Development of proto-type Jet-REMPI apparatus for on-line real-time monitoring of small amount of gaseous compounds at the incineration plants and observation of the correlation with the CO emission in the chimney

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Introduction

For monitoring of hazardous organic compounds, we have been developing a new type of analytical instrument based on a supersonic jet resonance enhanced multi-photon laser ionization (Jet-REMPI) mass spectrometry. The Jet-REMPI method has a great advantage, in principle, for in-situ and rapid response analysis, because no sample preparation for analysis is needed.

Most recently, Jet-REMPI has become a very promising technique for monitoring the emission of trace hazardous organic compounds. For example, the REMPI technique is applied for the on-line measurement for an incineration pilot plant[1,2], andon-line measurement of volatile organic compounds (VOC) of a diesel generator[3]. However, most of their REMPI setups cannot satisfy the function of real-time, on-line, high sensitivity and high selectivity detection simultaneously, even though all of the functions are important for the real-time, on-line monitoring of exhaust gas containing many compounds of the same mass number. When a particular emphasis is placed on the function of high sensitivity and high selectivity, the sample gas has to beintroduced by the conventional pulsed valve inletin most cases[3], because the pulsed valve can keep the differential pressure between the transfer pipe and the ionization chamber to create the jet-cooled state. However, this inlet greatly reduces the sample consumption in the transfer pipe, which is connected with the chimney of the incinerator and the REMPI chamber. The result is a time delay and also a worse time resolution. On the other hand, for real-time monitoring, the sample gas is, in general, introduced continuously by using the narrow inner radius transfer pipe, such as capillary[1,2]. Then the gas consumption is very large and the response speed is improved. However, the effusive molecular beam is produced and then the molecular selectivity and higher sensitivity are denied despite maintaining a high vacuum level in the ionization chamber. So such systems have been only applied for total gas monitoring with no isomer selectivity.

So far, we have been developing the continuous gas introduction system which consists of a pin-hole at the end of the transfer pipe and of an ionization chamber with a high vacuum pumping system. Then the pressure ratio between the transfer pipe (atmospheric pressure) and the ionization chamber was maintained enough to produce the jet-cooled state, even when introducing the sample gas and air continuously. As a result, we succeeded to rapidly flow the sample gas in the transfer pipe and achieve rapid response without losing the molecular selectivity.

To demonstrate this system, our REMPI setup was applied to monitor the exhaust gas emitted from a pilot scale waste incinerator. We mainly monitored the monochlorobenzene, which is a well known indicator of I-TEQ of PCDD/PCDF[4], and observed the correlation with CO emission in the chimney.

Methods and Materials

Setups of ionization laser and mass spectrometer: The setup of our Jet-REMPI has been described in detail elsewhere[5]. Briefly, 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 originally designed ion extraction electrodes, which consisted of conical ion lens and potential switch,[5] to a linear time-of-flight mass spectrometer (flight path, 1.4 m) and detected by a Daly-type detector[6]. The advantage of this detector is that high voltage can be applied for sensitivity improvement. We achieved the detection limit as 10 ppt of monochlorobenzene without any sample concentration, pulse counting but only averaging the signal on every laser pulse. We can obtain the data at a maximam of 1 point/sec at a maximum. The mass resolution of this mass spectrometer was almost 310 at m/z 112 in typical Jet-REMPI analysis condition. To monitor the exhaust gas from the pilot scale waste incinerator, the transfer pipe was inserted into a heating tube (NITTA MOORE 2242 44M05), which was able to control its temperature up to 200 °C. For quantification of the hazardous compounds, a gas generator (GASTEC PERMEATER PD-1B) was used to produce standard diluted gas.
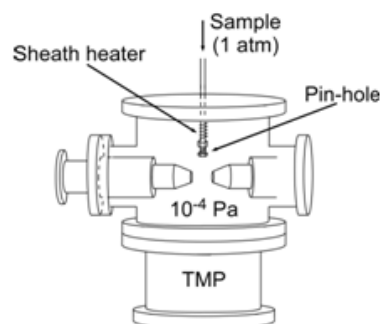

Fig 1: Schematic diagram of sample introduction

Sample introduction apparatus: Figure 1 shows the schematic diagram of the sample introduction system. The transfer pipe, which could be heated up to 200 °C, was inserted into the ionization chamber via Ultra-Torr (Swagelok) and the pin-hole, which had narrow radius compared with the transfer pipe, was set at the end of the pipe. The sample gas was expanded as a free jet into the ionization chamber through a pin-hole, which can be produced by precise and mechanical punching in the commercial stainless cap with the diameter of 100 mm. . We also applied a high speed pumping system, which consisted of 3000 L/sec Turbo molecular pump (TMP) and Rotary pump (EDWARDS E2M80). By using this pin-hole the resulting gas flow was 70 cm^3/min. To compare the response speed of the pin-hole and pulsed valve, we connected the conventional pulsed valve (General Valve Series 9) at the end of the transfer pipe instead of the pin-hole.

Results and Discussion

Response speed of the pin-hole and pulsed valve: Figure 2 shows the time delay for the signal detection of monochlorobenzene. At first, atmospheric air was introduced for 1 minute into the ionization chamber, and then the air containing about 20 ppmmonochlorobenzene was introduced for 1 minute, and finally atmospheric air was then introduced again during the measurement. We monitored the time for the sample gas to pass through the 11m long transfer pipe to the ionization

Fig 2: Time delay to detect the signal

chamber. When using the pulsed valve, it took ten minutes to obtain the signal. The full width at the half maximum (FWHM) in this case was 107 seconds, even though the monochlorobenzene was introduced for only 1 minute. This was the result of sample diffusion in the pipe. Because the sample gas took a long time to arrive at the chamber, the

Fig 3: REMPI spectra of each sample introduction method

diffusion phenomena appeared prominently. In contrast, when using pin-hole, the time delay was less than 45 seconds and FWHM was 62 seconds, so it shows a good ag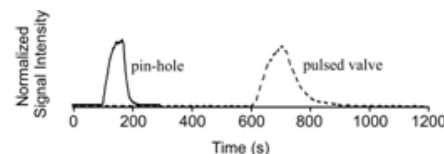reement with the monochlorobenzene introduction. Introducing the sample gas continuousl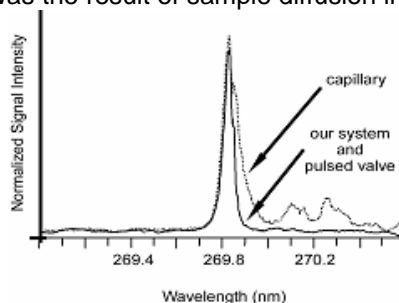y with a narrow transfer pipe, instead of pin-hole, will result in higher response speed, but the Jet-cooled state will not attained in this case as we can see in Figure 3. Figure 3 shows the REMPI spectrum obtained by using our sample introduction system as compared with a narrow capillary. In the case of the capillary, the vibrational state appeared and molecular selectivity was comparatively denied. This was caused by the pressure difference drop-off between the chamber and the transfer pipe due to the pressure decrease inside the transfer pipe because of air resistance. And the detected signal was ten times lower than that taken by our sample introduction system.

Emission phenomena of monochlorobenzene at waste incinerator: Figure 4 shows the results of real-time monitoring of the monochlorobenzene and CO in the stack gas. The irradiation laser wavelength was 269.8 nm, which is the resonance wavelength of monochlorobenzene. The laser power was 3 mJ/pulse, and the power was stable during the measurement. The signal intensity of the monochlorobenzene was averaged for ten seconds (200 laser shots) at each data point. The delay time between the gas emission and the gas detection through the 23m long transfer pipe was 150 seconds. CO emission was monitored by a conventional IR type CO monitor. The spectrum revealed that there were two types of monochlorobenzene emission. One is the fast transient emission obtained 550 seconds after beginning the data acquisition. The concentration of this fast transient emission was up to 2.5 ppb and extended to 30 seconds. Another small emission with the concentration of 100 ppt was monitored for about 40 minutes (from 1000 seconds to 3500 seconds of the data) successively. At the same time, the stack gas was measured by GC/MS for comparison. Needless to say, the GC/MS technique can only obtain the averaged value of the monochlorobenzene with the concentration of 100 ppt. We think that the fast transient high amount emission may be caused by the combustion condition such as imperfect combustion or declination of the temperature of the combustion chamber, because CO emission timing corresponded with this fast transient monochlorobenzene emission. The second emission may indicate the hysteresis of the incineration chamber, such as adsorption from the wall or from the unburned waste. As a result, monochlorobenzene was detected in small amounts of about 100 ppt, but continuously for a long time, and independent from CO emission.
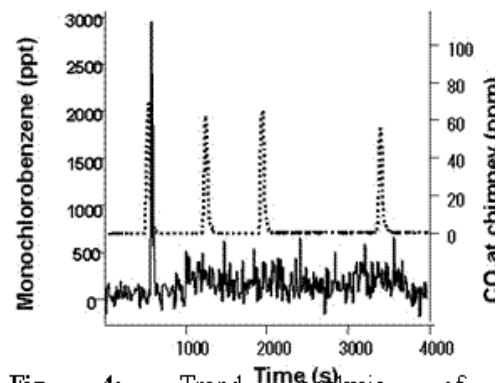

Fig 4: Trend analysis of monochlorobenzene and CO emission

Acknowledgements

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