

ANALYTICAL METHODS OF POLYCYCLIC AROMATIC HYDROCARBONS AND RELATED COMPOUNDS IN ENVIRONMENTAL SAMPLES

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ABSTRACT

The extraction of solid samples was performed to establish the analytical method of PAHs in environmental samples. The recovery efficiency of the soxhlet, accelerated solvent and microwave extraction were surveyed 64~120%, 68~100% and 22~81%, but the highest recoveries were obtained the dichloromethane(89, 90, 75%) and dichloromethane:methanol(10:1)(96, 94, 81%) in these three methods. The extraction recoveries of soxhlet and accelerated solvent extraction methods were surveyed high recovery efficiency compared to the microwave extraction method but the microwave extraction method can be used very easily. To establish the analytical method of the PAHs in the solid samples, the samples were extracted with the dichloromethane and dichloromethane:methanol(10:1) in the soxhlet, and eluted with 100 ml of the 10% dichloromethane:n-hexane. Two(A and B) different kinds of the methods were applied to the soil and waste samples. As the result, the internal standards recoveries were obtained 93~94%, therefore the established methods can be used to analyzed the PAHs in the environmental samples.

INTRODUCTION

Hundreds of polycyclic aromatic hydrocarbons (PAHs) result from incomplete combustion of organic materials during industrial processes and other human activities[1,2]. The studies of various environmentally related matrices, such as motor vehicle exhaust, used motor lubricating oil, tobacco smoke, soil contaminated oil, have shown the PAHs. The released PAHs into the environment has been determined by identification of a characteristic PAH concentration profile, but this has been possible in a few cases. Benzo[a]pyrene has frequently been used as an indicator of PAH[3]. The PAH has hydrophobic character with low solubility in water, therefore their affinity for the aquatic phase is low. The considerable concentration of PAHs are found in the hydrosphere because of their low Henry's constants in spite that the most of PAHs are released into environment via the atmosphere. Recently, only 16 kinds of PAHs by US EPA have been studied at most contaminated smpls, but the reports showed that many other toxic compounds can also be present, including other PAHs, methylated PAHs and heterocyclic PAHs containing oxygen, nitrogen or sulphur. Therefore, in this study, the analytical method of PAHs in solid samples (soil and waste) were established by considering the extraction method, extraction solvents and elution solvent, and the real sample analyzed using soil and waste using established method.

EXPERIMENTAL METHODS

The 16 kinds of PAHs were analyzed to establish the analytical method of solid samples. The various extraction methods (soxhlet, ASE, microwave), extraction solvents and elution solvents were used to take the highest recovery efficiency solvent in each extraction and cleanup step. The extraction and cleanup methods for solid sample represented in Figure 1. 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.

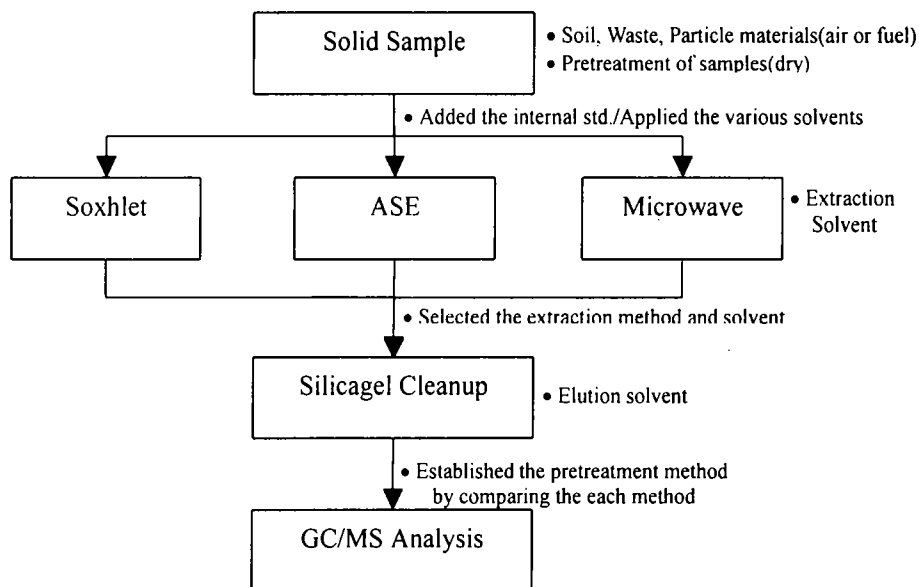


Figure 1. Experimental Procedures for Establishing the Analytical Methods in Environmental Solid Samples

RESULTS AND DISCUSSION

Analytical Method : The soxhlet extraction, accelerated solvent extraction and microwave extraction methods using various solvents were performed to establish the PAHs analytical methods. The 8 kinds of solvents (Dichloromethane, n-Hexane, Cyclohexane, Toluene, Dichloromethane:Acetone(1:1), n-Hexane:Acetone(1:1), Toluene:Methaneol(1:1), Dichloromethane:Methaneol(1:1), Dichloromethane:Methanol(10:1)) were selected to examine the extraction efficiency in three different extraction methods.

In soxhlet extraction as shown in Table 1, the average recovery was surveyed between 64 to 120%, and the highest recovery represented in toluene. But, fluorene, phenanthrene, pyrene and benzo(a)anthracen were not satisfied the recoveries, which compared the recovery of EPA 8270 method, therefore toluene is not satisfied as solvent of PAHs extraction using soxhlet. The average recoveries of PAHs were examined 88% using dichloromethane, and the each components recoveries were surveyed 75%~94%, and dichloromethane:acetone(1:1) was represented the

ORGANOHALOGEN COMPOUNDS

ANALYSIS II -POSTER

highest recoveries of 98%.

Table 1. Recovery of Soxhlet Extraction using Various Solvents(%)

Compounds	A	B	C	D	E	F	G	H
Naphthalene	87.82	63.70	55.27	90.91	93.05	73.12	55.04	58.27
Acenaphthylene	75.10	59.28	58.78	90.16	92.70	76.43	63.47	60.78
Acenaphthene	86.35	67.47	68.09	120.13	106.86	98.24	72.12	58.80
Fluorene	85.43	68.43	71.88	138.32	107.29	136.03	52.08	72.81
Phenanthrene	92.62	74.44	82.04	142.77	107.29	137.21	66.93	66.49
Anthracene	87.75	80.32	86.37	108.52	109.03	104.42	57.50	51.97
Fluorancene	93.21	81.97	85.21	134.30	101.00	131.43	79.66	56.48
Pyrene	93.53	83.91	84.87	121.44	97.69	118.81	77.20	55.84
Benzo(a)anthracene	92.64	92.98	81.08	140.63	87.89	129.10	101.93	69.52
Chrysene	93.64	91.10	81.33	137.41	87.76	125.35	90.03	59.72
Benzo(b)fluorancene	93.82	86.71	75.82	136.64	100.84	119.15	98.06	62.96
Benzo(k)fluorancene	92.66	96.69	74.45	136.05	99.41	118.71	109.84	63.53
Benzo(a)pyrene	88.73	88.46	70.64	90.89	95.47	75.97	89.92	61.88
Indeno(1,2,3-cd)pyrene	88.41	76.07	60.94	120.36	76.71	97.87	102.89	69.06
Dibenzo(a,h)anthracene	91.50	90.09	68.35	98.20	84.05	83.21	101.63	71.50
Benzo(g,h,i)perylene	85.63	77.47	65.55	117.48	91.33	90.36	101.23	72.87
Average	89.30	79.94	73.17	120.67	96.15	106.89	82.16	63.50

Table 2. Recovery of ASE using Various Solvents(%)

Compounds	A	B	C	D	E	F	G	H
Naphthalene	75.33	54.34	63.84	68.81	80.18	84.23	51.85	56.13
Acenaphthylene	77.11	61.05	92.93	68.23	87.89	91.78	56.93	68.05
Acenaphthene	77.50	70.80	95.34	80.60	94.83	98.78	67.12	79.08
Fluorene	92.86	71.46	126.89	81.89	98.87	118.72	60.21	79.11
Phenanthrene	82.82	75.36	111.58	73.40	97.79	115.15	63.41	90.35
Anthracene	76.00	73.67	88.84	75.34	93.13	93.84	52.73	75.30
Fluorancene	81.72	83.08	101.50	74.48	94.18	104.41	64.93	90.31
Pyrene	81.47	84.87	100.76	73.81	99.11	103.15	64.41	89.15
Benzo(a)anthracene	97.76	86.15	117.71	70.50	96.95	114.91	77.89	109.62
Chrysene	89.21	86.54	103.57	70.38	96.82	103.79	71.16	96.48
Benzo(b)fluorancene	94.96	88.93	108.75	74.14	96.36	101.24	89.00	103.82
Benzo(k)fluorancene	102.23	90.66	119.26	72.50	99.64	106.64	90.61	110.41
Benzo(a)pyrene	87.61	87.53	104.81	67.91	92.99	95.56	70.68	100.90
Indeno(1,2,3-cd)pyrene	88.28	77.24	105.15	59.56	88.89	92.81	72.86	105.13
Dibenzo(a,h)anthracene	87.93	84.04	99.95	63.27	91.08	93.83	72.70	101.87
Benzo(g,h,i)perylene	84.26	87.97	98.86	65.44	94.68	90.63	71.81	102.46
Average	89.87	78.98	102.49	71.27	94.00	100.60	68.45	90.52

The accelerated solvent extraction (ASE) method was well known to simple method compared with soxhlet extraction method because of using small amounts solvent, short extraction time, and easily establishing the analytical condition. In this extraction, the dichloromethane and dichloromethane:methanol(10:1) were obtained the 90% and 94%, respectively. As shown in Table 2, the small molecular mass compounds, such as naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluorancene, pyrene, were obtained the high recoveries in dichloromethane:methanol(10:1), but the large molecular mass compounds have no difference between two selected solvents.

Table 3. Recovery of Microwave using Various Solvents(%)

Compounds	A	B	C	D	E	F	G	H	I
Naphthalene	65.14	35.54	5.58	32.31	71.15	35.92	5.94	66.05	84.12
Acenaphthylene	77.88	38.96	46.92	57.17	72.52	46.10	39.78	65.01	83.27
Acenaphthene	85.87	50.74	67.19	57.19	79.41	55.64	43.73	77.44	80.41
Fluorene	85.50	42.99	71.08	64.83	77.67	54.30	50.19	68.85	87.79
Phenanthrene	80.06	41.51	58.37	65.08	71.16	58.47	66.68	61.06	82.42
Anthracene	79.37	37.43	58.32	62.50	72.59	61.60	39.93	61.72	81.35
Fluorancene	74.38	31.99	41.38	57.71	66.83	65.69	50.23	55.90	80.22
Pyrene	75.02	36.68	46.80	56.22	67.46	69.11	51.08	56.17	82.38
Benzo(a)anthracene	76.19	14.69	21.31	56.23	70.78	79.96	66.81	57.68	85.57
Chrysene	76.33	11.45	17.04	52.97	71.16	79.85	59.77	57.98	85.43
Benzo(b)fluorancene	76.41	3.83	6.68	53.52	65.28	81.03	71.83	59.19	81.40
Benzo(k)fluorancene	69.25	5.21	7.66	56.16	69.29	74.69	75.27	55.70	81.46
Benzo(a)pyrene	66.34	4.35	5.88	52.60	64.06	72.28	69.42	54.70	77.42
Indeno(1,2,3-cd)pyrene	64.64	0.00	2.55	57.55	67.61	61.31	84.04	54.44	73.93
Dibenzo(a,h)anthracene	79.94	0.01	0.00	59.08	78.02	72.50	85.82	64.63	80.17
Benzo(g,h,i)perylene	64.77	0.00	0.00	57.13	64.15	57.07	84.57	60.70	68.70
Average	74.51	22.21	28.55	56.00	70.57	64.10	59.07	61.08	81.01

A ; Dichloromethane, B ; n-Hexane, C ; Cyclohexane, D ; Toluene

E ; Dichloromethane:Acetone(1:1), F ; n-Hexane:Acetone(1:1), G ; Toluene:Methaneol(1:1),

H ; Dichloromethane:Methaneol(1:1), I ; Dichloromethane:Methanol(10:1)

The microwave extraction method recently used at various matrixes due to the simplicity. This method was needed short time to extraction, and could be applied to the samples, which containing the moisture. In this experiment, the sample extracted two times at 40°C for 15 min. As the result, the recovery ranged were surveyed 22~81%. The dichloromethane:methanol(10:1) was obtained the highest recovery, but the nhexane obtained the lowest recovery. The recovery of microwave extraction was not satisfied with the recovery of EPA 8270 method. From these results and clean-up results[4], the analytical method of solid was established as shown in Figure 2, and environmental samples were applied to this established method.

Cleanup Method : The clean up process of USA, Japan, Canada and Sweden were reviewed, and performed to the each method to make sure the experimental procedure. The silicagel column process were introduced to these country, and the country used various elution solvent to removed the interference compounds from extraction samples. The Figure 2 showed the results of each

method. As shown in Figure 2, the various countries' procedure showed that the EPA, Japan and Sweden methods had little differences even though they used various elution solvents, therefore we could choose the any of these methods. But, recovery of Canada methods showed little lower than the other countries.

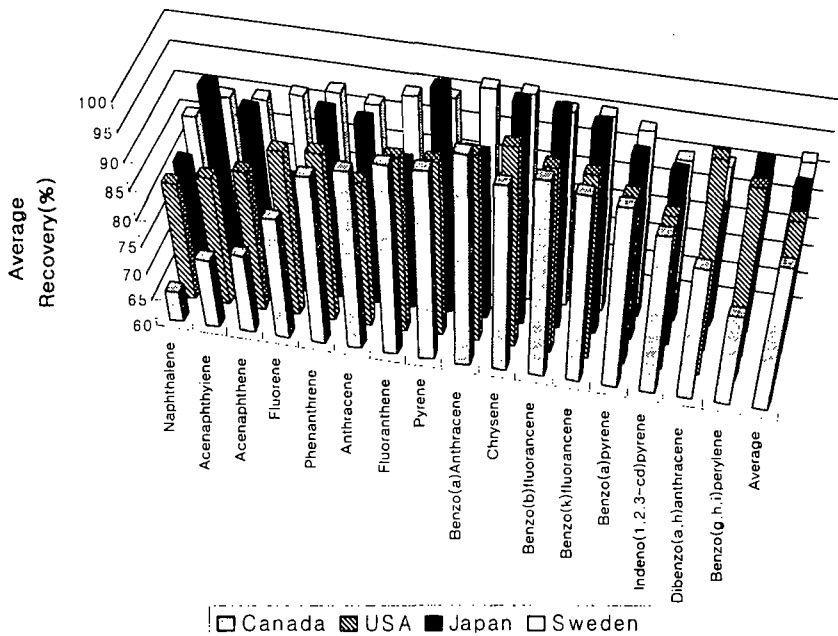


Figure 2. Comparison the Cleanup Process

Established Method : The analytical method was established, and the method was applied to the samples. The method was taken the soxhlet extraction with dichloromethane and dichloromethane:methanol(10:1), and silicagel cleanup process with 10% dichloromethane to soil and waste samples as shown in Figure 3. The average recoveries of applied four method(A,B,C,D) were surveyed to select the one method as shown in Figure 4. The designed method were represented the recovery ranges between 90% to 94%, and just few differences were represented in the designed methods. Therefore, the methods, which presented in Figure 4, could be applied to the environmental samples.

REFERENCES

1. IPCS, Environmental Health Criteria 202(Selected Non-Heterocyclic Polycyclic Aromatic Hydrocarbons).
2. M. Moller and I. Alfheim, *Environ. Sci. & Technol.*, 1982, 16, 221-225.
3. S. K. Shin et. al., " A Study on the Development of Analytical method for Unregulated Trace Pollutant(1)", 1999.

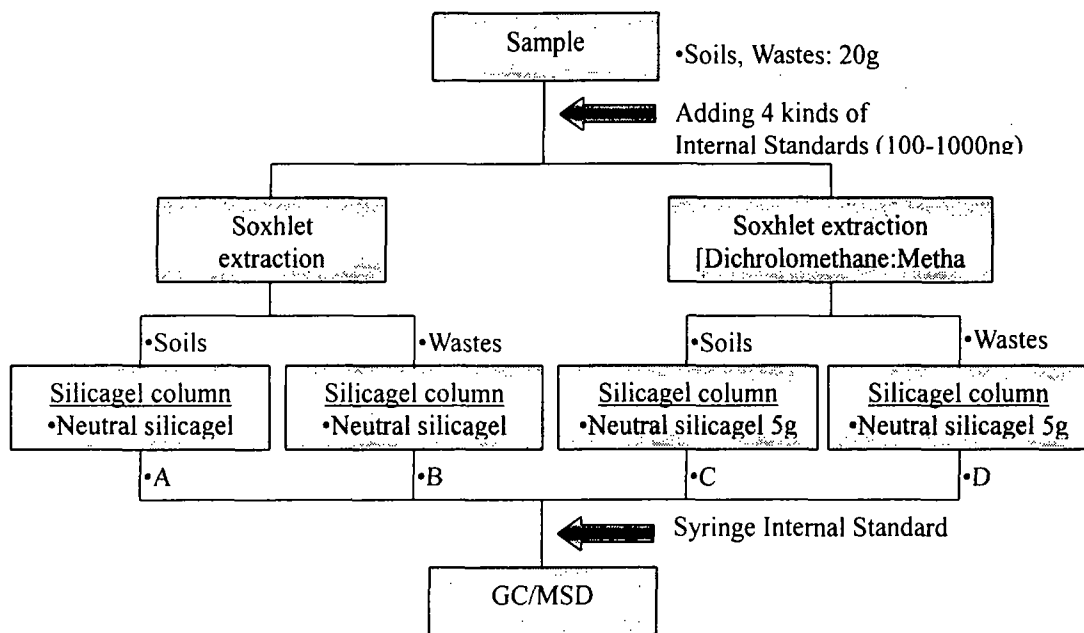


Figure 3. Designed Analytical Methods for Solid Sample

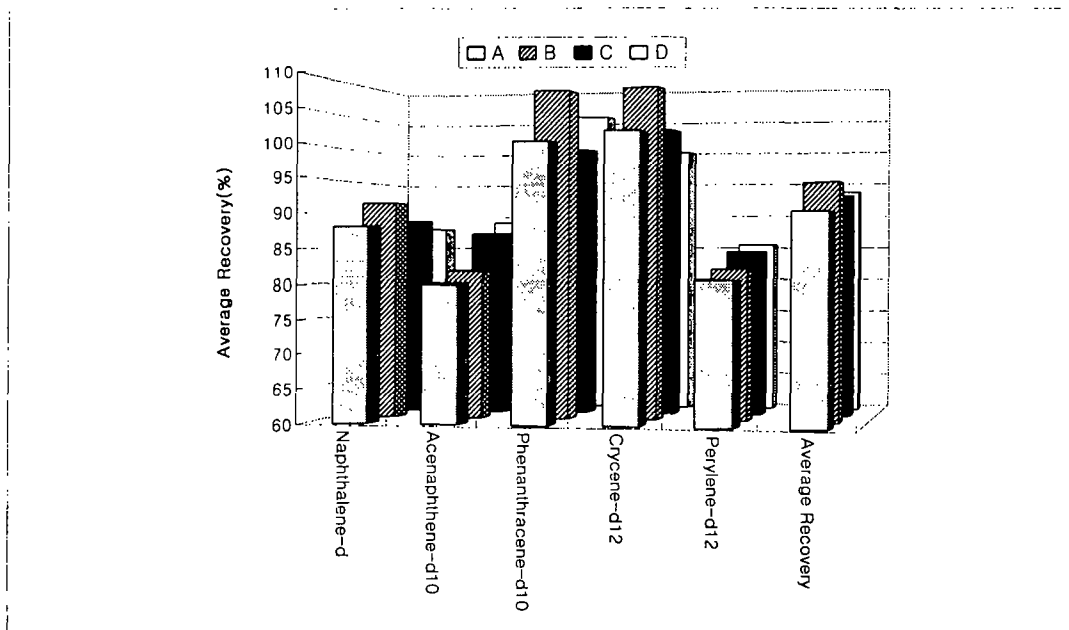


Figure 4. Recovery of Established Analytical method in Environmental Samples