ANALYTICAL METHOD OF POLYCYCLIC AROMATIC HYDROCARBONS IN ENVIRONMENTAL LIQUID SAMPLES

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ABSTRACT

The recoveries of extraction solvent, clean-up solvent and real sample were surveyed to establish the analytical method of PAHs(poly aromatic hydrocarbons) in liquid samples. The average recoveries of extraction solvent were surveyed 70~102% in the selected solvents. The dichloromethane and n-hexane as non-polar solvents, and dichloromethane:acetone, n-hexane:acetone, cyclohexane:acetone, dichloromethane:methanol(1:1) and dichloromethane: methanol(10:1) as combined solvents were examined the extraction recoveries over 80%. Also, in the silicagel column process, the dichloromethane:pentane(2:3), 10% dichloromethane:n-hexane and 40% dichloromethane:n-hexane as elution solvents were represented over 87% recoveries. The analytical method in liquid sample, which extracted with dichloromethane:methanol(10:1) and eluted with 10% dichloromethane:n-hexane selected to get the highest recovery.

INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are widespread environmental contaminants and PAHs have been measured in a variety of environmental matrixes including air, water, soil, waste and marine sediment[1~2] due to their mutagenic and carcinogenic properties. Recently only 16kinds PAHs listed by the USEPA have been studied at most contaminated site as priority pollutants. In this work, the analytical methods of USEPA, Japan, Canada and Sweden were considered to establish the suitable method, and the extraction and elution solvents were selected using various solvents in liquid sample. The established method was applied to the real environmental sample to check the method efficiency.

EXPERIMENTAL METHODS

The 16 kinds of PAHs were analyzed to establish the analytical method of liquid samples. The various extraction solvents and elution solvents were used to find the highest recovery efficiency solvent in each extraction and cleanup step. The instrument consisted of a Varian 3400CX GC/MS equipped with split injector, and a 60 meter DB-5 column(60m×0.32mm ID×3.0μm). The GC oven temperature program was 130°C for 1min, temperature-ramped to 260°C at 4°C/min for 1 min, then 290°C at 1°C/min and held for 5 min. The selected ion represents in Table 1.

Table 1. Selected ion group in GC/MS analysis.

Group	R.T	Analytical compound	Internal standard
1	3min ~ 13min	Naphthalene Acenaphthene Acenaphtyne Fluorene	Naphthalene-d8 Acenaphthene-d10
2	13min ~ 23min	Anthracene Phenanthracene Fluoranthene Pyrene	Phenanthracene-d10 Chrysene-d12
3	23min ~ 40min	Benzo(a)anthracene Chrysens Benzo(b)fluoranthene Benzo(k)fluoranthene Benzo(a)pyrene Indeno(1,2,3-cd)pyrene Benzo(g,h,i)perylene Dibenzo(a,h)anthracene	Perylene-d12

RESULTS AND DISSCUSSION

The recoveries of extraction solvent, clean-up solvent and real sample were surveyed to establish the analytical method of PAHs(polycyclic aromatic hydrocarbons) in liquid samples.

Extraction Solvents : Ten kinds of extraction solvents were used to find the highest recovery efficiency as shown in Table 2. The average recoveries of extraction solvent were surveyed 70~102% in the selected solvents. The dichloromethane and n-hexane as non-polar solvents, and dichloromethane:acetone, n-hexane:acetone, cyclohexane:acetone, dichloromethane:methanol(1:1) and dichloromethane:methanol (10:1) as combined solvents were examined the extraction recoveries over 80%.

Table 2. Solvent recoveries in liquid/liquid extraction(%).

Compound	A	B	C	D	E	F	G	H	I	J
Naphthalene	56.20	90.98	89.21	80.57	99.48	66.38	92.11	45.56	91.58	85.02
Acenaphthylene	99.11	95.00	93.24	74.32	100.42	77.43	92.22	54.53	90.80	90.46
Acenaphthene	98.32	96.25	94.32	88.31	100.32	76.73	93.17	57.69	92.68	90.43
Fluorene	109.53	96.92	94.89	98.12	101.26	80.41	92.97	63.26	95.63	92.22
Phenanthrene	109.06	97.02	98.59	93.53	103.76	84.62	93.15	66.33	92.49	95.31
Anthracene	108.08	96.80	98.93	103.28	101.58	88.13	93.61	35.79	91.01	92.39
Fluorancene	97.74	92.98	98.83	96.26	104.09	82.90	88.22	68.97	85.64	94.21
Pyrene	95.42	92.31	98.85	95.33	104.80	83.43	97.41	69.50	84.29	93.73
Benzo(a)anthracene	87.93	90.42	99.59	112.49	102.94	84.39	81.91	72.61	81.77	90.65
Chrysene	87.84	90.29	100.01	96.64	103.95	83.95	83.61	76.71	81.96	91.91
Benzo(b)fluorancene	85.68	88.77	99.56	94.08	107.62	81.29	76.19	86.29	81.52	92.39
Benzo(k)fluorancene	83.26	87.34	98.50	94.34	103.44	81.64	78.44	89.41	77.51	89.53
Benzo(a)pyrene	79.26	84.85	92.47	84.90	98.46	79.27	74.90	75.99	72.56	85.38
Indeno(1,2,3-cd)pyrene	78.72	79.10	90.26	93.29	96.54	74.57	67.72	97.63	69.70	82.59
Benzo(g,h,i)perylene	85.18	82.10	93.87	94.59	102.82	80.30	74.05	96.28	76.36	88.97
Dibenzo(a,h)anthracene	81.68	76.75	90.54	119.70	103.08	76.10	72.25	130.59	72.89	86.87
Average	90.19	89.87	95.73	93.34	102.16	80.10	83.87	70.46	83.65	90.13

A ; Dichloromethane, B ; n-Hexane, C ; Cyclohexane, D ; Toluene,
E ; Dichloromethane:Acetone(1:1), F ; n-Hexane:Acetone(1:1),
G ; Cyclohexane:Acetone(1:1), H ; Toluene:Methanol(1:1),
I ; Dichloromethane:Methanol(1:1), J ; Dichloromethane:Methanol(10:1)

Silicagel Column Cleanup : The analytical methods of other countries were considered, and the amounts of elution solvent were control to get the highest recoveries. The compared methods of other countries were represented the satisfied results except method I of Japan. In the silicagel column process, the dichloromethane:pentane(2:3), 10% dichloromethane:n-hexane and 40% dichloromethane:n-hexane as elution solvents were surveyed over 87% recoveries as shown in Table 3. The analytical methods of real environmental liquid sample were also performed as shown in Figure 1. The dichloromethane:methanol and n-hexane as extraction solvent and the 10% dichloromethane:n-hexane and dichloromethane:pentane(2:3) as column elution solvents, which were from previous analytical results, were selected to establish the PAHs. These A, B, C, D methods were applied to real samples to establish the analytical method, therefore the method A(dichloromethane:methanol as extraction solvent and the 10% dichloromethane:n-hexane as column elution solvents) was represented the highest recoveries of selected compounds. The recovery of internal standard is 87% as show in Table 4 in method A.

Table 3. Solvent recoveries of various countries

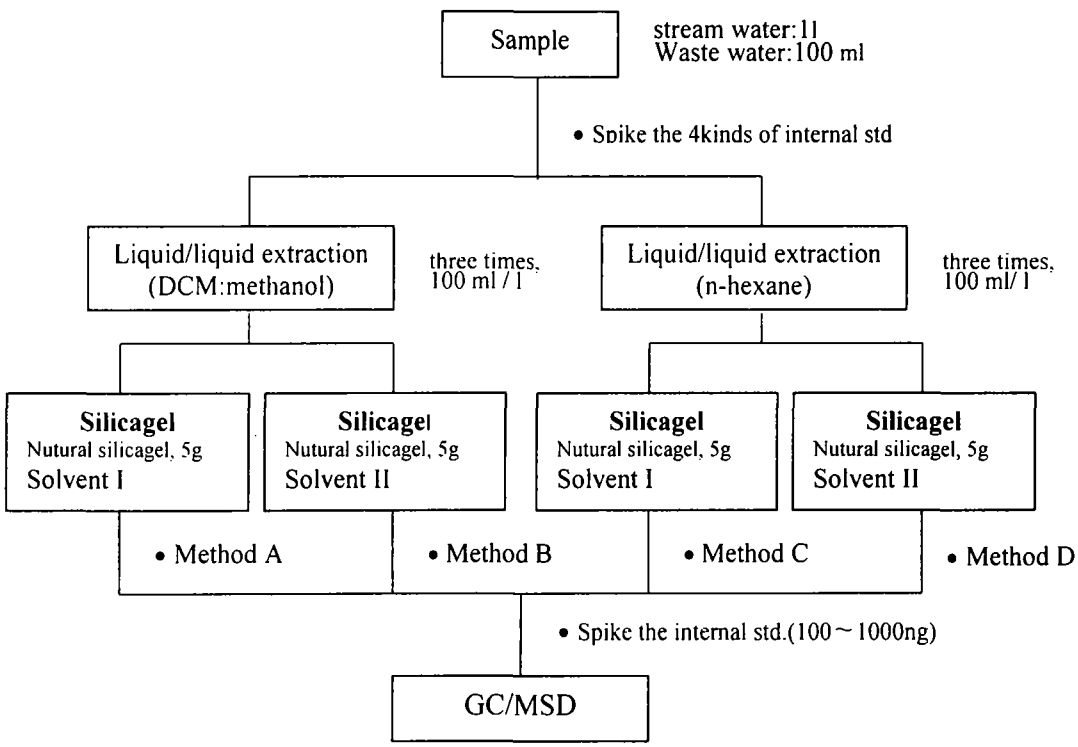
Compounds	USA [a)]	Japan		Canada [d)]	Sweden [e)]
		Method I [b)]	Method II [c)]		
Naphthalene	81.60	82.19	81.25	65.78	85.37
Acenaphthylene	83.61	68.49	95.06	72.87	89.50
Acenaphthene	85.55	68.32	92.06	74.77	90.00
Fluorene	90.04	72.28	80.86	82.46	91.56
Phenanthrene	90.64	66.75	93.60	90.73	92.98
Anthracene	86.62	68.33	92.94	92.63	91.80
Fluoranthene	91.75	61.02	86.72	94.61	94.10
Pyrene	91.93	58.40	99.79	94.58	94.57
Benzo(a)anthracene	94.14	63.73	89.77	98.15	97.02
Chrysene	96.40	63.91	99.40	94.07	96.97
Benzo(b)fluorancene	93.88	55.15	98.83	95.88	94.98
Benzo(k)fluorancene	93.58	58.01	97.44	94.42	95.23
Benzo(a)pyrene	90.94	53.46	93.58	93.38	93.74
Indeno(1.2.3-cd)pyrene	88.63	49.70	91.72	89.52	89.68
Dibenzo(a,h)anthracene	99.05	61.97	86.54	84.88	89.75
Benzo(g,h,i)perylene	95.29	47.61	94.95	77.40	88.25
Average	90.85	62.46	92.16	87.26	92.22

a) Dichloromethane:Pentane(2:3) 25ml→50ml[mℓ]
b) 2% Acetone:n-Hexane(decide the solvent amounts after elution) →300ml[mℓ]
c) 10% Dichloromethane:n-Hexane 50ml→100ml
d) Benznen 5ml(2 times)→20ml
e) n-Hexane 25ml+ n-Hexane:Dichloromethane 25ml : total 50ml→70ml[mℓ]
♣ The large amount of elution solvent was used to present the original analytical method.

Table 4. Internal standards recoveries in liquid/liquid extraction(%)

Compound	A	B	C	D
Naphthalene-d8	84.10	67.50	42.75	47.75
Acenaphthene-d10	76.56	63.75	61.69	60.24
Phenanthracene-d10	97.63	74.63	70.31	78.63
Crysene-d12	94.54	63.75	80.06	62.60
Perylene-d12	80.23	36.38	52.31	33.58
Average recovery	86.61	61.20	61.42	56.56

1. A method : dichloromethane:methanol(10:1) extraction / elution of 100 ml 10% dichloromethane:n-hexane
2. B method : dichloromethane:methanol(10:1) extraction / elution of 100 ml dichloromethane:pentane(2:3)
3. C method : n-hexane extraction / elution of 100 ml 10% dichloromethane:n-hexane
4. D method : n-hexane extraction / elution of 100 ml dichloromethane:pentane(2:3)



* DCM: Dichloromethane, Solvent I : 10% DCM : n-hexane, Solvent II : DCM : Pentane(2:3)

Figure 1. Analytical method of PAHs in liquid sample

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