs by LC-18 and ENVI-18 solid phase with 3 ml of dichloromethane

	Percentage recovery (mean±SD, n=3)	
PAHs	LC-18	ENVI-18
Naphthalene	59.18±7.84	32.39±5.63
Acenapthylene	58.48±8.68	29.43±2.94
Acenapthene	60.84±9.82	51.98±4.31
Fluorene	68.04±9.55	30.76±3.72
Phenanthene	74.40±9.87	41.01±3.87
Anthracene	70.74±9.93	34.53±5.01
Fluoranthene	76.37±8.02	47.63±0.93
Pyrene	77.04±10.04	46.62±3.90
Benzo[*b*[fluoranthene	86.85±8.49	95.37±2.74
Benzo[*a*]pyrene	99.83±8.15	91.49±5.05
Benzo[*ghi*]perylene	88.26±2.93	57.50±5.73

Table 3: The percentage recoveries of PAHs by LC-18 solid phase with various of eluting solvent

	Percentage recovery (mean±SD, n=3)				
PAHs	Cyclohexane	1:1 DCM + cyclohexane	1:1 DCM + hexane	1:2DCM +hexane	1:1:1 DCM + hexane + cyclohexane
Naphthalene	35.02±4.97	24.36±5.79	65.15±3.28	66.05±4.15	87.31±2.64
Acenapthylene	40.68±7.20	30.42±3.03	67.12 ±3.89	78.07±1.45	94.96±2.96
Acenapthene	50.00±2.88	37.78±4.18	68.90 ±5.54	77.59±3.46	93.99±3.29
Fluorene	52.87±0.84	34.51±5.12	73.56 ±5.76	80.19±1.38	93.51±5.36
Phenanthene	62.46±4.18	43.59±5.70	81.29 ±5.06	91.22±3.00	95.82±2.35
Anthracene	65.16±1.68	38.89±4.13	90.08 ±5.72	89.89±2.40	95.64±1.56
Fluoranthene	70.86±1.68	56.27±5.25	97.59 ±5.28	99.32±0.39	94.82±3.51
Pyrene	69.27±5.22	51.27 ±5.93	100.97±3.89	96.78±0.41	97.38±1.86
Benzo[*b*[fluoranthene	83.32±3.40	61.94±5.92	93.28±5.22	80.60±3.17	96.21±4.74
Benzo[*a*]pyrene	64.94±5.19	66.49±9.22	84.22±3.53	73.06±2.93	92.11±2.31
Benzo[*ghi*]perylene	81.01±5.52	73.42±3.80	98.73 ±5.52	74.05±9.85	93.34±4.15

DCM=dichloromethane

Table 4: The PAHs in water samples (mean±SD, n=3)

PAHs	Sample1	Sample2	Sample3	Sample4
Naphthalene	ND.	ND.	ND.	ND.
Acenapthylene	ND.	ND.	ND.	ND.
Acenapthene	ND.	ND.	ND.	1.06±0.28
Fluorene	ND.	ND.	3.42±0.20	ND.
Phenanthene	1.92±0.15	2.29±0.01	ND.	1.88±0.11
Anthracene	ND.	ND.	ND.	ND.
Fluoranthene	6.17±1.00	8.82±0.24	ND.	2.63±0.19
Pyrene	2.91±0.10	2.38±0.13	1.98±0.08	1.64±0.01
Benzo[*b*[fluoranthene	3.24±0.60	3.57±0.02	4.98±1.14	ND.
Benzo[*a*]pyrene	ND.	ND.	ND.	ND.
Benzo[*ghi*]perylene	ND.	ND.	ND.	ND.

ND = not detected

polar compounds, eluting the analytes is usually carried out with a non polar solvent.

The percentage recoveries with the various eluting solvent are shown in Table 3. The mixture of 3 ml (1:1:1) dichloromethane : cyclohexane : hexane showed good percentage recoveries for extraction of 11 PAHs in the ranges of 87.31-97.38 with the standard deviation in the ranges of 1.56-4.74. To achieve the optimum SPE procedure, the technique was applied to the analysis of water samples which collected from the water resources in Mahasarakham University. The concentration levels of PAHs detected were slightly varied from the location. The commonly found PAH compounds in water samples were acenapthene, fluorine, phenanthene, fluoranthene, pyrene, benzo[b]fluoranthene. Naphthalene, acenaphthylene, acenapthene, anthracence, Benzo[*a*]pyrene and benzo[*ghi*]perylene were not found in all samples.

CONCLUSION

The 11 PAHs can be extracted simultaneously by solid phase LC-18 using 3 ml of the mixture of (1:1:1) dichloromethane: cyclohexane: hexane as eluting solvent. The results show good recovery and low detection limit. The SPE procedures can purify the extraction of natural water samples prior analyzed by gas chromatographic and reduce the interference peaks in the analysis PAHs chromatogram. The advantages of SPE are solvent consumption, reuse in several times and trace analysis in ppb level.

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