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ONLINE MONITORING OF PCB IN AIR AND EXHAUST GAS FROM PCB DECOMPOSITION PROCESS

Masuyoshi Yamada[1], Masao Suga[1], Izumi Waki[1], Nobuyuki Shibata[2], Katsunori Kato[2]

[1] Hitachi, Ltd., Central Research Laboratory, 1-280, Higashi-Koigakubo, Kokubunji, Tokyo 185-8601, Japan
[2] Hitachi High-Technologies Corp., 24-14 Nishi-shimbashi, 1-chome, Minatoku, Tokyo 105-8717, Japan

Introduction

Polychlorinated biphenyls (PCBs) have been widely used in Japan in various applications such as insulating oil in electrical transformers and electrical capacitors since 1954. Once PCB was found to have biologically harmful effects, its production was stopped in 1972. Most of the existing PCBs have been stored since then. Several PCB decomposing processes have been proposed, which have been already used in large scale disposal plants and have been successful in decomposing PCB without the emission of pollutant compounds.[1]

High-speed online gas monitoring of PCB in gas is important in safely operating a PCB disposal plant. There are three sampling points where PCB monitoring is needed: (1) the working environment air in the process area of cleaning PCB-contaminated equipments; (2) the exhaust gas from PCB decomposition process; (3) the ambient air around the disposal plant. High-speed online monitoring at these points is effective to quickly alert workers in the plant or people living near the plant in an emergency. According to Japanese regulations, the monitor needs to have a detection limit lower than 100 $\mu g/Nm^3$ in the working environment air in the PCB disposal plant and in the exhaust gas from the decomposition process.

Similar to the analysis of dioxin in flue gas, the method for conventional GC/MS analysis of PCB requires a complicated enrichment/cleanup process of samples and takes several weeks. Therefore, this method is not applicable for the above–mentioned high-speed monitoring for PCB disposal plant. To respond in an emergency at a plant, hourly PCB pollutant emission monitoring is required.

We propose an online PCB monitor using atmospheric pressure chemical ionization (APCI) and ion trap mass spectrometry (ITMS). The combination of positive and negative ionization is used to increase the monitor's sensitivity. The APCI/ITMS system has been used to continuously measure chlorophenol[2] and chlorobenzene[3] in incinerator flue gas at one-minute time intervals. The system can measure these dioxin precursors at sub ppb levels.

In this paper, we investigated the sensitivity of the online monitor by analyzing PCB in the ambient air with positive and negative ionization modes. From di- to hepta- chlorinated biphenyls were analyzed because more than 95% of the PCB product (Kanechlor) was composed from di- to hepta- chlorinated biphenyls.

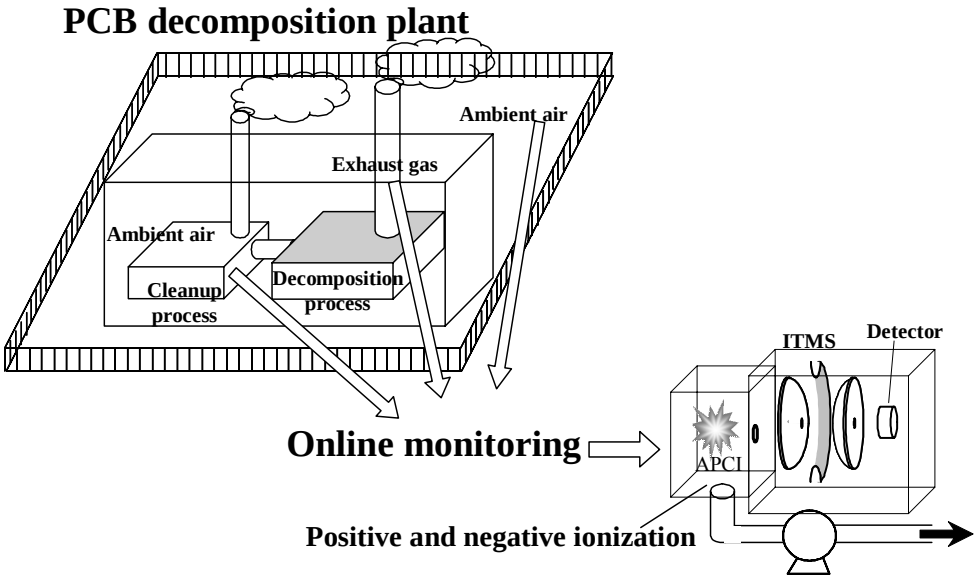

Fig.1: Concept of PCB online monitoring

Methods and Materials

Figure 1 shows the concept of the PCB online monitoring system that we developed. Samples from ambient air or exhaust gases are monitored directly. Without the PCB isomer separation done by GC, gas samples are continuously introduced into the APCI source. The ions are sent to the ion trap through a differential pumping region and then mass-analyzed. At the APCI source, positive or negative ionization mode can be selected to increase sensitivity. For a positive ionization mode, each PCB can be detected as a M^+ ion, where M designates a PCB molecular formula. Since positive ionization produces a large number of ions from the background gas, some of these positive ions may interfere with M^+ PCB ions as chemical noises. To improve the signal to noise ratio (S/N), tandem mass spectrometry MS/MS by collision induced dissociation (CID) is applied to M^+ ions. After Chlorine is abstracted from M^+ ions, the product ion $(M\text{-}Cl)^+$ is measured. This dechlorination from M^+ ions is also observed with chlorobenzene[3]. For negative ionization, PCB is mainly ionized as $(M\text{-}Cl+O)^-$. This ion is measured without MS/MS because the negative ionization has high selectivity due to each molecule's high acidity, resulting in very few chemical noises. Finally, the concentration of each PCB congener from di- to hepta- is obtained from the area of their mass-spectral peaks. The monitored mass number (m/z) of each congener is shown in table 1. We monitored the highest peak among the chlorine isotope peaks.

Table 1: Monitored mass numbers of PCBs with positive and negative ionization

Congener	Positive + MS/MS $M^+ \rightarrow (M\text{-}Cl)^{+}$ *1 m/z	Negative $(M\text{-}Cl+O)^-$ m/z
DiCB	222 → 187	203
TriCB	256 → 221	237
TetraCB	290 → 255	271
PentaCB	326 → 291	307
HexaCB	360 → 325	341
HeptaCB	394 → 359	375

*1: For example, "222 → 187" means that the precursor molecular ion m/z 222 M^+ is dissociated by CID. Product ion $(M\text{-}Cl)^+$ of m/z 187 is monitored.

We investigated the sensitivity of the online monitor. A PCB mixture, Kanechlor standard sample (KC-300, or 500, or 600) was put into a sample holder in which the temperature was controlled using an electric heater and a thermocouple. A trace amount of each sample was vaporized and added to ambient air flowing at a constant rate and sent to the APCI source. The temperature of the sample holder was stabilized to obtain a constant PCB concentration. Each PCB signal was measured for four hours using the online monitor with 10 seconds time resolution. Simultaneously, the sample gas was branched to be absorbed in 50 ml of hexane so that the PCB concentration could be quantified using GC/MS (GC column: DM-5MS, MS: Hitachi M-9000). The PCB concentration was varied from several ppt to sub ppb by changing the sample holder temperature. The limit of detection was obtained for each PCB congener.

Results and Discussion

Figure 2 shows the mass spectrum of KC-600 when negative ionization was applied. The concentration of penta-CB, hexa-CB, hepta-CB was 7, 20, 7 μg/Nm^3, respectively. As mentioned above, main peaks of (M-Cl+O)- ions were observed for penta-, hexa-, and hepta-CB. Very few fragment ions derived from the PCB's were observed.

Table 2 shows the limit of detection of when positive and negative ionization was applied. The detection limit was estimated at S/N=3, where N is the noise derived by the standard deviation of background noise level. With positive ionization, the limit of detection is in the range of 0.1-1.0 μg/Nm^3. With negative ionization, the highly chlorinated congeners have lower limit of detection, in the range of 0.1-8 μg/Nm^3. This result shows that negative ionization efficiency increases with the degree of chlorination.

Positive ionization gives lower limit of detection for di-, tri- and tetra-CB. Negative ionization gives lower limit of detection for penta- hexa-, and hepta-CB. Thus, switching the ionization polarity periodically according to above combination would give the best sensitivity. In this case, the sum of the limits of detection from di- to hepta-CB becomes 0.76 μg/Nm^3 which is low enough to measure the ambient air in the PCB decomposition plant.

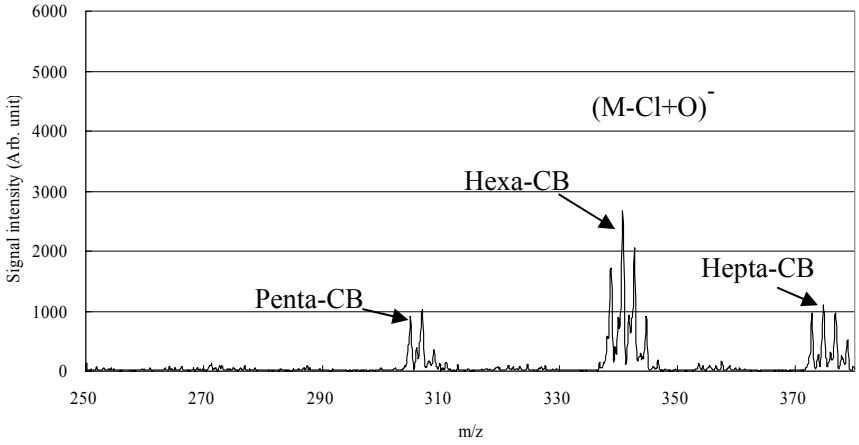

Fig. 2: Mass spectrum of KC-600 obtained by APCI/ITMS

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References

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Table 2: Limit of detection of each congener of PCB when positive and negative ionization is applied.

Congener	Limit of detection [μg/Nm^3]	
	Positive + MS/MS	Negative
DiCB	0.03	3.5
TriCB	0.16	7.7
TetraCB	0.27	1.5
PentaCB	0.98	0.14
HexaCB	0.24	0.08
HeptaCB	0.45	0.08