
Abstract

For monitoring of hazardous organic compounds, we have been developing an on-line analytical instrument based on a supersonic jet resonance enhanced multi-photon ionization (Jet-REMPI) mass spectrometry. We have attempted to apply this technique to monitor transient emission phenomena of hazardous organic compounds in the exhaust gas. The real time monitoring of the gaseous compounds in the atmosphere could be done by our instrument with a continuous sample introduction. We demonstrated the emission phenomena of monochlorobenzene generated from the chimney could be monitored every 10 seconds with below 100 ppt concentration level. This technique was proven to become pretreatment-free and high sensitivity analysis for hazardous organic compounds.

1. Introduction

It is expected that understanding the emission behavior of hazardous organic compounds contained in incinerator exhaust gas will provide important knowledge that is required not only for the optimization of incinerator operation conditions, but also for the development next-generation incinerators. In order to understand the emission behavior of actual exhaust gas correctly, it is important to implement dynamic monitoring of exhaust gas. This permits the feeding back of useful data about incinerator operation and clarification of the correlation between the operating condition of an incinerator and the emission of hazardous organic compounds. Generally speaking, the operating condition of an incinerator is judged from the in-furnace temperature, gas flow rate, atmosphere, carbon monoxide emission, etc. However, the correlation between the incinerator operating conditions that change by the moment and the emission of hazardous organic compounds is not yet thoroughly understood.

The dynamic monitoring of exhaust gas mentioned above calls for (1) highly sensitive (ppt - ppb) detection capability, (2) real-time detection capability, and (3) a high degree of molecular selectivity. Through the Creative Research Results Promotion Project of the Japan Science and Technology Agency (JST) and a subsidy for the industry-academia-government innovation creation projects of the Ministry of Education, Culture, Sports, Science and Technology, we developed new equipment for highly sensitive, real-time analysis of molecules applying the supersonic jet resonance-enhanced multi-photon ionization (Jet-REMPI) technique that permits identification of organic molecules without any pretreatment and that should enable extremely accurate detection of molecules.1, 2

2. Development of Jet-REMPI Equipment

2.1 Principle of Jet-REMPI

In the Jet-REMPI method, a sample gas containing the molecule being observed is jetted into a vacuum for adiabatic expansion of the gas to utilize the effect of cooling of the molecular thermal motion (rotation and vibration). In this process, the molecular thermal mo-
tion is transformed into a molecular translational motion and cooled. The speed of the molecular translational motion reaches tens of times the speed of sound; this motion is thus called a supersonic molecular jet. When a laser beam whose wavelength is tuned to the electron excitation level of the specific molecule irradiates the molecule after the thermal motion is cooled, the molecule under observation is selectively excited and absorbs more photons, and it then becomes ionized. Thus, when the laser wavelength resonates with the electron excitation state of the molecule under observation, the quantity of ions generated increases drastically. This phenomenon is called resonance-enhanced multi-photon ionization.11

With Jet-REMPI, it is possible to identify the molecule under observation and accurately determine its electron excitation wavelength by measuring the mass peak intensity of the molecule (REMPI spectrum) while sweeping the wavelengths by a wavelength tunable laser. As long as the molecule is sufficiently cooled, even a structural isomer of the molecule can be selectively detected by utilizing the slight difference in electron excitation levels between them. By applying this principle, it is possible to selectively detect, without any pretreatment, those structural isomers that have exactly the same mass number as the molecule under observation and that cannot be separated using a mass spectrometer. It has been reported that the effect of one particular structural isomer on the human body can be more than ten times greater than that of another structural isomer. Thus, it is important to detect these structural isomers separately and evaluate them in terms of their toxicity equivalence factors and their abundances.

2.2 Jet-REMPI equipment

The Jet-REMPI equipment consists of an ultrasonic molecular jet-generating chamber, a laser of variable (or fixed) wavelength, a laser ionization chamber, and a mass spectrometer. The ultrasonic molecular jet-generating chamber is a vacuum chamber that admits a gas (e.g., exhaust gas) at atmospheric pressure through a pulsed valve or suchlike and generates an ultrasonic molecular jet. The laser ionization chamber uses a pulsed laser to ionize the organic molecule under observation in the ultrasonic molecular jet. This chamber for laser ionization is also equipped with an optical system for collecting and admitting a variable-wavelength laser that excites the laser beam resonating with the electron excitation level of the molecule under observation. The mass spectrometer analyzes the mass of the laser-ionized molecule. In order to detect a molecule ionized by a pulsed laser as precisely as possible, a time-of-flight mass spectrometer (TOF-MS) is often employed. With this device, it is possible to obtain the mass of a specific molecule from the time at which its ions, which are generated immediately after laser pulse irradiation, reach the detector.

2.3 Points to consider in the development of the equipment

We developed equipment designed especially for highly sensitive, real-time analysis of hazardous organic compounds emitted from incinerators. Points to be considered regarding the development of the prototype equipment were as follows.

(1) Equipment provided with a mechanism that continuously admits exhaust gas into the equipment to permit constant monitoring of changes in gas flow and composition in the flue

(2) Highly sensitive Jet-REMPI equipment capable of detecting molecules in the order of ppb - ppt

Even before 2000, when we initiated the development of this equipment, several study groups in Europe and Japan were conducting R&D on environmental impact assessment techniques based on Jet-REMPI. However, there was still no equipment that enabled highly sensitive, real-time analysis of hazardous organic compounds.

2.3.1 Trial manufacture of the mechanism for continuous admission of gas

As already mentioned in the section on the principle behind Jet-REMPI, formation of an ultrasonic molecular jet makes the selective detection of a molecule possible. If the molecule is cooled insufficiently, it is impossible to secure the molecular selectivity or perform highly sensitive detection. The condition for molecular cooling in the ultrasonic molecular jet can be expressed by the following Poisson’s equation. Assuming the temperature of the molecular beam emitted from the nozzle to be \( T_0 \), the gas pressure inside the nozzle to be \( P_0 \), and the gas temperature inside the nozzle to be \( T_n \), then

\[
\frac{T}{T_0} = \left( \frac{P}{P_0} \right)^{\frac{\gamma-1}{\gamma}}
\]

(1)

In the above equation, \( P \) denotes the pressure inside the vacuum chamber and \( \gamma \) denotes the specific heat ratio. Assuming the specific heat at a constant pressure to be \( C_P \) and the specific heat at a constant volume to be \( C_v \), then \( \gamma = C_P/C_v \). The above equation can be rewritten as follows.

\[
\frac{P}{P_0} = \left[ 1 + \frac{\gamma-1}{2} M^2 \right]^{-\frac{\gamma}{\gamma-1}}
\]

(2)

In the above equation, \( M \) denotes the Mach number. \( M > 1 \) indicates a speed faster than the speed of sound.

Assuming the diameter of the nozzle used to be \( D_n \) and the Mach number at the cooling point reached when the molecule is cooled to be \( M_f \), then

\[
M_f = 1.17K_n^{-0.4}
\]

(3)

Here, \( K_n \) is called the Knudsen number, which is expressed as the ratio of the mean free path, \( \lambda \), of the molecule immediately before the nozzle port to the nozzle diameter, \( D_n \). Thus,

\[
K_n = \lambda / D_n
\]

(4)

In order to enhance the cooling effect on the molecule under observation in the jet, it is necessary to increase the Mach number, for which we must decrease the value of \( K_n \). In order to decrease the value of \( K_n \), it is necessary to raise the pressure this side of the nozzle or increase the nozzle diameter, as can be seen from Equation 4 above. To meet this requirement, Jet-REMPI has long used a pulsed valve. This enables the vacuum chamber load on the exhaust system to be kept from increasing too greatly even when the nozzle pressure is raised or the nozzle diameter is increased. For the continuous gas admission system that enhances the ability to operate in real time and the sensitivity of detection, a conventional pulsed valve that is almost devoid of gas flow cannot be employed. Therefore, a system for continuously feeding gas into the vacuum chamber is required. Here, since the mean free path, \( \lambda \), is proportional to the nozzle source pressure, \( P_0 \) (Equation 4 above can be rewritten as follows.

\[
M_f \propto (P_0D_n)^{0.4}
\]

(5)

The flow rate of the supersonic molecular jet from the nozzle is proportional to \( P_0D_n^2 \). Therefore, assuming the pumping rate of the vacuum exhaust system to be \( S \), it is necessary that the following condition be met.

\[
P_0D_n^2 \leq S
\]

(6)

Therefore, the Mach number is expressed as follows.

\[
M_f \leq \sqrt{\frac{S}{D_n}}^{2.4}
\]

(7)

Thus, in order to form a continuous supersonic molecular beam, it is
necessary to reduce the nozzle diameter or develop a vacuum chamber capable of pumping at higher speed. From the standpoint of admitting a large amount of gas into the system, it is advantageous to increase the diameter of the nozzle to form a supersonic molecular flow. On the other hand, in order to secure the degree of vacuum required of the vacuum chamber, it is important to restrain the admission of gas to the extent possible. However, if the nozzle diameter is reduced significantly, collisions between molecules at the exit of the nozzle may become insufficient, causing an “effusive beam.” If the pipe diameter is excessively small, resistance inside the pipe increases, causing $P/P_0$ to decrease near the exit of the nozzle. In either case, the cooling of molecules by adiabatic expansion becomes insufficient.

We installed a maglev turbomolecular pump with a large pumping capacity (3.0 m$^3$/s) in the vacuum chamber to ensure efficient differential pumping between the vacuum chamber and the time-of-flight mass spectrometer. In addition, we succeeded in developing an ion optical system capable of efficiently capturing the ions of the organic molecule under observation generated by the laser. Fig. 1 shows the REMPI spectra of monochlorobenzene obtained at room temperature, 100°C, and 150°C, respectively. When the molecular motion is insufficiently frozen, the vibrational levels and rotational levels, the so-called vibronic levels, are excited, causing the electron transition spectral line to widen and/or a vibronic spectral peak to appear. However, as can be seen from Fig. 1, we were able to detect monochlorobenzene in the hot gas from the heating pipe in a sufficiently cooled state, as well as at room temperature.

2.4 Development of a snout-type electrode for differential pumping

In order to ensure that the ions generated by the laser reach the detector efficiently, it is necessary to maintain the ion path with a high degree of vacuum. As shown in Fig. 2, the snout-type electrode we developed for differential pumping is covered in a mesh electrode installed in the system. Therefore, the nozzle can be set close to the snout electrode and the ions generated along the equipotential surfaces formed by the electrodes can be captured with high efficiency (50 times higher than the efficiency of conventional flat, parallel-plate electrodes available on the market) and let into the mass spectrometer. Therefore, the snout-type electrode greatly contributes to improvement in detection sensitivity.

In addition, we developed a new structure in which the ions generated in the laser ionization region are collected and fed into the electrode and the ion beams are focused inside the electrode. This structure made it possible to provide a pinhole, which helps enhance the effect of differential pumping between the vacuum chamber and the time-of-flight-type mass spectrometer. With this construction, it is possible to maintain the degree of vacuum inside the time-of-flight-type mass spectrometer at $5 \times 10^{-7}$ Torr when the degree of vacuum inside the vacuum chamber is $1 \times 10^{-4}$ Torr. Thus, we succeeded in building a system that is able to detect generated ions with high trans-

**Fig. 1** REMPI spectra of monochlorobenzene with the laser wavelength range of 269 to 270 nm
REMPI spectra were taken under room temperature, 100, and 150 degree of Celsius.

**Fig. 2** Schematic diagram of the snout type electrode and the curvature of equipotential surfaces formed when the high voltages were applied.

**Fig. 3** Ion signals versus concentrations of monochlorobenzene under on-resonance condition.
3. Demonstration Test with an Actual Incinerator

Using the flue gas of an actual incinerator fed into our system through a 23-m heating pipe from the flange, we carried out a real-time, on-site analysis of monochlorobenzene—one of the precursors of dioxin. The wavelength used for measurement by laser ionization was 269.83 nm. The detection signals of ions of mass number 112 amu were integrated for 10 seconds (200 pulses) with a digital oscilloscope and their average obtained. The measurement was conducted for a total of 5,000 seconds.

As shown in Fig. 4, 500 seconds after the start of measurement, a peak exceeding 2.5 ppb appeared. It then attenuated with a half-width of 30 seconds. In addition, in the time span from 1,000 to 3,800 seconds, the emission of monochlorobenzene in concentrations of 100 to 300 ppt was observed. Thus, two different phenomena—a short-lived peak of high concentration and a long-lived plateau of low concentration—were observed. In observing such emission behavior as well, we consider that our system can provide very useful information since it permits highly sensitive, real-time monitoring of hazardous organic compounds from incinerators.

On the other hand, as an indicator of the operating condition of an incinerator, the concentration of carbon monoxide is used. Carbon monoxide is used as an index of incomplete combustion. However, assuming that dioxin is formed from unburned carbon and aromatic molecules as a result of de novo synthesis, it might be better to use the emission of aromatic compounds, rather than carbon monoxide, as an index for the concentration of dioxin.

The concentration peak of monochlorobenzene about 500 seconds after the start of measurement perfectly coincides with the concentration peak of carbon monoxide. There is no correlation between the prolonged emission of low-concentration monochlorobenzene and the concentration of carbon monoxide.

We expect that through a detailed study of the correlations between the emission of hazardous organic compounds and the phenomena taking place in the incinerator, it will become possible to clarify the mechanism by which these compounds are formed.4-8)

4. Conclusion

The emission of highly hazardous organic compounds, including dioxin, has become a grave social problem. Nippon Steel naturally owns blast furnaces, coke ovens, sintering machines, and other high-temperature furnaces. It is therefore important for us to pay due attention to the emission of hazardous organic compounds from these furnaces. In order to develop methods for highly sensitive, real-time analysis of very hazardous organic molecules, we have proposed several national projects and have pressed ahead with the development of new equipment and new technologies.

In the Creative Research Results Promotion Project of the Japan Science and Technology Agency (JST) adopted in fiscal 2000, we successfully developed a new technology for the highly sensitive analysis of hazardous organic molecules based on the supersonic jet resonance-enhanced multi-photon ionization method. In addition, under the fiscal 2002-2004 subsidy for industry-academia-government innovation creation projects granted by the Ministry of Education, Culture, Sports, Science and Technology, we succeeded in developing equipment that allows highly sensitive, real-time analysis of hazardous organic molecules in high-temperature furnaces. In this project, the equipment developed during the fiscal 2000 project of JST was subjected to a major enhancement to provide it with a real-time measurement function. Then, the equipment was directly coupled to a garbage incineration furnace and subjected to experiments for demonstration purposes. As a result, we were able to observe for many hours the appearance and disappearance in 30 seconds of monochlorobenzene, a precursor of dioxin, from the incineration furnace.

Furthermore, we verified the validity of our new measurement technique by applying it to organic molecules of larger mass numbers. Through use of the real-time resolution of the technique, we also succeeded in observing fuel-specific organic molecules emitted from motor vehicles in specific driving modes.9-14)
It is expected that regulations on emissions of environmental pollutants will become increasingly stringent in the future. We intend to effectively utilize our on-site, real-time analytical equipment to help reduce the impact of the steelmaking process on the environment. In addition, we would like to apply our automotive exhaust measurement technology to the development of next-generation engines and catalysts.

Acknowledgements

The present study was partly funded by a subsidy for industry-academia-government innovation creation projects granted by the Ministry of Education, Culture, Sports, Science and Technology. We were also given extremely valuable guidance by Prof. Masaaki Fujii, Prof. Makoto Sakai, and Dr. Shunichi Ishiuchi at the Resources Chemical Laboratory of the Tokyo Institute of Technology, who were the project members. We wish to express our heartfelt thanks to all the people concerned.

References