

Trace Detection of Gaseous Chlorobenzene and Biphenyl using Laser Photoionization

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Introduction

Since their development in 1881, polychlorinated biphenyls (PCBs) have been widely used in electrical equipments such as transformers and capacitors because of their high stability and electrical insulation characteristics. However, the adverse effect of PCBs on human health has been feared recently owing to their toxicity. Therefore, PCB-containing equipment has appropriately been stored and PCB decomposition process has been developed until today. Toshiba has developed UV/catalyst PCB decomposition process for PCB detoxification facility, which was approved as one of the appropriate methods by Japanese government. Recently, monitoring methods of PCB concentration in atmosphere or in industrial process have gradually become important. From the viewpoint of environmental protection and human health, several variations of monitoring technique for trace chlorinated organic compound have been studied. However, conventional analysis methods like gas chromatography require several days to analyze a sample. On the other hand, laser-based methods have a potential to be better suited for real time analysis¹. Especially, laser photoionization with simple Time of Flight Mass Spectrometry (TOF-MS) is thought to be one of the most powerful methods^{2,3}. With this idea in mind, measuring time and sensitivity of TOF-MS for gaseous monochlorobenzene (MCB) and biphenyl (BP) has been evaluated in the present experiments. PCB measuring feature can be predicted based on its photochemical similarity to MCB and BP.

Methods and Materials

Photoionization and Detection: Schematic diagram of experimental apparatus is shown in Figure 1. After the reaction cell was evacuated to less than 1.33 mPa (10^{-5} Torr), sample gas was introduced at 10 Hz through pulsed valve. A frequency-quadrupled Nd:YAG laser (Quanta-ray GCR-190-10, wavelength 266 nm) was used for photoionization of target trace molecules in sample gas. The laser was operated at 10 Hz with typical laser energy of 1-30 mJ/pulse. Pulse duration of the laser was approximately 5 ns (FWHM). Pulse generators synchronized the timing of sample gas introduction and laser irradiation. The laser beam (typically 2-6 mm diameter) was unfocused, which was passing through the region of sample gas introduced from the pulsed valve. Photoionization characteristics of target molecules in sample gas were measured by secondary

electron multipliers (SEM) with/without a quadrupole mass (Q-mass) filter. Target molecules were ionized by laser irradiation and their ions were extracted into the SEM with Q-mass filter system or the SEM without Q-mass filter system by the electrostatic field. The laser wavelength is chosen so that the photon energy could be enough for two-photon ionization processes of MCB, BP and PCB.

Sample gas: Sample gas for the photoionization experiment was a mixture of trace amounts of target molecules in the gas phase and nitrogen (N_2) gas. All chemicals used in this experiment, MCB and BP, were analytical reagent grade, and they were used without further purification.

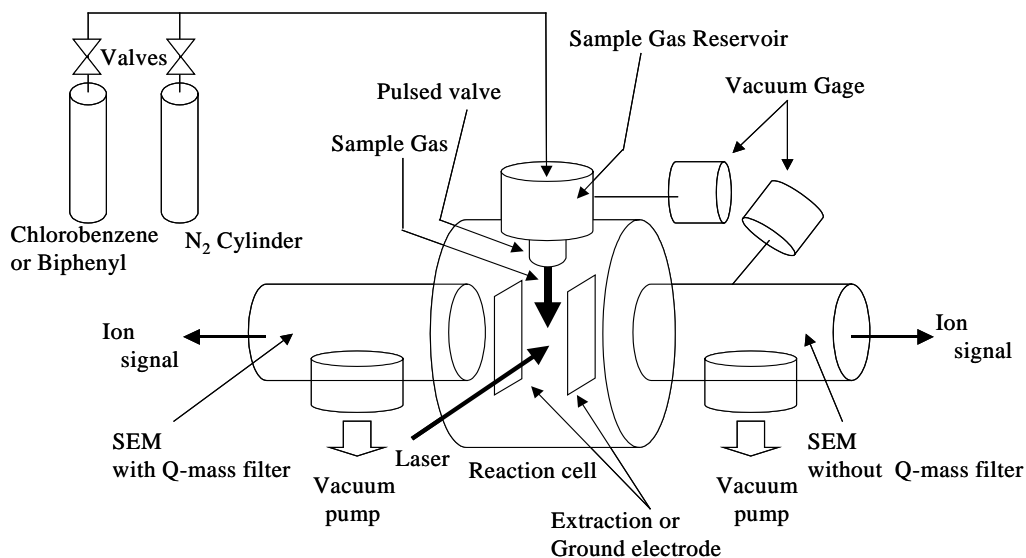


Figure 1: Schematic diagram of experimental apparatus

Results and Discussion

Figure 2 shows the mass spectra of gaseous MCB with 2.4 kPa (18 Torr) N_2 gas observed 10 μ s after laser irradiation. The MCB concentration of this sample gas was prepared to 1ppbv by gas mixing. The spectrum (A) obtained by the Q-mass filter + SEM system was measured in the mass number scanning mode of the system. It took about 3 minutes to capture all of the mass-different ions, which are identified as MCB ion (mass 112: $C_6H_5Cl^+$) and their fragments (mass 77: $C_6H_5^+$, mass 51) by the comparison of the Electron Impact MCB Mass Spectrum reported in the NIST Standard Reference Database⁴. For the spectrum (B) measured by the SEM system, the x-axis unit in the figure was converted from the time of flight (μ s) to mass number (amu) using peak fitting calibration between (A) and (B). Measuring time for the SEM system was about 30 seconds. It is clear that the fragmentation patterns of these two spectra are very similar. However, mass resolution of the spectrum (A) is much higher than that of the spectrum (B). On the other hand, ion

signal intensity of the spectrum (B) is about 50 times larger than that of the spectrum (A). Since the difference between $\text{C}_6\text{H}_5\text{Cl}^+$ and C_6H_5^+ was clearly observed as shown in Figure 2, it is thought that the selectivity of the SEM without Q-mass filter system is enough to distinguish between PCB homologues that have different number of chlorine atoms.

Figure 3 shows the mass spectrum of the gaseous BP with 2.4 kPa (18 Torr) N_2 gas obtained by the SEM system. The BP concentration of the sample gas was 40ppbv. As shown in Figure 3, no fragments were observed except BP ion (mass 154: $\text{C}_{12}\text{H}_{10}^+$) in this experiment while the observation

of fragment ions for the Electron Impact BP Mass Spectrum has been reported in the NIST Standard Reference Database⁴. In addition, the mass spectrum of gaseous Isopropyl alcohol (IPA) with N_2 gas was measured by the same system. However, neither IPA ion (mass 60: $\text{C}_3\text{H}_8\text{O}^+$) nor their fragments were observed. Because the energy of two UV photons (9.3eV) is less than the ionization potential of IPA (10.2 eV), UV laser light cannot ionize IPA molecules. The ionization potentials of MCB and BP are 9.1eV and 8.2eV

respectively. Therefore, MCB ions and BP ions are observed using laser photoionization technique. For applying TOF-MS in UV/catalyst

PCB decomposition process where a large amount of IPA is used as PCB solution, interference by IPA ion must be avoided to attain higher performances. Since no interference by IPA is occurring for measuring mass spectra, and the ionization potential of PCB is around 8 eV, this laser-based technique is thought to be suitable for monitoring PCB concentration even in IPA vapor gas atmosphere.

Figure 4 shows the mass spectra of gaseous MCB in different concentration observed by the SEM system. The MCB concentration of the sample gas was changed between 0.089 ppbv and 1 ppbv.

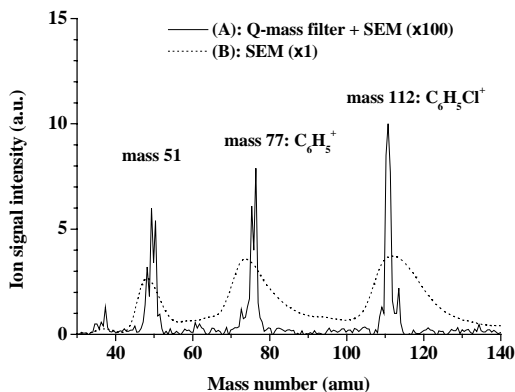


Figure 2: Mass spectra of gaseous MCB with N_2 gas observed by Q-mass filter + SEM system (A) and SEM system (B)

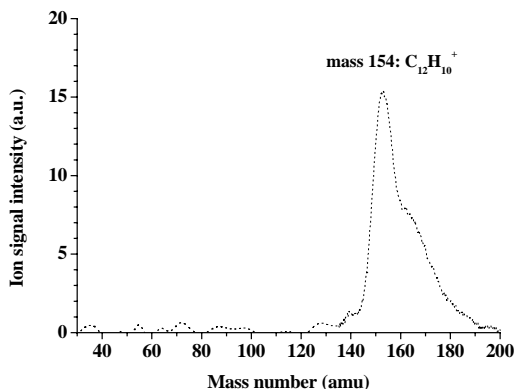


Figure 3: Mass spectrum of gaseous BP with N_2 gas obtained by SEM system

The ion signal intensity in the mass spectrum gradually increased with increasing MCB concentration.

Figure 5 shows plots of the ion signal intensity versus MCB concentration by the SEM system. Three peaks of MCB ion (mass 112: $\text{C}_6\text{H}_5\text{Cl}^+$) and their fragments (mass 77: C_6H_5^+ , mass 51) were selected for the quantitative evaluation. The plots for three ion signal peaks show a good linear relation in the range of 0.089-1 ppbv. The results mean that the detection limit of MCB is located in the range of 1ppb in our system. Relative intensity of these three peaks has not changed at all in the different concentration. This suggests that two fragments (mass 77: C_6H_5^+ , mass 51) are formed by the decomposition process of MCB. Especially, in case of C_6H_5^+ ion, the first step of the photoreaction is thought to be a fission of the C-Cl bond into Cl and C_6H_5 as reported in the literature⁵. Successive C_6H_5 photoreactions might lead to the formation of C_6H_5^+ .

In summary, laser photoionization with simple Time of Flight Mass Spectrometry has been applied to detect trace gaseous MCB with N_2 gas in low ppbv range. The high linearity of ion signal versus concentration has been measured over the range (0.089-1 ppbv). The developed system is applicable for real time gas monitoring of MCB, BP and is expected to be applied to gaseous PCB monitoring in near future.

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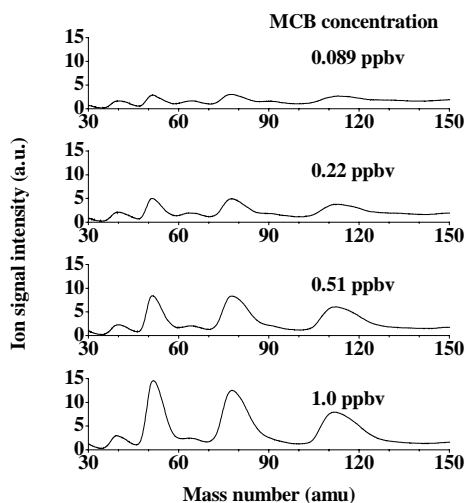


Figure 4: Mass spectra of gaseous MCB in different concentration observed by the SEM system

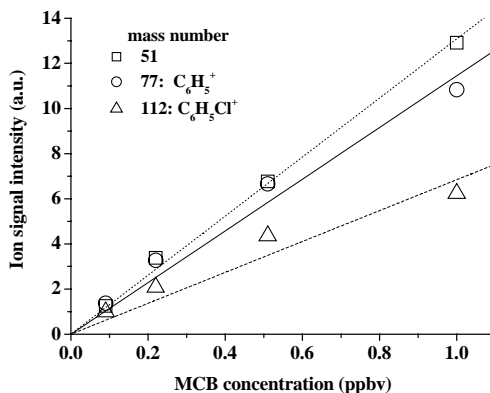


Figure 5: Ion signal intensity versus MCB concentration plots by the SEM system

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