METHOD FOR THE ANALYSIS OF DIOXIN-LIKE POLYCHLORINATED BIPHENYLS(PCBS) IN ENVIRONMENTAL SAMPLES

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Abstract

The analytical method of 14 kinds of coplanar-PCBs was established and applied the soil sample. The three kinds of extraction solvents (toluene, acetone: hexane, dichloromethane) were selected to apply the soil sample. The silica gel, florisil and alumina column cleanup also performed to compare the elution recovery.

The average recovery of selected solvents was surveyed the order of toluene, acetone: hexane, dichloromethane as 77.94 %, 58.59 %, and 54.20 %. Also, the coplanar PCBs were obtained the highest recovery in the toluene. The average recovery is represented 49.99 % for silica gel (n-hexane 100mL), 69.65 % for florisil (6 % ether/n-hexane 100 mL), and 65.23 % for alumina (2 % DCM:n-hexane 100 mL, 50 % DCM 150mL). In silica gel (n-hexane) and florisil (6 % ether:n-hexane) cleanup, the 14 kinds of coplanar PCBs eluted until 40 mL. These two columns cleanup, the amounts of elution solvent can be reduced from these results, but the researcher has to confirm the elution amounts before performing the experiments. In alumina cleanup process, which was selected many country's official methods, the PCBs eluted until 2 % DCM 100mL and 50 % DCM 40 mL, and therefore the change of elution solvent is necessary to develop the simple procedure.

Introduction

The dioxin-like polychlorinated biphenyls (PCBs) are called the coplanar-PCBs, which is highlighted the pollutants of environmental contamination for decades[1~4] The toxicity of PCBs differs dramatically depending on the substitution pattern, especially the number of *ortho*-chlorine substituents. PCBs with many *ortho*-chlorines possess Phenobarbital type induction, whilst PCBs without ortho-chlorines (non-*ortho* PCBs) possess methylchoanthrene type induction and "dioxin-like" effects. Mono-*ortho* PCBs induces both system, bur to a lesser extend.

Also, the structure of PCB molecules depends on the substitution in *ortho*-position. The non-*ortho* substituted PCBs does more easily adopt a planar configuration than the other congeners, as reflected by the rotational energy barriers that decrease in the order non-*ortho* < mono-*ortho* < di-*ortho* << tri-*ortho* < tetra-*ortho*.[1~8]

In this study, the analytical method of 14 kinds of coplanar-PCBs was established and applied the soil sample. The extraction methods were used to the soxhlet, and the cleanup method was used to the column cleanup, and the analytical instruments were used GC/MSD. The 14 kinds of PCBs standards were used to establish the analytical methods to perform the experiments of recoveries and detection limits in soil samples

Experimental Methods

The 14 kinds of coplanar-PCBs (Table 1) were analyzed to establish the analytical method of the soil samples. The various extraction extraction solvents and elution solvents for column cleanup were

used to take the highest recovery efficiency solvent in each extraction and cleanup step. The instrument consisted of a HP5890N GC/MS equipped with split injector, and a 60-meter DB-5 column (60m´0.32mm ID´3.0mm). The GC oven temperature program was 105 °C for 1min, temperature-ramped to 245 °C at 10 °C/min for 2 min, and temperature-ramped 300 °C/min at 3 °C/min. The experimental conditions are represented in Table 2.

Table 1. Selected 14 kinds of coplanar PCBs[2]

Type		IUPAC No.	TEF(1993)	TEF(1997)	Cas No.	Character ion mass
Non-	81	3,4,4',5-	–	0.0001	70362-50-4	289.9, 291.9, 393.9
ortho	77	3,3',4,4'-	0.0005	0.0001	32598-13-3	289.9, 291.9, 393.9
	126	3,3',4,4',5-	0.1	0.1	57465-28-8	325.9, 323.9, 327.9
	169	3,3',4,4',5,5'-	0.01	0.01	32774-16-6	359.8, 361.8, 357.8
	105	2,3,3',4,4'-	0.0001	0.0001	32598-14-4	325.9, 323.9, 327.9
Mono-	114	2,3,4,4',5-	0.0005	0.0005	74472-37-0	325.9, 323.9, 327.9
ortho	118	2,3',4,4',5-	0.0001	0.0001	31508-00-6	325.9, 323.9, 327.9
	123	2',3,4,4',5-	0.0001	0.0001	65510-44-3	325.9, 323.9, 327.9
	156	2,3,3',4,4',5-	0.0005	0.0005	38380-08-4	359.8, 361.8, 357.8
	157	2,3,3',4,4',5'-	0.0005	0.0005	69782-90-7	359.8, 361.8, 357.8
	167	2,3',4,4',5,5'-	0.00001	0.00001	52663-72-6	359.8, 361.8, 357.8
	189	2,3,3',4,4',5,5'-	0.0001	0.0001	39635-31-9	393.8, 395.8, 397.8
Di-	170	2,2',3,3',4,4',5-	0.0001	–	35065-30-6	393.8, 395.8, 397.8
ortho	180	2,2',3,4,4',5,5'-	0.00001	–	35065-29-3	393.8, 395.8, 397.8

Table 2. Experimental conditions of PCBs.

Exp. Methods	Contents
Extraction	soxhlet ·n-hexane, dichloromethane, toluene
Clean up	Column ·Silica gel : n-hexane 100mL ·Florisil : 6 % ether:n-hexane 100mL ·Alumina : 2% DCM:n-hexane 100mL, 50% DCM 150mL
Instrument	·GC/MS ·HP5890N
·Column	·DB-5MS(60m×0.32mm×0.25um)
·Column temp	·105°C(1min) → 10 °C/min → 245 °C(2min) → 3 °C/min → 290 °C(8min)
·Injector temp	·300°C
·Ion source	·MS Source 230°C, MS Quad. 150 °C
·Ionization volt	·70eV
·Ionization	·EI
·Injection mode	·Splitless mode
·Carrier gas	·He(1mL/min)

Results and Discussion

Solvent Extraction

The soxhlet extraction and microwave extraction methods using various solvents were performed to establish the coplanar-PCBs analytical methods. The 3 kinds of solvents (toluene, acetone: hexane, dichloromethane) were selected to examine the extraction. The 14 kinds of PCBs standards were used to establish the analytical methods to perform the experiments of recovery. The average recovery of selected solvents was surveyed the order of toluene, acetone: hexane, dichloromethane as 77.94 %, 58.59 %, and 54.20 %, which represented in Figure 1.

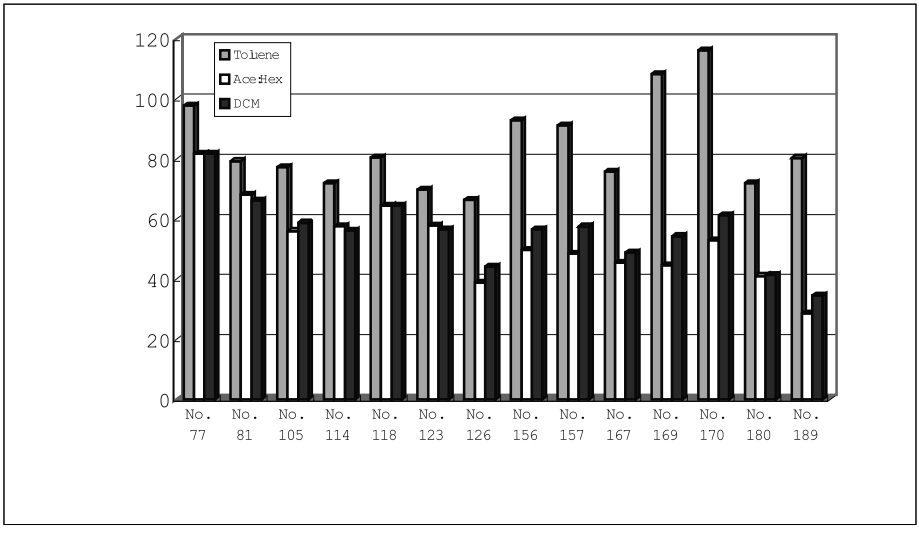

Figure 1. The recoveries of coplanar-PCBs in cleanup process

Cleanup Method

The clean up process of USA and Japan were reviewed, and performed to the each method to make sure the experimental procedure. The silica gel, florisil and alumina column process were performed to apply the various environmental samples, and various elution solvents also applied to remove the interference compounds from extraction samples. The Figure 2 showed the results of each method. As shown in Figure 2, the average recovery is represented 49.99 % for silica gel (n-hexane 100 mL), 69.65 % for florisil (6 % ether/n-hexane 100 mL), and 65.23 % for alumina (2 % DCM:n-hexane 100 mL, 50 % DCM 150 mL). In silica gel cleanup, the 14 kinds of coplanar PCBs eluted until 40 mL of n-hexane, and the coplanar PCBs eluted until 40 mL of 6 % ether:n-hexane in florisil cleanup, which was adopt in EPA method for analysis of individual isomer. These two columns cleanup, the amounts of elution solvent can be reduced from these results, but the researcher has to confirm the elution amounts before performing the experiments. In alumina cleanup process, which was commonly applied to remove the non-polar compounds and selected this method many country's official methods, the PCBs eluted until 2 % DCM 100 mL and 50 % DCM 40 mL, therefore the change of elution solvent is necessary to develop the simple procedure.

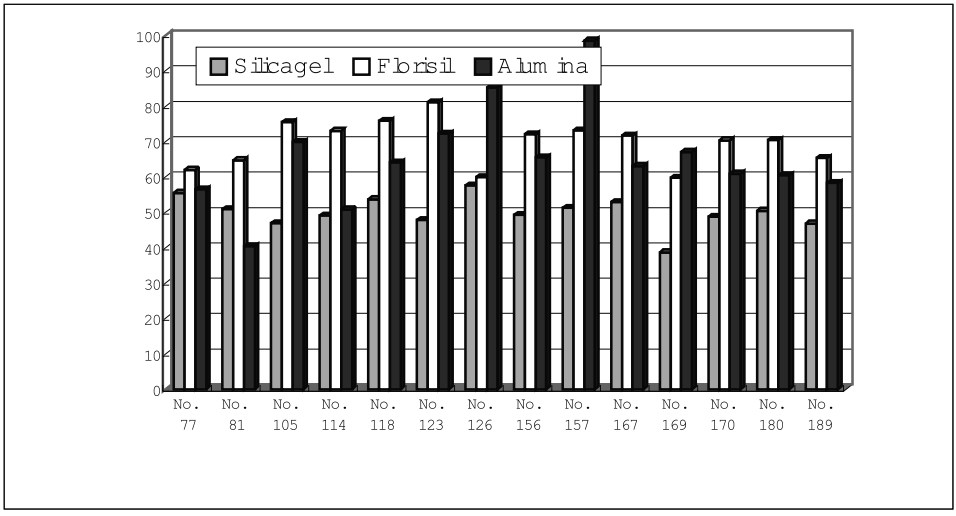

Figure 2. Recoveries of PCBs in cleanup process

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