The simultaneous measurement of both monochlorobenzene and phenol in the stack gas by using Jet-REMPI-TOFMS

Tetsuya Suzuki[1,2], Hideaki Kusano[3], Yuichi Yoshimoto[4], and Shun-ichi Hayashi[5]

[1]Nippon Steel Technoresearch Corporation, Chiba
[2]Tohoku University Graduate School of Environmental Studies, Sendai
[3]SHIMADZU CORPORATION, Tokyo
[4]Nippon Steel Corporation, Steel Plant & Environmental Engineering Division, Fukuoka
[5]Nippon Steel Corporation, Advanced Technol. Res. Labs., Chiba

Introduction

Online, real-time monitoring of the hazardous compounds emitted from combustion engines has been garnering increased public interest from the perspective of not only human health, but also understanding of its emission mechanism. The waste in an incineration chamber is not always homogeneous and it is therefore necessary to monitor the toxic products successively. In addition, a waste incinerator is usually operated at intervals of around 15 minutes (for example, the interval required to charge waste). Therefore, it is very important to monitor the emission phenomena of hazardous compounds with real-time responsiveness.

Jet-REMPI technique is expected as a high-isomer-selectivity, high-sensitivity analytical method for the online measurement of trace amounts of organic compounds in a complex gas mixture down to the around ppb from ppt concentration[1)].

We have developed online and real-time monitoring apparatus for the analysis of small amounts of organic gaseous compounds at incineration plants. The apparatus is based on the supersonic jet resonance-enhanced multi-photon laser ionization time-of-flight mass spectrometry (Jet-REMPI-TOFMS) technique. We have succeeded in monitoring the emission phenomena of the trace amounts of monochlorobenzene by using the resonant ionization process, and have shorten the delay time between the emission of the exhaust gas and its detection in order to simultaneously realize high isomer selectivity, high sensitivity and high time responsiveness by developing a new jet inlet system[2)].

We had succeeded in online, real-time monitoring of monochlorobenzene in the stack gas as reported in elsewhre[3)]. In this study, the simultaneous measurement of both monochlorobenzene and phenol were successfully demonstrated to compare the difference in the process between chlorination and hydroxylation. Additionally, the dichlorination and chlorination process was

considered by simultaneous monitoring of both monochlorobenzene and meta-dichlorobenzene.

Methods and Materials

Setups of ionization laser and mass spectrometer: The setup of our Jet-REMPI has been described in detail elsewhere[2)]. The pump laser employed a frequency-doubled dye laser (Sirah: Cobra-Stretch) pumped by the third harmonic of a YAG laser (Spectra Physics: INDI-HG) operated at 20 Hz. The pump laser beam was focused on a supersonic jet, which was created in the ionization chamber, using a 300 mm focal lens. The produced cation was introduced by the ion extraction electrodes to a linear time-of-flight mass spectrometer (flight path, 1.4 m) and detected by a Daly-type detector. To monitor the exhaust gas from the pilot scale waste incinerator, the transfer pipe was inserted into the heating tube (NITTA MOORE 2242 44M05), which was able to control the temperature of the tube up to 200 ˚C. For quantification of the hazardous compounds, a gas generator (GASTEC PERMEATER PD-1B) was used to produce standard diluted gas.

The stack gas analysis was demonstrated by monitoring a pilot-scale waste incinerator. This waste incinerator was a 30–t/day coke bed type gasification and melting incinerator. The composition of the matrix gas was, typically, 6% CO_2, 59% N_2, 9% O_2, and 26% H_2O. The general household waste was combusted at 1,400 degree Celsius. The flue gas was again burned in the post-combustion chamber to reduce the hazardous compounds, and cooled at the heat exchanger, the dust was reduced at the dust precipitator (pore size was 2 μm), and finally, emitted into the atmosphere from the smoke stack. We set a sampling probe between the dust precipitator and the chimney. The sample gas was transported to ionization chamber by pump ability of the chamber.

Results and Discussion

Mass Spectrum of the stack gas: Figure 1 shows the mass spectrum of the stack gas. The irradiation laser wavelength was 269.8 nm, which was resonant wavelength of monochlorobenzene. The monochlorobenzene signal was strongly appeared with resonant ionization process, and some other mass peaks was appeared with non-resonant ionization process due to high-concentration compared with monochlorobenzene.

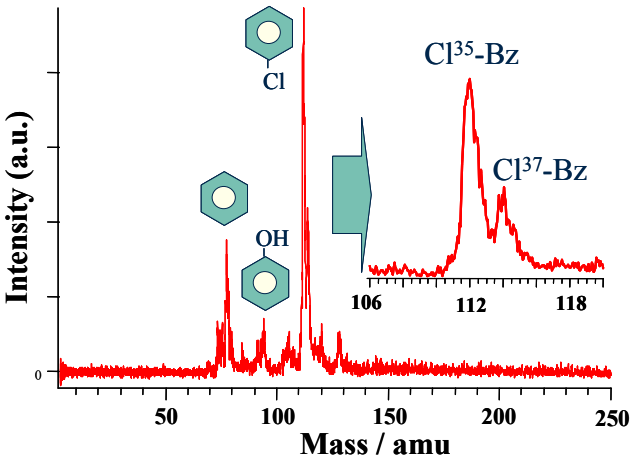

Figure 1 Mass spectrum of stack gas

The result of the simultaneous measurement: Figure 2 shows the result of online real-time monitoring of both monochlorobenzene with resonant ionization process and phenol with non-resonant ionization process. Both spectra commonly showed two types of emission. One was the fast-transient and high amount emission, and another was long-time and low concentration emission. We had reported that only the first transient emission was correlated to the CO emission in the chimney[3]. In figure 2, the emission of monochlorobenzene does not always correspond to the waste charging in the combustion chamber, but the one of phenol definitely coincides with it. This difference would be suggested the difference in the process of between chlorination and hydroxylation. Figure 3 shows the simultaneous measurement of meta-dichlorobenzene and monochlorobenzene. The irradiation wavelength was 269.13 nm which was the resonant wavelength of higher-vibration state of meta-dichlorobenzene. The spectra showed the same emission phenomena between meta-dichlorobenzene with resonant ionization process and monochlorobenzene with non-resonant ionization process. This result would be suggested that the process of dichlorination and chlorination was as same as each other.

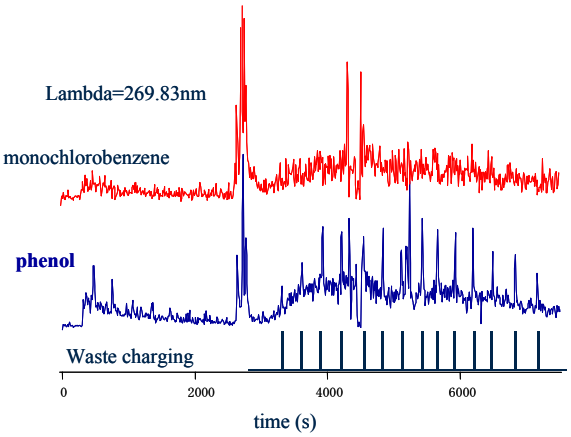

Figure 2 Simultaneous measurement of monochlorobenzene and phenol

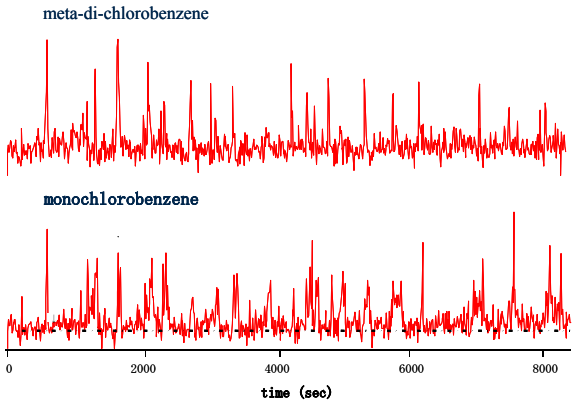

Figure 3 Simultaneous measurement of metadichlorobenzene and monochlorobenzene

Acknowledgements

We acknowledge the financial support from the Japan Science and Technology Agency (JST) and a Grant-in-Aid for the Creation of Innovations through the Business-Academic-Public Sector Cooperation from the Japanese Ministry of Education and Culture, Sports, Science and Technology (No. 14304). We thank the Plant Management Division of Nippon Steel Corporation for giving us the chance to confirm the usefulness of our instruments for monitoring the exhaust gas from the pilot scale waste incineration plant. We also thank Drs. K. Saito, Y. Fujioka, M.

Nishifuji, K. Kanehashi and Mr. M. Aimoto to help us the experiments at the pilot scale plant. And finally, we are indebted to Prof. M. Fujii and Dr. Ishiuchi (Tokyo Institute of Technology, Japan) for their numerous discussions and contributions.

References

1. Hafner, K.; Zimmermann, R.; Rohwer, E. R.; Dorfner, R. and Kettrup, A. *Anal. Chem.* **2001**, *73*, 4171-4180.
2. Tetsuya Suzuki, Shun-ichi Hayashi, Shun-ichi Ishiuchi, Morihisa Saeki, and Masaaki Fujii *Anal. Sci.*, ***21***, 991-996(**2005**).
3. Tetsuya Suzuki, Hideaki Kusano, Yu-ichi Yoshimoto, Shun-ichi Hayashi, *25th Int. Symp. On Halogenated Environmental Organic Pollutants and POPS*, Toronto, August 2005.