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Continuous monitoring of polychlorinated biphenyls in air using direct sampling APCI/ITMS

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Abstract

We report a continuous monitoring system of polychlorinated biphenyls (PCBs) in air, which uses direct sampling atmospheric pressure chemical ionization (APCI)/ion trap mass spectrometry (ITMS). In APCI, humidity in the atmosphere, which fluctuates from 0 to 10 vol.%, influences PCB sensitivity. In dry air (0.5% humidity), the detection limits of Di- to Hp-chlorinated biphenyls (CB) are 0.01–0.44 μg/Nm^3 (μg/m^3 at normal condition) with time resolution of 1 min, whereas the sensitivity decreases to less than 1/10 when water vapor concentration is 10 vol.%. The sensitivity decrease is calibrated in real-time using an internal standard, trichlorophenol. In order to obtain the calibration accuracy of ±30%, we dilute the sample gas by dry air, decreasing the water vapor concentration below 1%. We applied the monitor to measure Di- to Hp-CB in ventilation air from a PCB decomposition plant. The monitored PCB concentration levels agreed well with that by high-resolution gas chromatography/high resolution mass spectrometry (HRGC/HRMS).

Keywords: APCI; Ion trap; Environmental analysis; Real-time monitoring; Polychlorinated biphenyls

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1. Introduction

Polychlorinated biphenyls (PCBs) were widely used for electrical equipment, heat transfer systems, plasticizers, etc. [1]. Although PCBs production was stopped in 1970s, they persist in the environment for many years and can be found in the air, water, soil, and food [1–3]. In 1978, U.S. Environmental Protection Agency (EPA) began to regulate the storage and disposal of PCBs [4], where PCBs are disposed by incineration. In Japan, wastes containing PCBs have remained untreated for a long time [5]. Recently, several PCB decomposing processes have been proposed [5,6], some of which have already been used in large-scale decomposition plants and have been successful in decomposing PCB.

For safer operation of PCB decomposition plant, it is desirable to measure PCB emission from the PCB decomposition plants by on-site monitoring. Japanese regulation [7,8] specifies that: (1) the ambient air of the working environment in the plant is less than 100 μg/Nm^3 (μg/m^3 at normal condition); (2) the exhaust gas from the PCB decomposition process is less than 150 μg/Nm^3. To constantly ensure the safety of the workers in the plant and people living nearby, it is desirable that the sensitivity of the monitoring system was about 10 μg/Nm^3, and the monitoring is continuous with time interval of less than 1 h.

There are several analytical methods to measure PCB in the environment. One method to analyze PCB in aqueous samples is described in the EPA method 1668A [9], which uses high-resolution gas chromatography and high-resolution mass spectrometry (HRGC/HRMS). For a routine analysis, combination of gas chromatography and other mass spectrometers are used [10,11]. These analyses of PCB require a

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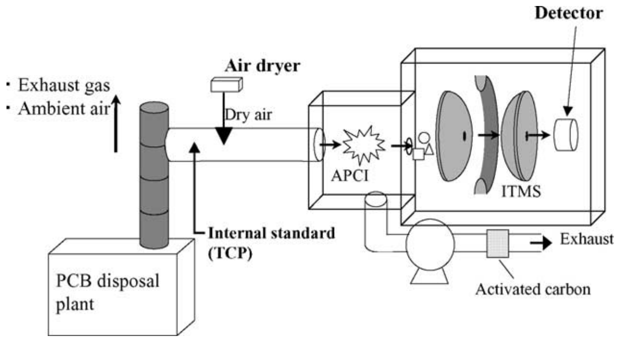

Fig. 1. Schematic drawing of PCB online monitor, which uses direct sampling atmospheric pressure chemical ionization coupled with ion trap mass spectrometry.

complicated enrichment/cleanup process of the samples and take more than 5 h. Therefore, these methods cannot be applied for the aforementioned continuous monitoring at a PCB decomposition plant. For this purpose, Kira et al. reported a laser-ionization/TOF-MS system for Di- to Hx-chlorinated biphenyls (CB) [12,13] in gas with time resolution of minutes. Their sensitivities for Di-CB, Tr-CB, and Te-CB in clean nitrogen were 0.11, 0.48, and 0.80 μg/Nm^3, respectively. In a field test, they monitored steady levels of PCB concentration below 10 μg/Nm^3 in exhaust gas of a PCB decomposing process.

In this paper, we report a PCB continuous monitoring system for ambient air using atmospheric pressure chemical ionization (APCI) and ion trap mass spectrometry (ITMS), whose sensitivity is 0.01–0.44 μg/Nm^3 for Di- to Hp-CB. These homologues are target compounds for monitoring because they cover 95% of the PCB product Kanechlor [14]. We applied this system to the monitoring of ventilation air from sodium-dispersion-process in a PCB decomposition plant, where we observed transient emission of PCB in the range of ∼5 μg/Nm^3 synchronized with the PCB decomposition process.

2. Experimental

2.1. Direct sampling online gas monitor

Fig. 1 shows the schematics of PCB online gas monitoring system. Sample gas is mixed with dry air and an internal standard upstream of an APCI ionization source. At the APCI source, flow rate of gas is 1 L/min and the temperature is 200 °C.

The produced ions are sent into an ion trap through a differential pumping region and then mass analyzed with 1 s time resolution [15,16]. Different degree of chlorination can by separated by ITMS. PCB isomers cannot be distinguished, however, since there is no GC separation prior to ionization.

APCI can ionize PCBs as either positive or negative ions. The PCB sensitivity differs between the two ionization polarities. In positive-APCI, PCB is ionized as an M$^+$ ion by the following reactions [17], where M designates a PCB molecular formula:

$$\mathrm{N_2 + e^- \rightarrow N_2{}^{+\bullet} + 2e^-} \quad (1)$$

$$\mathrm{N_2{}^{+\bullet} + 2N_2 \rightarrow N_4{}^{+\bullet} + N_2} \quad (2)$$

$$\mathrm{M + N_4{}^{+\bullet} \rightarrow M^{+\bullet} + 2N_2} \quad (3)$$

Because positive ionization produces a large number of ions from the background gas, some of these positive ions may interfere with M$^+$ ions as chemical noise. Tandem mass spectrometry MS/MS by collision induced dissociation (CID) can distinguish the PCB ions from the chemical noise better than single MS [16]. In our MS/MS of PCBs, chlorine is extracted from the M$^+$ ions by CID, after which the monitor measures the fragment ions (M–Cl)$^+$. Fig. 2 shows an example of the mass spectra for Hx-CB.

In negative-APCI, PCB is mainly ionized as (M–Cl + O)$^-$ by the following reactions [18]:

$$\mathrm{O_2 + e^- \rightarrow O_2{}^{-\bullet}} \quad (4)$$

$$\mathrm{M + O_2{}^{-\bullet} \rightarrow (M{-}Cl + O)^- + OCl^\bullet} \quad (5)$$

The monitor measures the phenoxide ions (M–Cl + O)$^-$, because few CID fragment ions are produced from (M–Cl + O)$^-$ by MS/MS. Very few chemical-noise ions are observed on the negative-APCI mass spectrum as shown in Fig. 3, which illustrates an example of negative ionization of Pe-, Hx-, and Hp-CB. Monoisotopic *m*/*z* value is 305, 339, and 373, respectively.

We obtain the concentration of each PCB congener from the area of their mass-spectral peaks. The monitored mass number (*m*/*z*) of each congener is shown in Table 1.

2.2. Detection limits in air

To compare the detection limits between positive and negative ionization, we measured PCB mixtures of Kanechlor standard sample KC-300, 500, and 600 (equivalent to Aroclor 1242, 1254, and 1260, respectively [14]). The samples were placed in a sample holder whose temperature was controlled to vaporize ppb concentration of the PCB mixtures. The produced PCB gas was mixed with laboratory environmental air (water concentration: 0.5%) flowing at a constant rate and sent to the APCI source. Simultaneously, the sample gas was branched to an impinger and collected in 50 ml of hexane, so that the PCB concentration could be analyzed by GC/MS (GC column: DB-5MS, MS: Hitachi M-9000). Table 2 shows the monitor's detection limit (S/N = 3, N: standard deviation of background noise) of each PCB congener for detection period of 1 min. With positive ionization, the detection limit was in the range of 0.01–0.44 μg/Nm^3. With negative ionization, the detection limit was in the range of 0.04–3.4 μg/Nm^3. The negative ionization efficiency increased as the degree of chlorination increases, which is similar to the increment of ionization efficiency of chlorinated benzene [18].

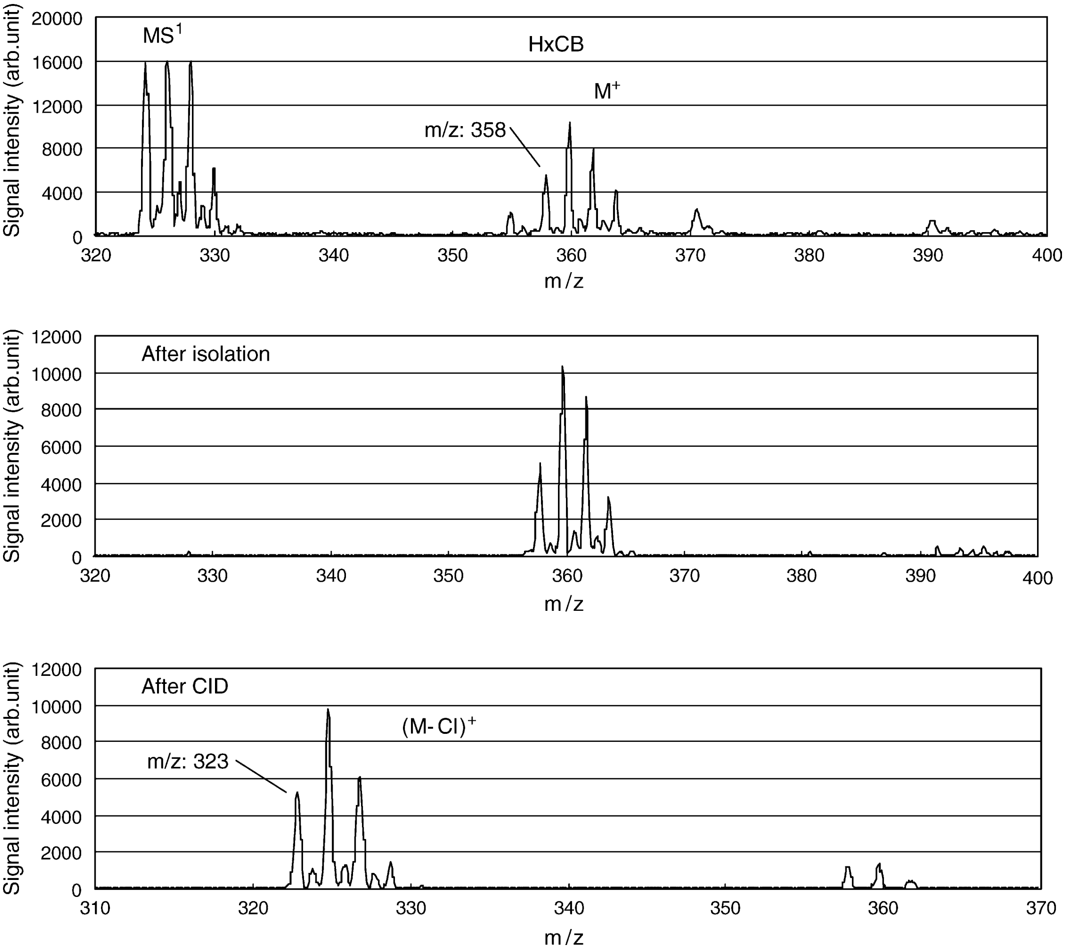

Fig. 2. Mass spectrum of positive-ionized hexa-chlorinated biphenyl before and after CID. The concentration of sample was 20 μg/Nm^3.

2.3. Interference of water vapor on PCB ionization

In APCI, impurities in sample gas interferes the ionization of target compounds, resulting in fluctuation of sensitivity [15,16]. In ambient air, the main impurity is water vapor, which fluctuates from 0 to 10 vol.%. To calibrate the sensitivity fluctuation in real-time, we used internal standard trichlorophenol. We did not choose ^{13}C-labeled PCBs to calibrate each congener because the cost of ^{13}C-labeled PCBs is high and they may be environmentally harmful effect.

We obtained the calibration accuracy of sensitivity fluctuation due to water as shown in Fig. 4. A constant concentration (about 10 ppb) of each PCB congener was introduced into the APCI source. Water vapor was added from a temperature-controlled impinger. One liter per minute of dry air from a gas cylinder was forced through the impinger. The water vapor concentration was changed by varying the temperature of the water.

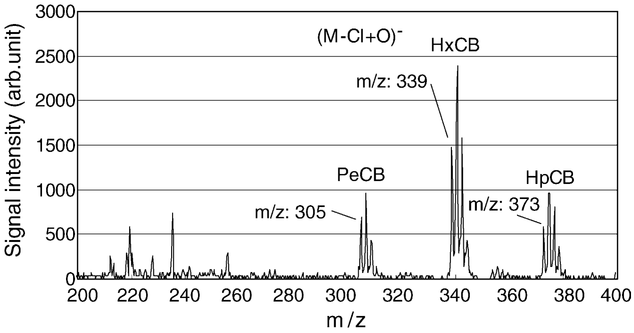

Fig. 3. Mass spectrum of negative ionized penta-, hexa-, and hepta-chlorinated biphenyl. The concentration of sample was 7, 10, and 7 μg/Nm^3, respectively.

Table 1
Monitored mass numbers of PCBs by positive and negative ionization

Congener	Positive + MS/MS M$^+$ → (M—C1)$^+$	Negative (M—Cl + O)$^-$
Di-CB	222 → 187 (187)	203 (203)
Tr-CB	256 → 221 (221)	237 (237)
Te-CB	290 → 255 (255)	273 (271)
Pe-CB	326 → 291 (289)	307 (305)
Hx-CB	360 → 325 (323)	341 (339)
Hp-CB	394 → 359 (357)	375 (373)

For example, “222 → 187” means that the precursor molecular ion *m/z* 222 M$^+$ is dissociated by CID. Fragment ion (M—Cl)$^+$ of *m/z* 187 is monitored. The values in the parenthesis indicate the monoisotopic *m/z* values.

Table 2
Detection limits (S/N = 3) of PCB in laboratory environmental air (water concentration: 0.5%) when positive (with MS/MS) and negative (without MS/MS) ionization are applied

Congener	Positive + MS/MS	Negative (µg/Nm^3)
Di-CB	0.01	1.6
Tr-CB	0.07	3.4
Te-CB	0.12	0.67
Pe-CB	0.44	0.06
Hx-CB	0.11	0.04
Hp-CB	0.20	0.04

They were obtained from the standard sample gas with PCB concentration 0.5–5.5 µg/Nm^3; S/N = 3; time resolution, 1 min.

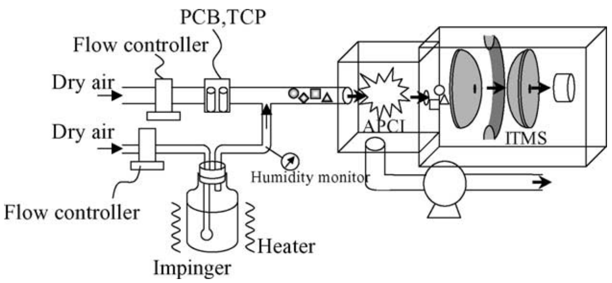

Fig. 4. Experimental setup to measure PCB and TCP sensitivity with various water vapor content ratios.

Figs. 5 and 6 show the response of PCB and TCP to H_2O concentration (vol.%) for positive and negative APCI. For negative APCI, Di-CB and Tr-CB are not measured because the sensitivity for the two congeners was too low to give reliable data. We define the normalized sensitivity (Sn) for each water concentration as the signal intensity divided by the signal intensity without water vapor. For both positive and negative ionizations, normalized sensitivities of each PCB congener decrease as the water concentration increases.

In positive APCI, water vapor influences the ionization process of N_2 by the following reactions (6)–(9) [17,19]:

$$H_2O + N_4^{+\bullet} \rightarrow H_2O^{+\bullet} + 2N_2 \quad (6)$$

$$H_2O^{+\bullet} + H_2O \rightarrow H_3O^{+} + OH^{\bullet} \quad (7)$$

$$H_3O^{+} + H_2O + N_2 \rightarrow (H_2O)_2H^{+} + N_2 \quad (8)$$

$$(H_2O)_{n-1}H^{+} + H_2O + N_2 \rightarrow (H_2O)_nH^{+} + N_2 \quad (9)$$

The reaction (6) suppresses the ionization reaction (3) of PCB and the internal standard TCP.

In negative APCI, we conjecture the following reaction can decrease the PCB's ionization efficiency.

$$O_2^{-\bullet} + nH_2O \rightarrow (H_2O)_nO_2^{-\bullet} \quad (10)$$

$$M + (H_2O)_nO_2^{-\bullet} \rightarrow (M\text{–}Cl + O)^{-} + OCl^{\bullet} + nH_2O \quad (11)$$

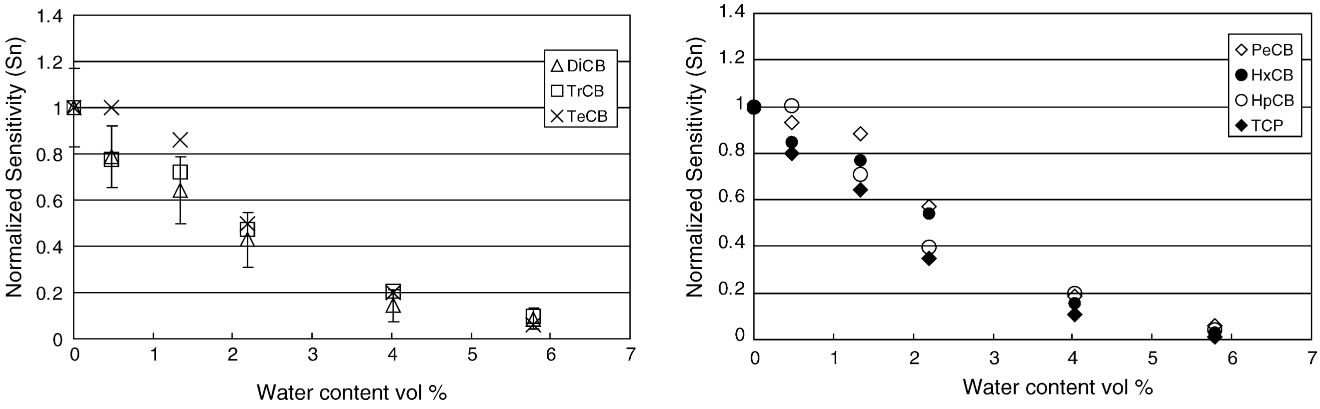

Fig. 5. Normalized sensitivity of PCB and TCP vs. water vapor content ratio, for positive APCI.

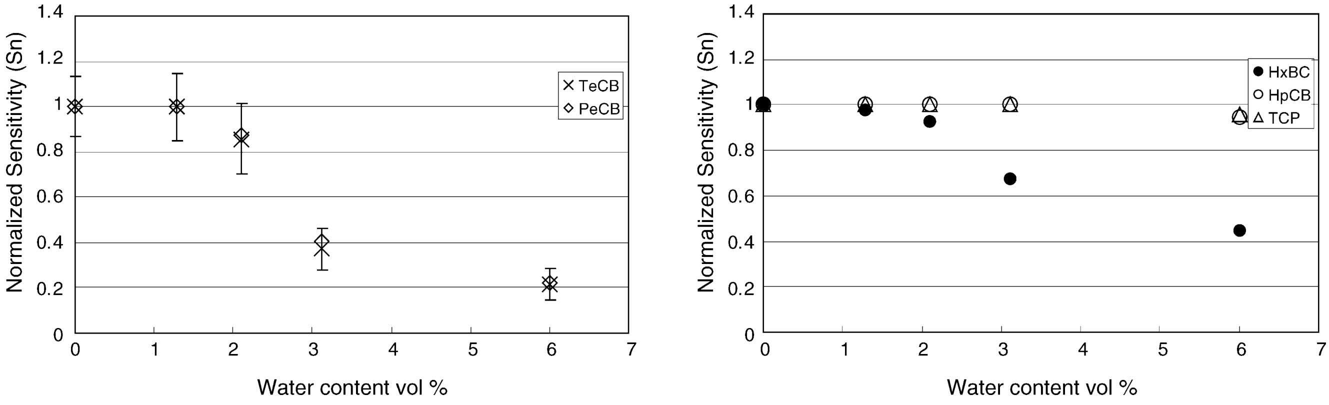

Fig. 6. Normalized sensitivity of PCB and TCP vs. water vapor content ratio, for negative APCI.

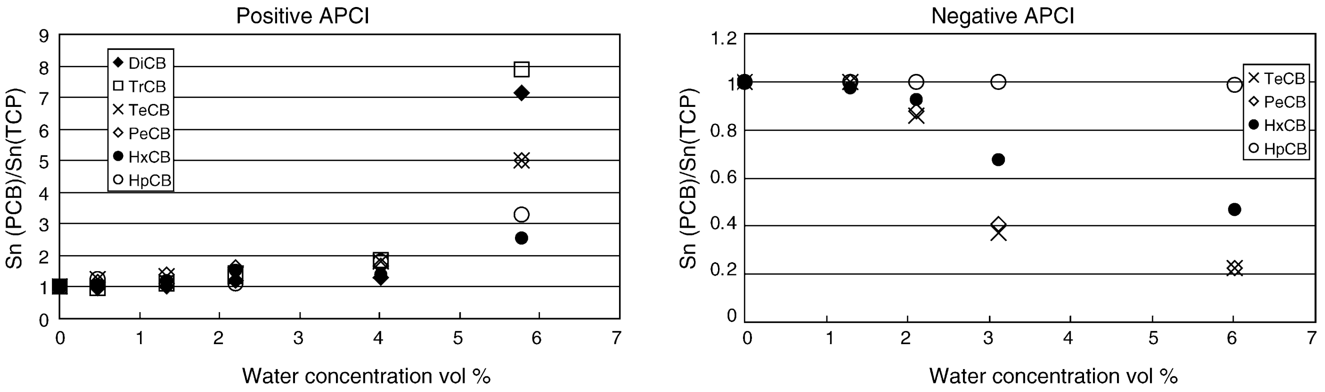

Fig. 7. The ratio of Sn(PCB)/Sn(TCP) versus water vapor content ratio.

The sensitivities of Te-CB and Pe-CB are significantly decreased as shown in Fig. 6, because the reaction rate of (11) may be lower than that of (5).

Fig. 7 shows the ratio between normalized sensitivities of PCB congeners and TCP Sn(PCB)/Sn(TCP). If the ratio is equal to 1, the calibrated PCB concentration is accurate. Fig. 7 shows that, at high water vapor concentration of more than 3 vol.%, the ratio of Sn(PCB)/Sn(TCP) moves significantly away from 1.0 and the monitor's calibration is not accurate, for both positive and negative ionization. When positive ionization is applied and water vapor concentration is less than 1 vol.%, the ratio of Sn(PCB)/Sn(TCP) for Di- to Hp-CB are in the range of 1.0 ± 0.3. Therefore, the sample gas needs to be diluted by dry air to decrease the water vapor concentration less than 1% to obtain quantitation accuracy of ±30%.

When negative ionization is applied and water vapor concentration is less than 2.5 vol.%, the ratio of Sn(PCB)/Sn(TCP) for Te- to Hp-CB are in the range of 1.0 ± 0.3. Negative ionization is, however, not applicable to obtain total PCB detection limit of 10 μg/Nm^3 because the sensitivity of Di- and Ti-CB is low.

3. Results and discussions

We applied the positive-APCI/ITMS system to monitor Di- to Hp-CB in ventilation air from a PCB decomposition plant. Dry air of 2.3 L/min was added to 1 L/min sample gas and introduced to the ion source, so that the water vapor concentration decreased to less than 0.3%. Fig. 8 shows typical mass spectrum at decomposition process. Dominant peaks on the spectrum originated from water vapor, which is seen as $(H_2O)_2H^+$ and $(H_2O)_3H^+$. $(H_2O)H^+$ is not observed because it was below the mass range of ITMS. In addition to water-origin ions, minor peaks related to isopropyl alcohol could be observed.

Fig. 9 shows the correlation between the PCB concentration in ventilation air obtained by APCI/ITMS monitoring system and the concentration analyzed by HRGC/HRMS. The PCB concentration obtained by APCI/ITMS is calibrated by TCP internal standard as described in the previous section. Each APCI/ITMS point indicates the average concentration for 1 h continuous monitoring. The sampling period for HRGC/HRMS analysis is also 1 h. Because the PCB emission level in the process gas is lower than several μg/Nm^3, we intentionally added pure PCB (Kanechlor 300–600) samples to the gas to obtain the PCB concentration higher than 4 μg/Nm^3. The correlation factor R^2 between the concentration analyzed by APCI/ITMS and that analyzed by HRGC/HRMS are from 0.96 to 0.99.

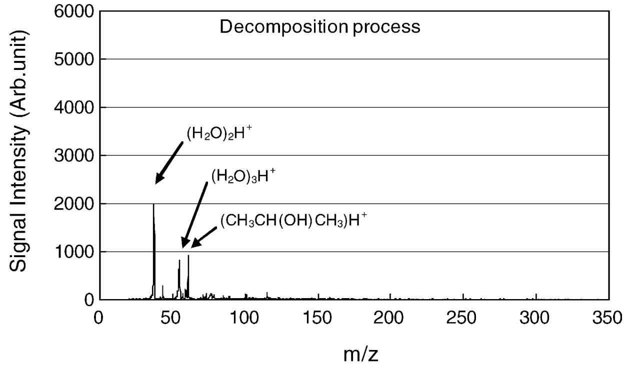

Fig. 8. Mass spectrum of the ventilation air from PCB decomposition process.

The limit of detection (S/N = 3) of each PCB congener is listed in Table 3. The total detection limit as defined by

Table 3
Detection limits (S/N = 3) of PCB in ventilation air from PCB decomposition process

Congener	Positive + MS/MS (μg/Nm^3)
Di-CB	0.27
Tr-CB	0.66
Te-CB	0.09
Pe-CB	0.15
Hx-CB	0.17
Hp-CB	0.17

They were obtained from the gas with PCB concentration 1.0 – 6.1 μg/Nm^3; S/N = 3; time resolution, 2 min.

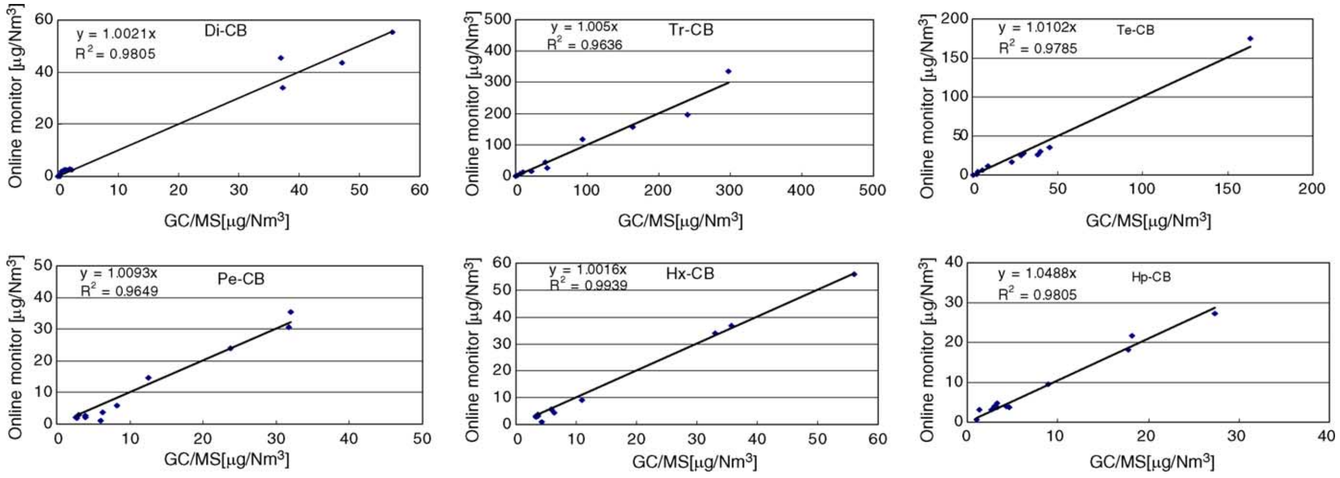

Fig. 9. Comparison of the calibrated PCB concentrations by APCI/ITMS monitor with the results by HRGC/HRMS.

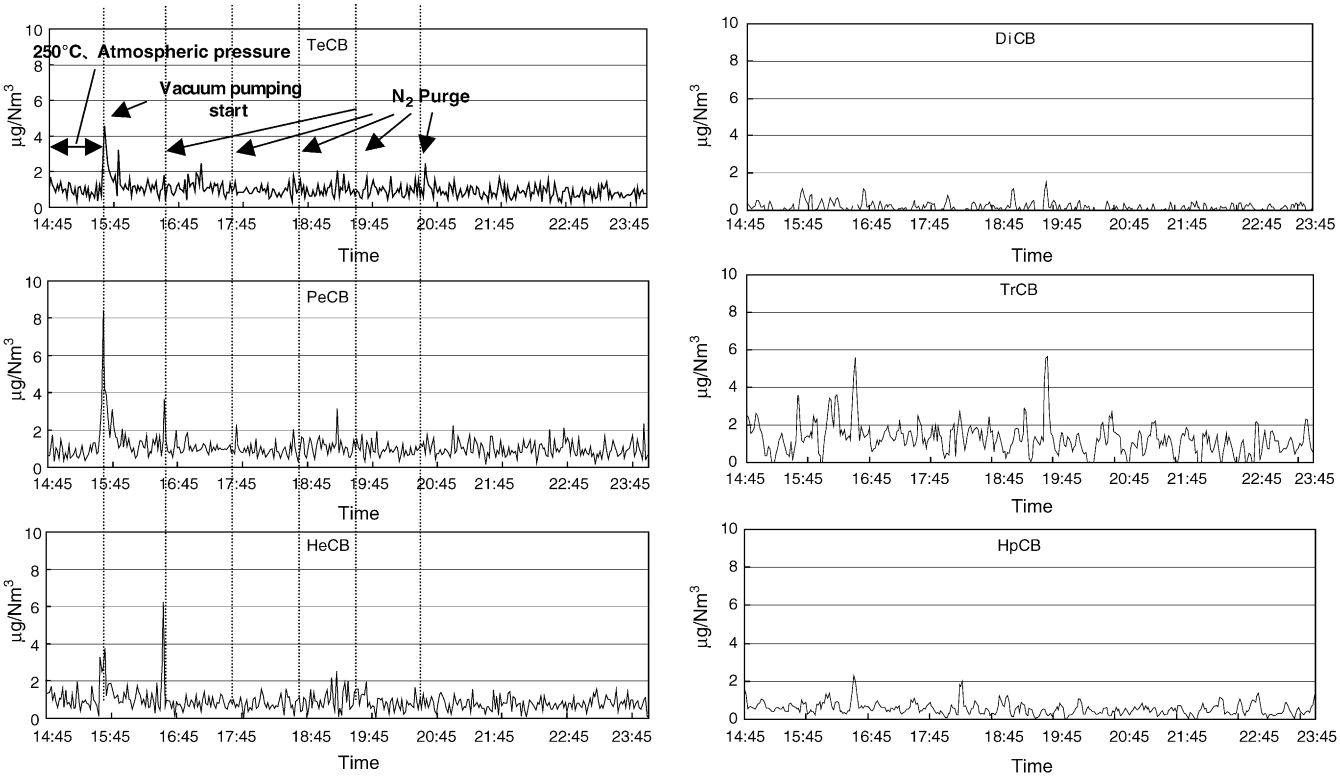

Fig. 10. Transient emission of PCB during vacuum heating process.

summing all the congeners' detection limits is 1.5 μg/Nm^3 with time resolution of 2 min.

Fig. 10 shows real-time monitoring of PCB in the ventilation air during vacuum heating process. We observed spiky increment of Te-CB, Pe-CB, and Hx-CB when vacuum pumping started and a PCB vacuum chamber was purged with nitrogen. These three homologues of PCB were the main component of KC-500, which was used in the disposed equipment. We interpret that the residual Te-CB, Pe-CB, and Hx-CB was spikily emitted from the chamber and detected by APCI/ITMS.

4. Conclusion

We developed a high-speed monitoring system of polychlorinated biphenyls in air that uses direct sampling APCI/ITMS with dry air dilution. After the water vapor concentration in the gas was diluted to less than 1%, concentration of Di- to Hp-CB could be calibrated by trichlorophenol with quantitation accuracy of ±30%. We showed sub-ppb sensitivity ($0.1 - 0.66$ μg/Nm^3) for Di- to Hp-PCB in the ventilation air from a PCB decomposition plant.

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