MONITORING METHOD OF MONO- TO DECA-CHLORINATED BIPHENYLS / MONO- TO OCTA-CHLORINATED NAPHTHALENES USING SPE CARTRIDGE IN ATMOSPHERE

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summary

The Sep-Pak PS Air cartridge column was utilized to the analysis of PCB and polychlorinated Naphthalene in indoor atmosphere. Sampling was conducted for 24 hours at a flow-rate of 1-6 L/min yielding sample volumes of 2-9m^3. Eluting and adding an internal standard solution after, analysis was carried out with HRGC/HRMS. As a result, the isomer specific analysis was possible and even the simultaneous analysis of HCB were possible.

At that time, the rate of recovery was ranges from 80 to 110% even either isomer. Low chlorinated congeners like mono- through tri- chlorinated congeners, were possible to collect without doing break-through. The range of the detection limit was 0.8-2.0pg/m^3, in the case that collect 5 m^3 of atmosphere and calculated as 0.1mL of final solution quantity.

Introduction

Polychlorinated biphenyl (PCB) have been persisted during environment even now, although it was prohibited the production and the use of PCB about 30 years ago. Also, the accident that the condenser of fluorescent light that contains PCB with elementary school etc., explode is reported. Generally, the high-volume air sampler (Hi-Vol) is used, to the monitoring of environment atmosphere.(*1-5*) Even we are monitoring it by using Hi-Vol.(*6-8*) Levels of PCB in indoor and outdoor air is given by Currado and Harrad (*9*). However, to be not able to use in the space like indoor, that an apparatus is large-scale in this method, and also there is the risk that the substance of the low molecular weight like mono- through tri-chlorinated congeners causes brake through. The establishment of the monitoring method of the PCB that even included the low chlorinated congener is necessary to assess the risk to the human body in indoor and general environment.

Thereupon, the Sep-Pak PS Air cartridge column (*made of Waters*) that used to analyzing for the brominated benzene and the like before was utilized to the analysis of PCB and polychlorinated Naphthalene (PCN) in indoor atmosphere. After eluting, HRGC/HRMS was utilized to the isomer specific analysis of PCB and PCN.

Materials and Methods

sample collection and elution method

Connecting two pieces of the Sep-Pak PS Air (PS A) cartridges made of Waters was connected to a flow meter and pump. *(See Scheme 1, Picture 2)* We collected atmosphere for 24 hours with 1-6L/min of flow rate. The cartridges were connected to a syringe, and eluted with 30mL of 5% acetone in hexane or 5mL of dichrolomethane. *(See Scheme 2)* The eluate was concentrated to 0.1mL under nitrogen stream and added a solution of ^{13}C labeled PCB as an internal standard (*MBP-CG made of Wellington: 10 Congeners were mixed solution that one of each mono- through deca-chlorinated congeners.*) *(See Table 1)* It was the solution for analytical sample.

Preparation of the standard solution

It was used for PCB calibration standard that was 19 congeners mixture of mono- through deca-chlorinated PCB (*BP-WD made of Wellington Laboratories*). *(See Table 1)* It was diluted to the range from 0.1 to 20ng/mL with nonane, added a solution of ^{13}C labeled PCB as an internal standard. It was used for PCN calibration standard that was 18 congeners mixture of mono- through octa-chlorinated PCN (*PCN MX-B made of Wellington Laboratories*). It was diluted and added like in the case of PCB.

GC/MS-SIM Conditions

HRGC/HRMS-SIM analyses of PCB and PCN congeners were carried out on a JMS-700 mass spectrometer (*JEOL*) connected to a HP5890 gas chromatograph (*Hewlett Packard*). Gas chromatographic separation of samples was carried out on 25m fused silica capillary column of 0.2mmID. coated with a 0.33um film of 5% diphenyl polydimethylsiloxane (*HP Ultra-2, Hewlett Packard*). Helium was used as carrier gas at a flow late of 1.2ml/min. An aliquot of 1uL of the sample was injected. The injection port temperature was 250°C. The interface temperature was 250°C. The chamber temperature was 250°C. The HRGC was temperature programmed from 120°C (2min) - 6°C/min - 300°C (0min) (total 32min). The mass spectrometer was operated in electron impact ionization mode with ionization energy of 38eV. The resolution was more than 10,000 (at m/z 293 of perfluorophenanthlene). The monitored ions (m/z) were shown in Table 2-1 and 2-2.

Results and Discussion

Recovery test

It connected 3 pieces of PS A cartridges and added a solution of ^{13}C labeled PCB standard (*MBP-CG*) and a solution of PCN standard (PCN MX-B) to one on the side of atmosphere, furthermore, 3 pieces of PS A cartridges were connected on the side of atmosphere. Then indoor atmosphere was collected about 4m^3. Although the result of a recovery test is shown in Figure 1, the rate of recovery was ranges from 80 to 110% even either isomer. Low chlorinated congeners like mono- through tri- chlorinated congeners, were possible to collect without doing break-through. The PS A Cartridge was as well possible to collect 9 m^3 of atmosphere for 24 hours, because the pressure drop is small. Accordingly, it was discovered, that it is an excellent adsorbent to collect more than 1 m^3 of atmosphere.

Detection Limit Values

The detection limit is 3 times as the standard deviation in the time that measured 1pg each PCB congeners the repetition 7 times with HRGC/HRMS. The range of the detection limit was 0.8-2.0pg/m^3, in the case that collect 5 m^3 of atmosphere and calculated as 0.1mL of final solution quantity. *(See Table 3)*

Homologue Distributions and Isomeric Pattern in Atomosphere

About 4m^3 of the indoor atmosphere was collected with PS A Cartridges and was measured with HRGC/HRMS. The homologue distribution of PCB was shown in Figure 2. Tri-chlorinated congeners were predominant. Similarly the homologue distribution of PCN was shown in Figure 3.

Figure.4 shows the example of component ratios of the PCB congeners in indoor air. Predominant PCB congeners were #5/#8, #11, #18, #17, #16/#32, #28/#31, #20/#33, #22, #73/#52, #43/#49, #47/#48/#75, #44, #41/#64/#68, #70, 76/#80/#66, 83/#95, #101/#90, #110, #118. Predominant PCB congeners of di-chlorinated isomers in indoor air were #5/#8, #11, #12/#13, and #15, as in the case of ambient air.(*8*)

Conclusion

As a result that the PCB and PCN in indoor atmosphere is measured by using PS Air the advantage like the following was found out.

1 Low chlorinated congeners like mono- through tri- chlorinated congeners, were possible to collect without doing break-through.
2 Because the pressure drop is small, the PS A Cartridge was as well possible to collect 9 m^3 of atmosphere for 24 hours.

Accordingly, it was discovered, that it is an excellent adsorbent to collect atmosphere.

References

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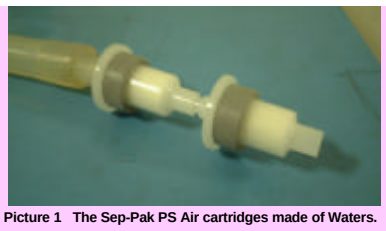
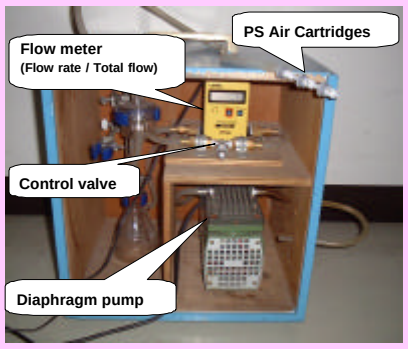
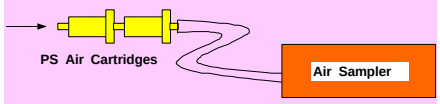


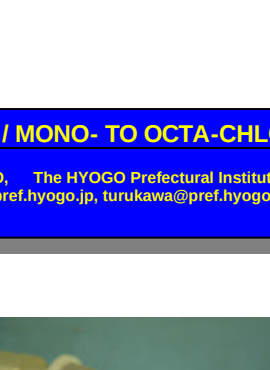
Picture 1 The Sep-Pak PS Air cartridges made of Waters.



Picture 2 Air sample collection with PS Air cartridge.



Scheme 1 Apparatus of the atmosphere collection method that used PS Air cartridge.



Scheme 2. Elution method from PS Air cartridges.

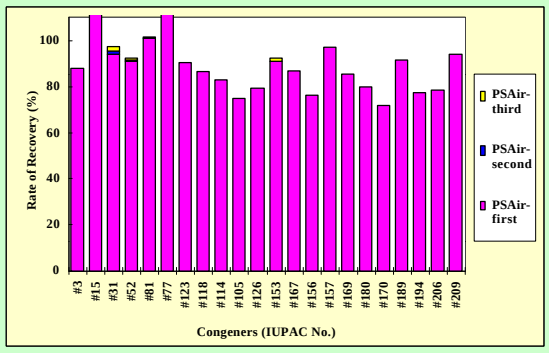


Figure 1 The result of recovery test in 13C labeled PCB congeners (IUPAC designation).

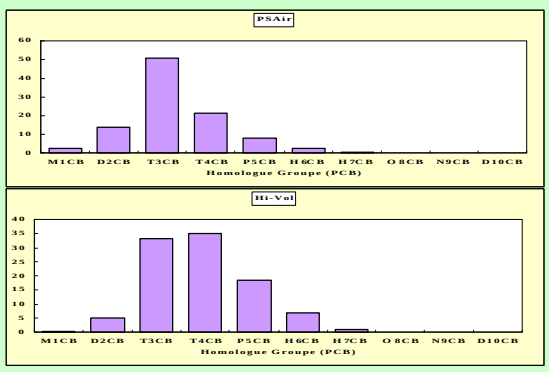


Figure 2 The homolog distribution of PCB case that collected 4m^3 of the indoor air by PS Air cartriges and 1,000m^3 of the indoor air by Hi-Vol.

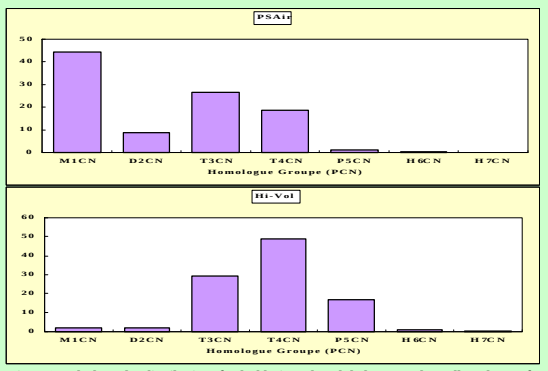


Figure 3 The homolog distribution of polychlorinated naphthalene case that collected 4m^3 of the indoor air by PS Air cartriges and 1,000m^3 of the indoor air by Hi-Vol.

Table 1 PCB standard solutions for analyzing.

MBP-CG (Wellington)	
Mass-Labelled Mono- To Decachloro PCB Solution/Mixture (13C12)	
IUPAC #3	4-Chloro[13C12]biphenyl
IUPAC #15	4,4'-Dichloro[13C12]biphenyl
IUPAC #31	2,4',5-Trichloro[13C12]biphenyl
IUPAC #52	2,2',5,5'-Tetrachloro[13C12]biphenyl
IUPAC #118	2,3',4,4',5-Pentachloro[13C12]biphenyl
IUPAC #153	2,2',4,4',5,5'-Hexachloro[13C12]biphenyl
IUPAC #180	2,2',3,4,4',5,5'-Heptachloro[13C12]biphenyl
IUPAC #194	2,2',3,3',4,4',5,5'-Octachloro[13C12]biphenyl
IUPAC #206	2,2',3,3',4,4',5,5',6-Nonachloro[13C12]biphenyl
IUPAC #209	2,2',3,3',4,4',5,5',6,6'-Decachloro[13C12]biphenyl
BP-WD (Wellington)	
PCB-Window Defining Solution/Mixture for DB-5 or Equivalent Column (Native)	
IUPAC #1	2-Chlorobiphenyl
IUPAC #3	4-Chlorobiphenyl
IUPAC #10	2,6-Dichlorobiphenyl
IUPAC #15	4,4'-Dichlorobiphenyl
IUPAC #19	2,2',6-Trichlorobiphenyl
IUPAC #37	3,4,4'-Trichlorobiphenyl
IUPAC #54	2,2',6,6'-Tetrachlorobiphenyl
IUPAC #77	3,3',4,4'-Tetrachlorobiphenyl
IUPAC #104	2,2',4,6,6'-Pentachlorobiphenyl
IUPAC #126	3,3',4,4',5-Pentachlorobiphenyl
IUPAC #155	2,2',4,4',6,6'-Hexachlorobiphenyl
IUPAC #169	3,3',4,4',5,5'-Hexachlorobiphenyl
IUPAC #188	2,2',3,4',5,6,6'-Heptachlorobiphenyl
IUPAC #189	2,3,3',4,4',5,5'-Heptachlorobiphenyl
IUPAC #202	2,2',3,3',5,5',6,6'-Octachlorobiphenyl
IUPAC #205	2,3,3',4,4',5,5',6-Octachlorobiphenyl
IUPAC #206	2,2',3,3',4,4',5,5',6-Nonachlorobiphenyl
IUPAC #208	2,2',3,3',4,5,5',6,6'-Nonachlorobiphenyl
IUPAC #209	2,2',3,3',4,4',5,5',6,6'-Decachlorobiphenyl

Table 2-1 Monitored ions of PCBs (Injection 1)

G#:1 Repeat:1.20[sec], m/z: 265.0- 405.8 (1.53M)	
Compound name	m/z
HCB	283.8102
HCB	285.8072
13C6-HCB	289.8303
PCB4	289.9224
PCB4	291.9194
Lock Check	292.9824
Mass Lock	292.9824
PCN-5	299.8648
PCN-5	301.8619
13C-PCB4	303.9597
PCB5	325.8805
PCB5	327.8776
PCN-6	333.8258
PCN-6	335.8229
13C-PCB5	337.9207
PCB6	359.8415
PCB6	361.8386
PCN-7	367.7869
PCN-7	369.7839
13C-PCB6	371.8817
PCB7	393.8025
PCB7	395.7996
13C-PCB7	405.8428

Table 2-2 Monitored ions of PCBs (Injection 2)

G#:1 Repeat:1.00[sec], m/z: 160.0- 268.0 (1.68M)	
Compound name	m/z
PCN-1	162.0236
PCN-1	164.0208
Lock Check	180.9888
Mass Lock	180.9888
PCB1	188.0393
PCB1	190.0364
PCN-2	195.9847
PCN-2	197.9818
13C-PCB1	200.0795
PCB2	222.0003
PCB2	223.9979
PCN-3	229.9457
PCN-3	231.9428
13C-PCB2	234.0406
PCB3	255.9613
PCB3	257.9587
PCN-4	263.9067
PCN-4	265.9038
13C-PCB3	268.0016

G#:2 Repeat:0.70[sec], m/z: 392.0- 509.7 (1.30M)	
Compound name	m/z
PCN-8	401.7479
PCN-8	403.745
PCB8	427.7636
PCB8	429.7606
13C-PCB8	441.7999
Lock Check	454.9729
Mass Lock	454.9729
PCB9	461.7246
PCB9	463.7216
13C-PCB9	475.761
PCB_10	497.6826
PCB_10	499.6797
13C-PCB_10	509.723

Table 3 The detection limit (pg/m3) of the polychlorinated biphenyl in the time that did atmosphere a/th 5m^3 collection by using PS Air cartridge.

Compounds	Detection limit
Mo1CBs	0.8
Di2CBs	0.8
Tr3CBs	0.8
Te4CBs	2
Pe5CBs	2
Hx6CBs	2
Hp7CBs	2
O8CBs	2
N9CBs	2
De10CBs	2

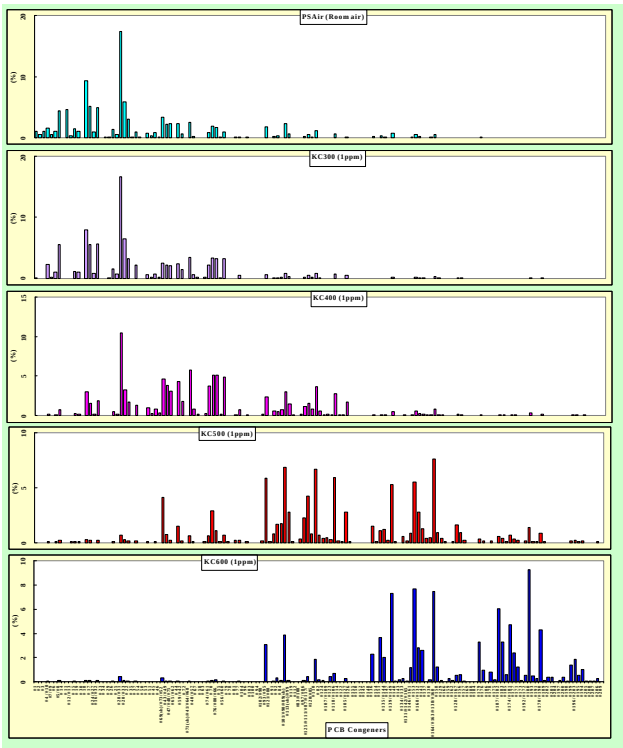


Figure 4 Isomer distribution in during atmosphere. Horizontal axis is IUPAC number of PCB congener.

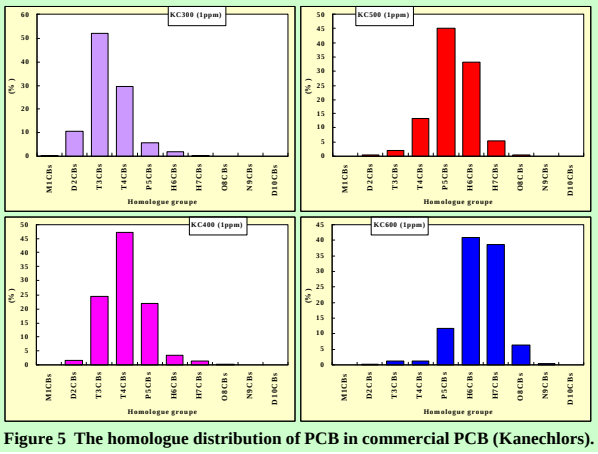


Figure 5 The homologue distribution of PCB in commercial PCB (Kanechlors).