

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

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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. Sampling was conducted for 24 hours at a flow-rate of 1-6 L/min yielding sample volumes of 2-9m³. 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.

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) We collected atmosphere for 24 hours with 2~9L/min of flow rate. The cartridges were connected to a syringe, and eluted with 30mL of 5% acetone in hexane. The eluate was concentrated to 0.1mL under nitrogen stream and added a solution of ¹³C 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.) It was the solution for analytical sample.

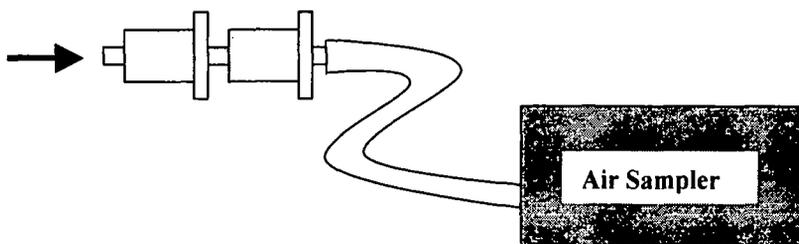
Preparation of the standard solution It was used for PCB calibration standard that was 19 congeners mixture of mono- through deca-chlorinated PCB (BP-WD made of Wellington Laboratories). It was diluted to the range of 0.1~20ng/mL with nonane, added a solution of ¹³C labeled PCB as an internal standard. 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

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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 rate 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).



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

Results and Discussion

Recovery test It connected 3 pieces of PS A cartridges and added a solution of ^{13}C labeled PCB standard (PCN MX-B) 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 of 80~110% 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 9m^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 1m^3 of atmosphere.

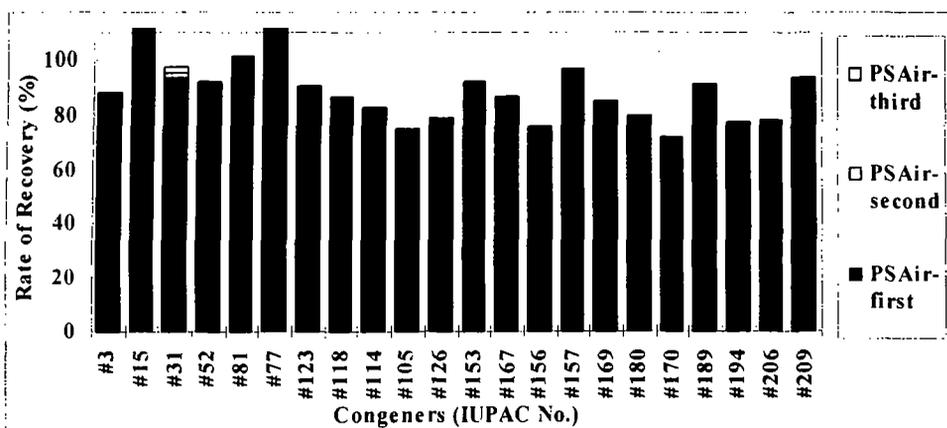


Figure1 The result of recovery test in ^{13}C labeled PCB congeners (IUPAC designation).

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/m³, in the case that collect 5 m³ of atmosphere and calculated as 0.1mL of final solution quantity.

Homologue Distributions and Isomeric Pattern in Atmosphere

About 4m³ 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. Trichlorinated 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)

Table 1 The detection limit of the polychlorinated biphenyl in the time that did atmosphere a/the 5m³ collection by using PS Air cartridge.

Compounds	Detection limit (pg/m3)
Total-PCBs	2
Mo1CBs	0.8
Di2CBs	0.8
Tr3CBs	0.8
Te4CBs	2
Pe5CBs	2
Hx6CBs	2
Hp7CBs	2
O8CBs	2
N9CBs	2
De10CBs	2

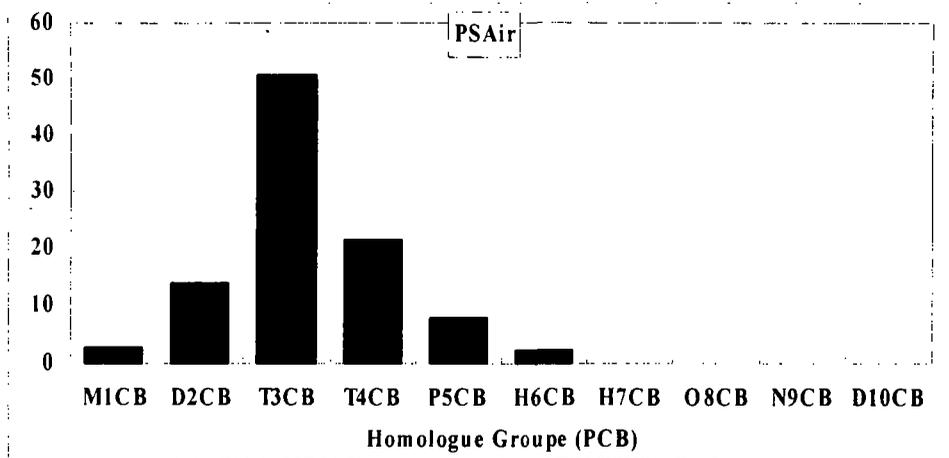


Figure 2 The homolog distribution of polychlorinated biphenyl case that collected 4m³ of the indoor air by PS Air cartridges.

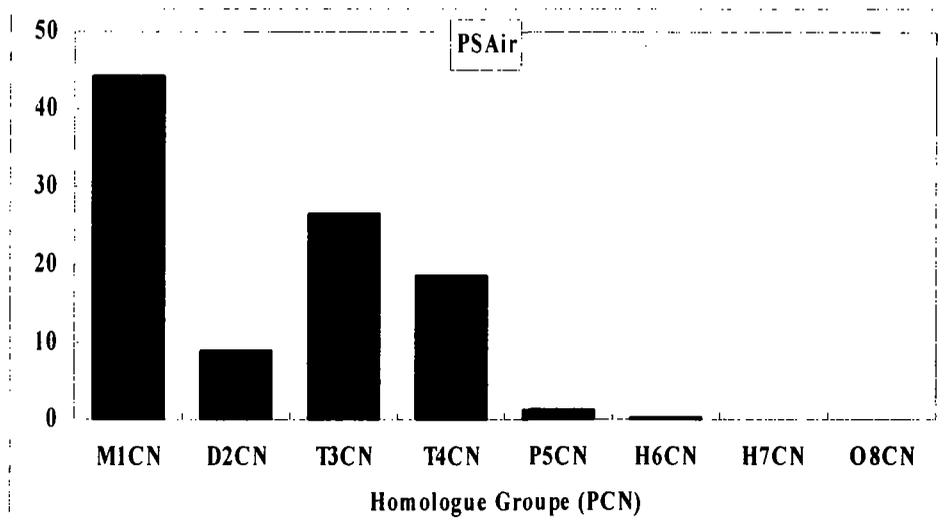


Figure 3 The homolog distribution of polychlorinated naphthalene case that collected 4m³ of the indoor air by PS Air cartridges.

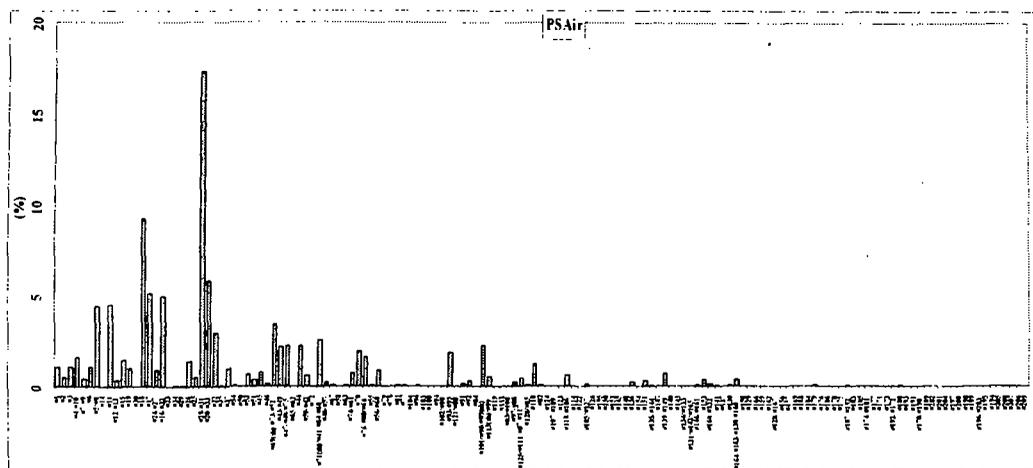


Figure 4. It is isomer distribution in during atmosphere. Horizontal axis is IUPAC number of PCB congener. PS Air Cartridges

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