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MEASUREMENT OF TRACE HYDRO-CARBON COMPOUNDS BY VACUUM ULTRA VIOLET (VUV) LIGHT IONIZED ION TRAP TIME OF FLIGHT MASS SPECTROMETRY (IT-TOFMS)

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Introduction

We have developed a VUV light ionized IT-TOFMS for real-time analysis of trace hydro-carbon compounds in real flue gas of incinerators. The feature of this spectrometer is a use of a VUV light from a discharge lamp to ionize the hydro-carbons. Energy of the VUV light used in this study is 10.2eV. Using the VUV light, almost all hydro-carbons are able to be ionized, but rarely dissociated to fragments. So this method enables soft and efficient ionization. The efficiency is not degraded with number of halogen atoms in a purpose molecule, as is often the case of laser ionizations[1]. Also, since the efficiency is not sensitive to co-existing molecules as is the case in chemical ionizations, no internal-standard injection is required[2]. The VUV lamp doesn't need any delicate adjustments or frequent mechanical maintenances.

Ion trap is used to accumulate and enrich the ions to achieve high sensitivity. Although the intensity of the VUV lamp is feeble relative to the lasers, the ion trap can accumulate considerable amount of ions ionized by photons from the continuously emitting lamp. It is also a merit of using the trap that by applying appropriate RF waveforms to end cap electrodes of the ion trap, interfering ions, which have same mass with purpose ions, can be removed from the ion trap so that only the purpose ions can be detected.

Methods and Materials

The VUV light ionized IT-TOFMS is shown in Figure 1. The VUV light is the Lyman-α emission from hydrogen (122nm) excited by H_2/He microwave discharge (2.45GHz). Intensity of the VUV light was adjusted by the microwave power. Sample gas was introduced into the ion trap located in an ionization chamber and ionized by VUV light and enriched for 0.1-0.3s. The ions whose mass were different from the purpose ions (for example, T3CBs) were removed by applying a SWIFT[3, 4] (stored waveform inverse Fourier transform) signal to the end cap electrodes of the ion trap. The frequency spectrum of the SWIFT signal corresponds to the secular frequency band of mass range other than T3CBs. After an accumulation period, the accumulated T3CB ions were dissociated to fragment ions by giving another waveform, whose frequency spectrum corresponds to the secular frequencies of the T3CBs, to the end cap electrodes. The optimization of the voltage of the waveform was sensitive, so had to be adjusted in unit of 0.1V. In this way, impurity ions were removed from the ion trap, so only fragment ions from T3CBs were able to be detected.

N_2 diluted T3CB standard gas mixture was supplied from a commercial gas cylinder. The T3CB flow rate was controlled by a mass flow controller. The gas line, the mass flow controller and the ionization chamber were heated to 200 to prevent T3CB from adsorption. The ionization chamber was maintained at 10^{-2} Pa, which was optimized to form fragment ions signal as much as possible.

For measuring P5CDF, the gas chromatogram (GC) was adapted to the sampling line of the TOFMS. P5CDF solution (diluted by hexane) was vaporized by GC and introduced into the ionization chamber. The GC condition was optimized to enrich the P5CDF and obtain the strongest signal. Through the capillary tube made of silica glass, P5CDF out of GC oven was introduced to ionization chamber. The capillary tube was heated to 300 to prevent P5CDF from adsorption.

Results and Discussion

(1)T3CB

Using the commercial standard gas, measurement condition was optimized and detection sensitivity was investigated. Figure 2 shows the T3CB fragment mass spectrum. T3CB fragment signals were detected at m/e=74, 109, 111, 145, 147. The fragment signals at m/e=145, 147 correspond to T3CB-Cl, which stands for the fragment eliminated Cl from T3CB. The signals at m/e=109, 111 correspond to T3CB-HCl_2. The signals at m/e=74 corresponds to T3CB-HCl_3. The fragment patterns depended on the RF voltages given to the end cap electrodes of the ion trap. So as to get strong signal intensity, the RF voltage was optimized. To obtain high fragmentation efficiency, 4.0 V was the best voltage. Figure 3 shows the relationship between T3CB concentrations and signals. Good linearity was recognized between T3CB standard gas concentrations and signals when T3CB standard gas concentration was from 0 to 8000 ng/m^3N. To increase the signal, longer trap time is preferred, but too long trap time cause saturation of the signal. So in order to get linearity like Figure 3, it is important to optimize the trap time. In this case, the trap time was optimized as 0.3 s. As a result, T3CB detection sensitivity was 80ng/m^3N (S/N=3) in 20s.

This system is applied to measure T3CB concentration of a real flue gas, which was extracted at a furnace outlet of a small-scale stoker-type incinerator. Figure 4 shows the T3CB fragment mass spectrum. T3CB signal was detected at the same m/e as the standard gas shown in Figure 2. In addition to them, new signals were detected at m/e=87, 89, 99, 101, 127, 128, 129, 130, which were believed to be caused by water vapour in flue gas but their formation mechanism was not clear. Since the gas contains considerable amount of interfering molecules, which have the same mass with T3CB, some fragments originated from them are also observed. T3CB concentration of the flue gas was calculated to be 1200 ng/m^3N.

(2) P5CDF

Using a commercial standard solution, P5CDF detection sensitivity was measured. Figure 5 shows the P5CDF fragment mass spectrum. P5CDF fragment signals were detected at m/e=205, 207, 275, 277, 279. The fragment signals at m/e=275, 277, 279 correspond to P5CDF-COCl. Those at m/e=205, 207 correspond to P5CDF-$COCl_3$[6, 5]. Other signals were impurity ions which were mainly originated from a liquid layer of the capillary tube. Figure 6 shows the relationship between P5CDF concentrations and signals. Good linearity was recognized between the P5CDF standard sample concentrations and the signals when P5CDF standard gas concentration was from 0 to 200pg. In the similar way of T3CB, trap time is optimized as 0.1 s. As a result, the P5CDF detection sensitivity reached 1pg (S/N=3).

Conclusions

A VUV light ionized IT-TOFMS was proposed for real-time analysis of trace hydro-carbon compounds in real exhaust of incinerators. Detection sensitivity of 80 ng/m^3N was achieved with a standard tri-chlorobenzene (T3CB) gas mixture by averaging data for 20s. Measurement of T3CB in real exhaust, extracted at a furnace exit of a stoker-type incinerator, was demonstrated. Analysis of P5CDF was also demonstrated, and the detection sensitivity of 1pg was achieved.

Figure 1: VUV light ionized IT-TOFMS.

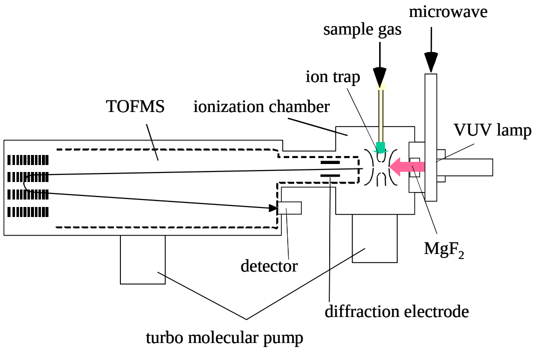


Figure 2: T3CB mass spectrum (standard gas).

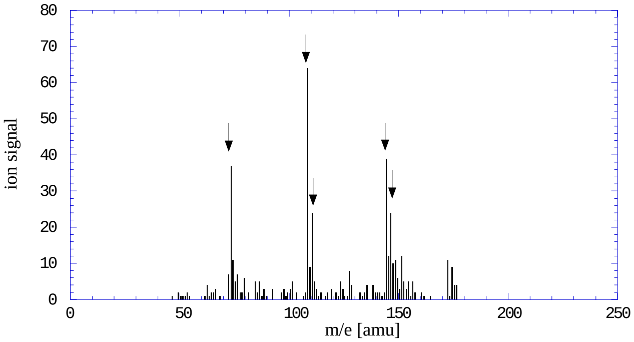


Figure3: relationship between T3CB concentrations and signals.

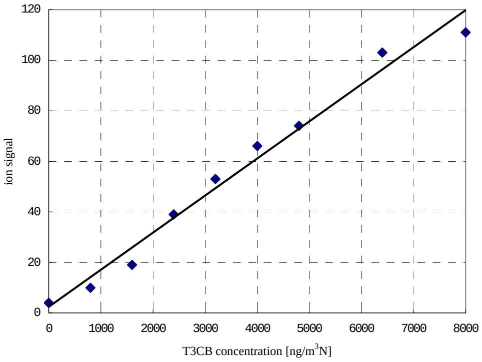


Figure 4: T3CB mass spectrum (flue gas).

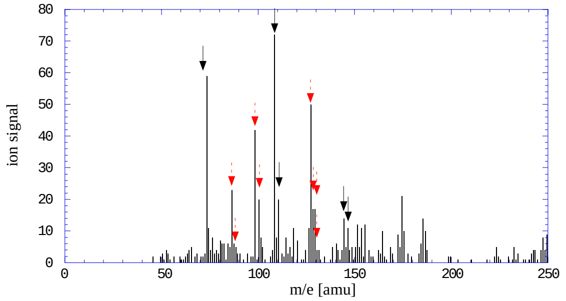


Figure 5: P5CDF mass spectrum.

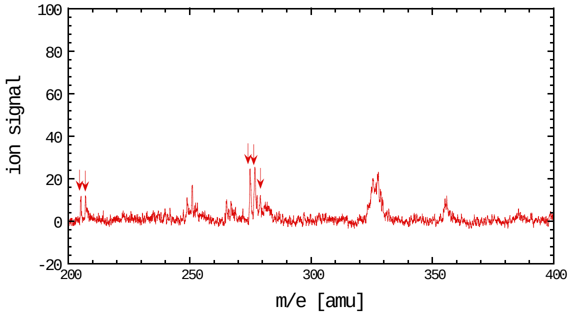
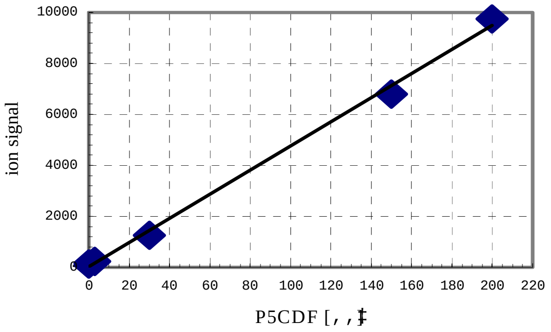


Figure6: relationship between P5CDF concentrations and signals.



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