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Determination of polychlorinated biphenyl congeners in environmental samples

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Abstract — A modified separation method has been developed for determinating polychlorinated biphenyl congeners in environmental samples. Direct treatment of extract with concentrated H_2SO_4 was employed in the first step for removal of lipids and other interfering substances, then a joint column of alumina-silica gel(Ag^+) was applied to separate PCBs fraction from HCH, DDT and its analogs. After this separation, the PCBs fraction was analyzed by capillary gas chromatography with ECD detector and confirmed by GC/MS. The recoveries of individual congeners in Aroclor 1254 through the separation are about 79%—84%. The method is very efficient and useful for determination of trace amount of PCB congeners in environmental samples.

Keywords: polychlorinated biphenyl; capillary gas chromatography; environmental samples.

1 Introduction

Polychlorinated biphenyl (PCBs) are a group of mixture manufactured formerly in several countries. A very large number of PCB congeners are presented in commercial products. In environmental samples, chlorobenzenes and other chlorinated hydrocarbons, such as DDT and its analogs often interfere the determination of PCBs (Oliver, 1989), so it is important to separate the interfering material from samples before determining PCB congeners, especially when only trace of PCBs existed in environmental samples. There are a lot of papers which reported the clean-up procedure. The most common method was column chromatography with florisil, alumina, silica gel, active carbon or gel resin as packing material, but the separation was not always satisfactory. In this report a new method consisting of two separation steps is described.

2 Experimental

2.1 Reagents

Aroclor 1254, Aroclor 1242(Supelco. Inc.); PCB_3 standard sample (Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences); hexane was redistilled in glass system; basic alumina, 100-200 mesh, was deactivated with 2% water. $AgNO_3$; silica

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gel (Ag^+): the silica gel (A. R.), 120—200 mesh was treated according to Needham (Needham, 1980), and sealed in bottle before use.

2.2 Procedure

2.2.1 Preseparation and clean-up

Water samples were preconcentrated by passing through a column packed with GDX-502 resin as described in the literature(Wang, 1990), then the resin was extracted in Soxhlet extraction apparatus with hexane.

Sediment and soil samples were ground to about 60 mesh after drying, extracted with hexane for 12 hours.

Mussels and fish samples were ground, homogenized and reflexed for 1 hour with ethanol-KOH. After saponification, the mixture was extracted three times with hexane.

The extract was concentrated to about 10 ml, dried and concentrated to approximately 0.5 ml. The sample in hexane was shaken with concentrated H_2SO_4 in a test tube, and then the sulfuric acid layer was discarded. This treatment should be repeated several times until the hexane layer was clean. The latter was then dried and concentrated.

The Al_2O_3-silica gel (Ag^+) column used in the second step was 300×11 mm i. d. glass column with Teflon stopcock. 2% water deactivated basin alumina was packed on the upside of silica gel (Ag^+), with 1 g anhydrous Na_2SO_4 placed at the top. Then the column was washed with 40 ml hexane and the retention volumes of Aroclor 1254, Aroclor 1242, PCB_3, HCH, DDT and DDE were determined with their respective standard. After that, the samples were treated similarly and the PCBs fraction was collected and concentrated to 0.2 ml for gas chromatographic analysis.

2.2.2 Gas chromatographic analysis

A Varian 3740 gas chromatograph with ^{63}Ni electron capture detector was used. The fused silica capillary column (18×0.25 mm i. d.) coated with SE-54 (J & W Scientific Inc. USA) was connected to splitless injector. The temperatures of injector and detector were 300℃ and 350℃, respectively. The GC temperature program was as follows: 50℃ with 2 min holding, 50—150℃ at 10℃ min^{-1}, 2 min holding at 150℃, 150—280℃ at 4℃ min^{-1}, and 10 min holding at 280℃. Splitless injection was applied. Data acquisition was accomplished through a Shimadzu Chromatopac C—R3A.

2.2.3 Gas chromatography/mass spectrometry

A VG TRIO 2000 mass spectrometer was used for the gas chromatography-mass spectrometry analysis of the PCBs fraction and the gas chromatographic procedure was similar to that described above. Confirmation of the presence of PCBs was carried out with mass spectrometry and selected ion monitoring (SIM) technology.

3 Results and discussion

3.1 Concentration and clean-up

The environmental samples should be pretreated in different ways according to their types.

Resin adsorption is often employed for preconcentration of water sample, since the concentration of PCBs in water is very low, liquid-liquid extraction is not always a satisfactory method for analyzing trace PCBs in environmental water samples.

Soxhlet extraction is considered to be the most useful procedure for extraction of organic compounds from sediment and soil, but fish and other biota samples need saponification before extraction, as the biota samples have complex structure(Vassilaros, 1982). If the latter is only Soxhlet extracted with organic solvent, some portion of the compounds in interest may be lost.

In this paper, two steps are employed to clean-up samples. In the first step, 90% of the lipid in samples can be destroyed, while PCBs remain almost the same(because PCBs have high stability). Table 1 shows the recovery of Aroclor 1254 treated with concentrated H_2SO_4. In this step, HCH, DDT and its analogs are also not destroyed.

Table 1 The recovery of Aroclor 1254 treated with concentrated H_2SO_4

	1	2	3	4	$\bar{X}$
Amount added, μg	1.033	1.033	1.033	1.033	
Amount recovered, μg	0.991	1.050	1.082	0.955	
Recovery, %	95.9	101.6	104.7	92.4	98.7

The samples from environmental system often contain a large number of individual PCB congeners and interfering contaminants. An efficient separation procedure are necessary to separate HCH, DDT and its analogs from PCBs fraction before the determination of PCB congeners. Needham (Needham, 1980) employed silver nitrate on silica gel to determine PCBs in human serum, but the capacity of the silica gel column was comparatively small and easily affected by different samples. In this paper a joint column of alumina silica gel(Ag^+) for clean-up was employed to solve this problem. In this way HCH, DDT, and its analogs were adsorbed on the column and not eluted by hexane, and sulfur containing coextractants were also removed from sample, so PCBs could be completely separated from interfering compounds. Fig. 1 shows that the gas chromatograms of PCBs fraction of a water sample under different separation steps of this method. It can be seen that the separation is very efficient.

3.2 Gas chromatography

It is almost impossible to separate all PCB congeners on a single capillary column, however, it provides the most potential method for analyzing them. SE-54 column was recommended by some analysts as efficient standard column for determining some PCB congeners (Huhnerfuss, 1992). The electron-capture detector (ECD) continues to be one of the most sensitive and valuable selective detector for PCBs detection. In this paper, a capillary column with SE-54 stationary phase and ECD as the GC detector gives satisfactory chromatograph.

3.3 Detection and quantification

Aroclor 1242 and Aroclor 1254 were used as standard, of which their weight-percent

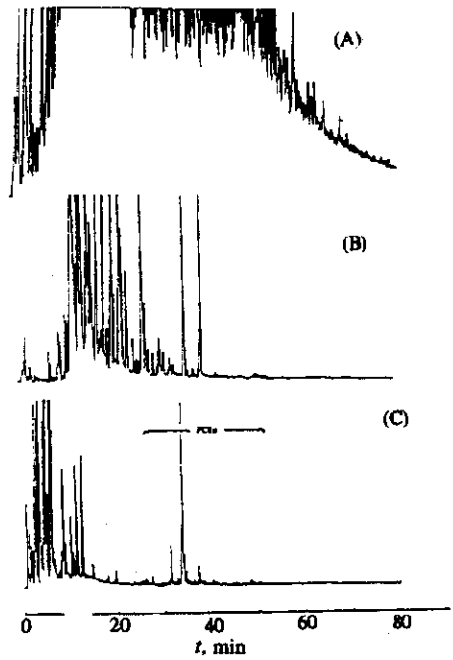

Fig. 1 Gas chromatogram of PCBs fraction under different separation steps
A. gross hexane extract; B. extract after treated with concentrated H_2SO_4;
C. extract after clean-up with alumina-silica gel(Ag^+) column

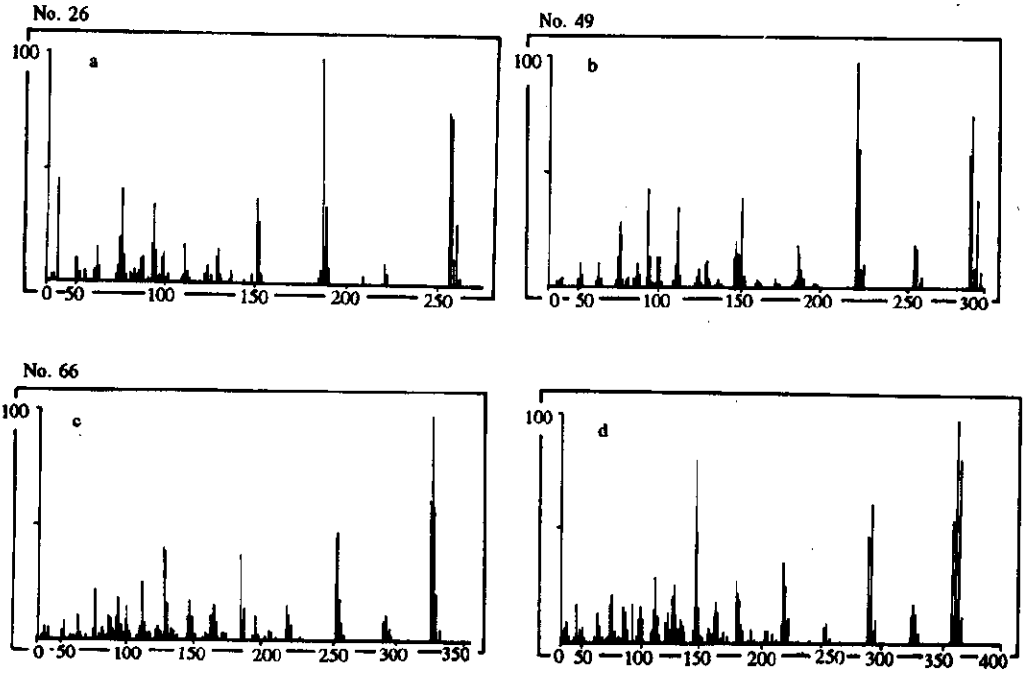

Fig. 2 Mass spectra of PCB congeners fraction in fish tissue

composition had been previously determined by Capella and his co-operators (Capel,

1985) for qualitative and quantitative analysis. Confirmation of the presence of PCBs in sample was carried out by using GC/MS. Fig. 2 shows electron impact mass spectra of some PCB congeners (with respective IUPAC No. indicated) in fish tissue. Selected ion monitoring is also used to determine some trace congener in the samples. Fig. 3 shows the mass chromatograms of PCBs fraction of the fish tissue.

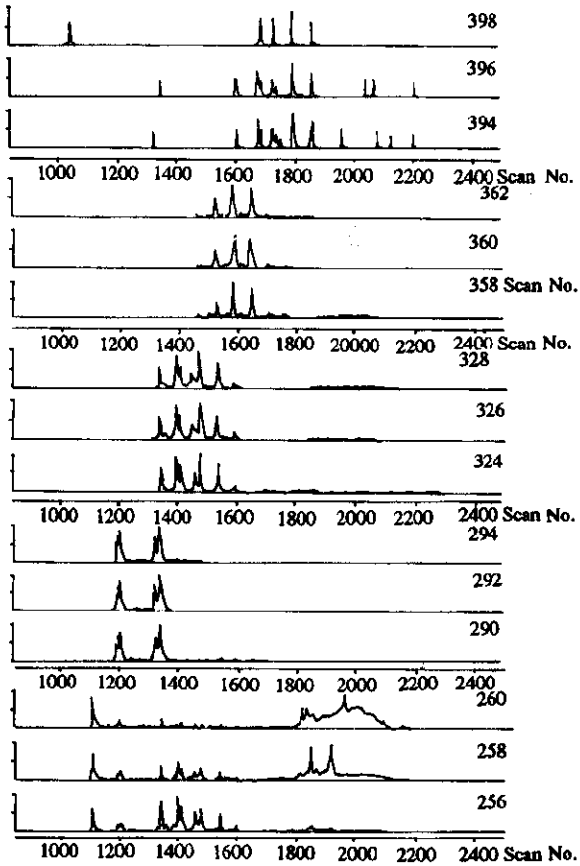

Fig. 3 Mass chromatogram of PCBs fraction in fish tissue

3.4 The recoveries of PCBs

A standard sample of Aroclor 1254 was treated for investigating the recoveries of individual PCBs through the two step clean-up procedure. Fig. 4 shows the gas chromatograms of Aroclor 1254 before and after the separation procedure. There are no obvious difference between the chromatograms in Fig. 4 except that some peaks come out in the first 6 min. interval from the solvent in Fig. 4(B). This shows that the method does not exert apparently different effect on the individuals PCBs congeners. Table 2 shows the recoveries of PCBs through the procedure.

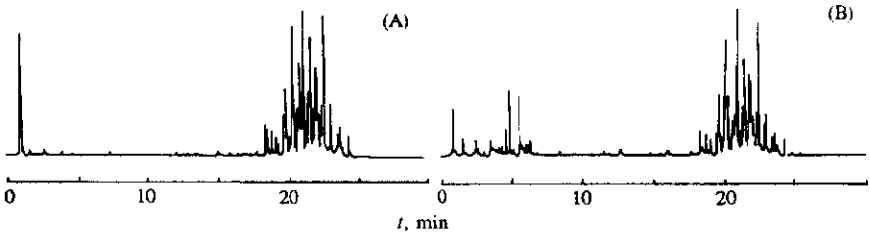

Fig. 4 The GC chromatograms of Aroclor 1254 (A) before and (B) after separation procedure

Table 2 Recovery of Aroclor 1254 through the procedure

	1	2	3	4	5	6
Added, μg	1.03	1.03	1.03	0.413	0.413	0.413
Recovered, μg	0.817	0.911	0.869	0.326	0.324	0.334
Recovery, %	79.3	88.4	84.4	78.9	78.5	80.9
$\bar{X}$, %		84.0±4.6			79.4±1.3	

3.5 Determination of PCBs in environmental samples

The two-step separation method has been satisfactorily applied in our laboratory to investigate the distribution of PCBs in environmental samples such as soil, water, shell and fish. Fig. 5(A) is the GC chromatogram of PCBs in fish sample (*Crucian Carp*).

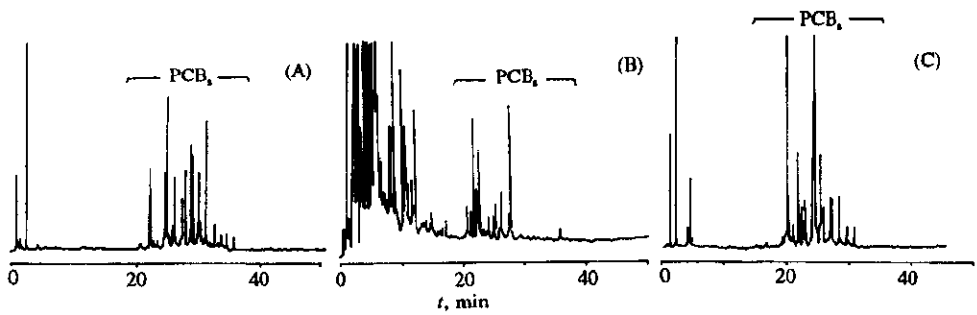

Fig. 5 The GC chromatogram of PCBs fraction from (A) a fish sample; (B) surface water samples and (C) sediment sample

Fig. 5(B) and Fig. 5(C) are the GC chromatograms of PCBs from surface water and sediment samples respectively from nearby the spot where the fish was from. Table 3 lists the concentration of individual PCB congeners in the above samples. Most of the earlier quantitative analyses only gave a relatistic value for total PCB concentration, provided that the PCB pattern in the sample was similar to that found in the commercial PCB standard. There were only few of papers mentioned that this speculation would result very possibly in an erroneous report because the PCBs residues in the environmental samples could not be adequately described precisely by the commercial PCBs standard (Schwartz, 1987). In this paper the results also support the speculation. If a cursory look is made at the chromatograms

in Fig. 5(A), (B), (C), it is obvious that a shift of peaks to more highly chlorinated PCBs occurs from water to sediment, and to fish. The relative concentration of lower chlorinated PCBs in water is higher than those in sediment because the solubility of lower chlorinated PCBs in water is higher than of higher chlorinated PCBs; and the higher chlorinated PCBs have higher tendency to be bioaccumulated in fish.

Table 3 Concentration of PCBs in different environmental samples

IUPAC No.	Fish, μg/kg	Water, ng/kg	Sediment, μg/kg	Mussel, μg/kg
4	0.16			
7	0.05			
6	0.06			
8	0.21		0.37	0.07
19	0.14		0.34	
18+17	0.41		0.20	0.03
16+32	0.08			
26	0.24		0.35	
25			0.18	
31+28	4.80	0.10	23	0.02
33		0.07	8.3	
22		0.10	1.9	
45			0.22	0.02
52	78	0.44	58	0.14
49	45	0.13	36	0.07
47+48	30	0.56	20	0.04
44	8.2	0.07	19	0.02
37+42	2.7	0.06	18	
41+64	7.3	0.05	19	0.01
40	1.0		0.95	
100	4.5		5.9	0.01
74	51	0.11	57	0.05
70	25	0.14	80	0.15
66	116	0.22	85	0.14
60+56	12	0.04	16	0.01
101	51	0.31	33	0.07
99	35		23	0.03
83	3.9		4.4	0.03
97	9.0	0.11	20	0.02
87	22		18	0.04
85	11	0.26	17	0.03

Table 3 (Continued)

IUPAC No.	Fish, μg/kg	Water, ng/kg	Sediment, μg/kg	Mussel, μg/kg
110	52	0.05	37	0.07
82	6.7		6.1	0.01
118+108	90		59	0.07
146	50		17	0.08
153	14		20	0.02
141	5.4		3.0	
137	4.0		0.94	
138	76		26	0.11
178	5.2		2.8	
175	6.5		7.5	0.01
187+159	2.2		1.9	0.01
128	11		4.8	0.01
185	1.6		2.3	0.01
177	6.8		5.8	0.01
180	5.0		7.8	
170	8.7		8.5	
196			3.2	
201			5.2	
194			1.7	
Total	864	3.0	786	1.4

Blue mussels (*Mytilus edulis*) are usually used as biota samples for monitoring coast pollution (Goldberg, 1978). Table 3 also lists the concentration of PCB congeners in a mussel (*Mytilus edulis*) sample from southeast coast of China.

4 Conclusion

The methods used in this study, including two-step pre- separation procedure and capillary gas chromatography, is efficient for determination of PCBs in various environmental samples. This method will meet the need for quantifying individual PCB congeners, and also for researches on environmental pathway, fate of PCBs and so on.

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References

Capel PD, Rapaport RA, Eisenreich ST, Looney BB. Chemosphere, 1985; 14:439

Goldberg D, Bowen VT, Farrington JW *et al.* Environ Conservation, 1978; 5(2):101

Huhnerfuss H, Kallenborn R. J Chromatogr, 1992; 580:191

Needham LL, Smerk ALS, Hesad SL, Burse VW, Liddle JA. Anal Chem, 1980; 52:2227

Oliver BG, Baxter RM, Lee Hingbiu. Analysis of trace organics in the aquatic environment (Ed. by Alfghan, Alfred SY Chau). Boca Raton Fla:CRC, 1989:31

Vassilaros DL, Staker PW, Boath GM, Lee ML. Anal Chem, 1982; 54:106

Wang Xikui, Jin Zuliang, Wang Hai, Xu Xiaobai. Collections of scientific studies on the activities relating to the environmental behavior and eco-toxicology of toxic organics (Ed. by Xu Xiaobai *et al.*) Beijing: China Science and Technology Press. 1990:374

Schwartz TR, Stalling DL. Environ Sci Technol, 1987;21:72

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