

## DEVELOPMENT OF A RIMMPA-TOFMS: ISOMER SELECTIVE SOFT IONIZATION OF PCDDs/DFs

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### Introduction

Laser mass spectrometry is an excellent technique for analyzing the dioxin discharge that changes continuously in a waste incinerator because of its rapidity and sensitivity. This instrument is being developed by many research groups<sup>1-4</sup> around the world. A laser has also been proposed that uses a pico-second or femto-second pulse width in order to ionize softly for the polychlorodibenzo-*p*-dioxins and polychlorodibenzofurans (PCDDs/DFs) because of the short excitation lifetime of their molecules<sup>4</sup>.

In contrast, we have developed a new laser mass spectrometer, RIMMPA-TOFMS (Resonance Ionization with Multi-Mirror-System Photon Accumulation coupled with Time of Flight Mass Spectrometry)<sup>5</sup>, based on a two-color-two-photon ionization scheme and using a nano-second pulse laser, which enables isomer selective soft ionization for the PCDDs/DFs, and which has high-sensitivity performance with a minimum limit of detection of 3.7 pptv (signal-to-noise ratio S/N = 3, 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (2,3,7,8-TeCDD)). In particular, a pulse valve has been developed that can operate under a high-temperature condition and produce a supersonic jet under the choke-flow condition<sup>6,7</sup>, enabling isomer selective soft ionization of the PCDDs/DFs. If the supersonic jet gas ejected from our short pulse valve can not only be cooled to cryogenic temperature, but also be ordered uniformly so that the collisions between particles are minimized and the excitation lifetime of its compounds becomes longer, then the nano-second pulse width laser will also ionize softly.

In this paper, we report the experimental results of the following PCDDs/DFs detected by RIMMPA-TOFMS: 2,3,7,8-TeCDD, 1,2,3,7,8-pentachlorodibenzofuran (PnCDF) and 2,3,4,7,8-PnCDF, and the mass and wavelength two-dimensional map database for the 14 kinds of PCDDs/DFs.

## Methods and Materials

**Experimental Setup:** The RIMMPA-TOFMS instrument has been described in detail elsewhere<sup>5</sup>. Figure 1 shows the schematic diagram of RIMMPA-TOFMS for analyzing PCDDs/DFs. Briefly, the set-up consists of a Nd:YAG pumped dye laser including frequency doublers (tunable laser

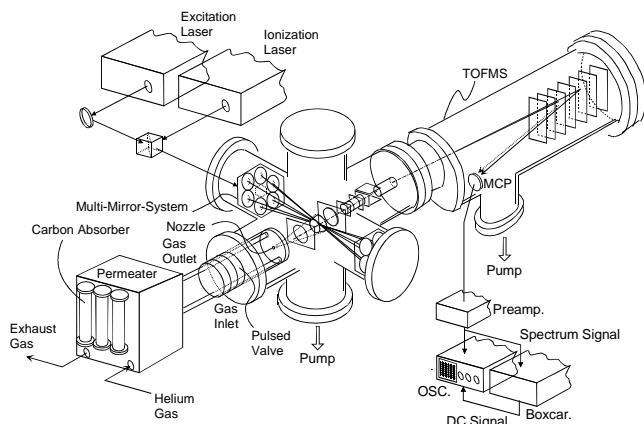


Fig. 1 Experimental apparatus of RIMMPA-TOFMS

radiation, tuning range between 270 – 370 nm, 5 – 8 nano-second pulse width, 10 Hz repetition rate, under  $0.1\text{ cm}^{-1}$  @285 nm optical linewidth, 2 mJ maximum output energy) for exciting sample molecules and a frequency quintupled Nd:YAG (213 nm laser radiation, 3 – 5 nano-second pulse width, 10 Hz repetition rate, 4 mJ maximum output energy) for ionizing excited molecules, a multi-mirror-system<sup>8</sup> by which an optical image relaying system is constructed using 14 reflective mirrors, a PCDDs/DFs sample gas generator (Permeator PD-230, Gastec Corporation) that the concentrations of PCDDs/DFs can

be arbitrarily changed by heating temperature (50 – 230 C) and carrier gas flux (Helium, etc.), a special pulsed valve for the sample inlet system (Gentry-Giese design type, heatable up to 200 C), a reflectron type time-of-flight mass spectrometer including a mass gate system and a z-gap type MCP (R.M. Jordan, mass resolution of 600), a preamplifier for amplifying an ion signal (bandwidth: 400 Hz to 140 MHz, gain: 46 dB, noise: < 0.6 dB), a digital oscilloscope for recording the mass spectrum (500 MHz, 2 GS/sec), and a boxcar gated integrator.

**Detection Methods:** A supersonic molecular beam produced from a pulsed valve with 10 Hz repetition rate, 1 atm of helium gas, and 40 micro-second gas pulse, obtained a flat-topped peak using a fast ionization gauge at the high temperature of 200 C, indicating that choked flow is occurring. This means that under the given conditions, the maximum flow rate through the nozzle orifice (1.1 mm diameter) is reached and the maximum cooling is achieved<sup>7</sup>. The molecular beam interacted with two multi-reflected synchronous laser beams for about 40 nano-second, and the molecules are selectively ionized in the ionization region, and the ionized molecules were detected at the time-of-flight mass spectrometer. The molecular ions injected to the MCP are converted to electrical signals, which are then amplified by a preamp and transmitted to the oscilloscope and boxcar integrator. The time-of-flight mass spectrum is observed at the oscilloscope.

## Results and Discussion

**Mass spectrum:** Figure 2 shows a time-of-flight mass spectrum of 2,3,7,8-TeCDD gas, under the experimental condition of exciting laser energy of 3.0 mJ and wavelength of 310.99 nm, ionizing laser energy of 0.5 mJ, and sample gas concentration of 260 pptv. The inlet shows an enlarged view near a parent spectrum and the isotope ones including the pulse signal that shows the gate width of the boxcar integrator. The figure shows that soft ionization of 2,3,7,8-TeCDD is successfully achieved, and the dissociation of molecules is minimized even with the laser irradiation time of about 40 nano-seconds with neither a pico-second nor femto-second pulse laser.

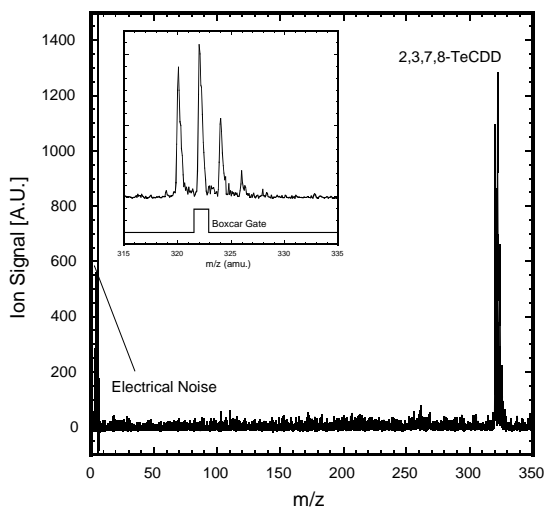


Fig. 2 2,3,7,8-TeCDD Mass spectrum detected by RIMPPA-TOFMS

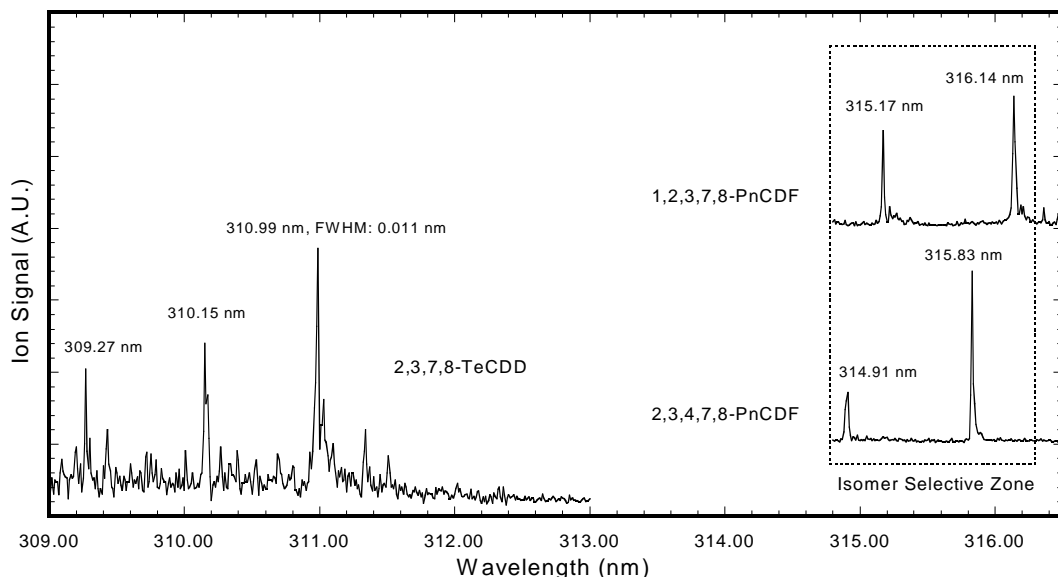


Fig. 3 Wavelength dependence of 2,3,7,8-TeCDD (lower trace), 2,3,4,7,8-PnCdf (middle trace) and 1,2,3,7,8-PnCdf (upper trace)

**Wavelength dependence:** Figure 3 shows the wavelength dependences of 2,3,7,8-TeCDD (lower trace), 1,2,3,7,8-PnCdf (upper trace) and 2,3,4,7,8-PnCdf (middle trace) standard samples. Since the laser energies differed in our experiment, the signal intensity does not mean the amount of ions. In this figure, the first transition wavelength of 2,3,7,8-TeCDD, 2,3,4,7,8- and 1,2,3,7,8-PnCdf are 310.99 nm (corresponding to 3.9866 eV), 315.83 nm (3.92553 eV) and 316.14 nm (3.92168 eV), respectively. The spectrum width (full width at half maximum: FWHM) of 2,3,7,8-TeCDD at 310.99 nm peaks is 0.011 nm. Isomer selective ionization between 2,3,4,7,8- and 1,2,3,7,8- PnCdf can be performed at 316.14 nm and 315.83 nm or 315.17 nm and 314.91 nm respectively.

**Working curve for 2,3,7,8-TeCDD:** Figure 4 shows a working curve of the ion signal plotted against concentration for 2,3,7,8-TeCDD in seeded helium gas. Signal intensity is read by the DC signal from the boxcar integrator. The figure shows that the minimum limit of detection is 3.7 pptv at S/N = 3. A

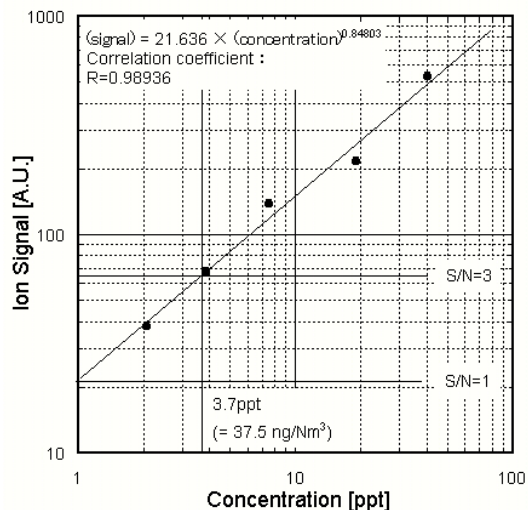


Fig. 4 Working curve for 2,3,7,8-TeCDD

good accuracy is obtained and correlation coefficient  $R = 0.989$ . The laser powers are kept constant throughout the series of experiments.

**Two-dimensional map:** The 14 kinds of PCDDs/DFs are measured by the RIMMPA-TOFMS. The first transition wavelength ( $S_0$  to  $S_1$ ) of these compounds is obtained. Figure 5 shows the two-dimensional map of the parent ion mass and the first transition wavelength for 14 kinds of PCDDs/DFs. In this figure, the closed squares show the PCDDs and the open circles show the PCDFs. Good correlations are observed between the mass and the first transition wavelength.

If the gas cooling of the target molecule is insufficient with the increase in mass, the isomers of this one may not be separated clearly by the laser wavelength.

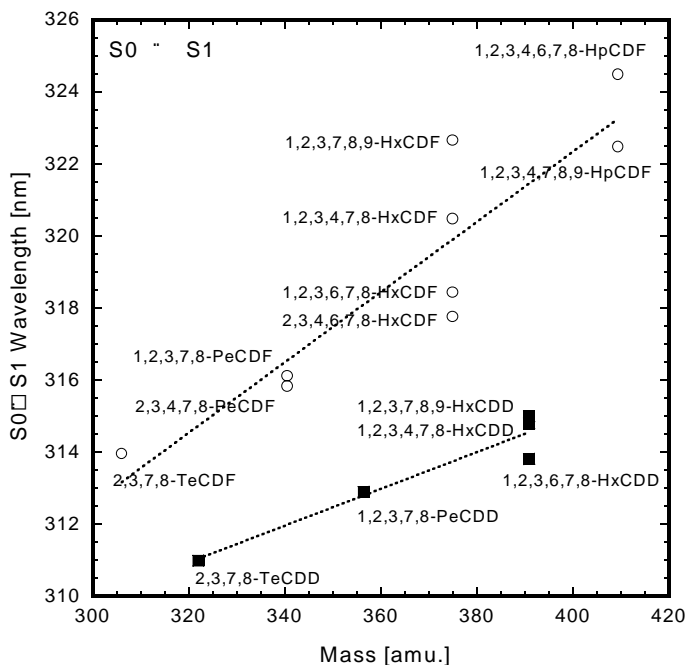


Fig. 5 Two-dimensional map of the parent ion mass and the first transition wavelength for 14 kinds of PCDDs/DFs

**Excitation Lifetime:** Figure 6 shows the absorption wavelength spectra and the mass spectra of 2,3,7,8-TeCDD in cases of sufficient or insufficient cooled gas. The upper, middle and lower spectra are the two-color-two-photon ionization spectrum under the conditions of either insufficiently or sufficiently cooled gas, and one-color-two-photon ionization spectrum under the condition of sufficiently cooled gas, respectively. Moreover, the inlet upper and lower mass spectra are the two-color-two-photon ionization mass spectra in the cases of insufficiently and sufficiently cooled gas, respectively. The mechanism of the soft ionization of up to four or more chlorinated PCDDs/DFs seems to depend on whether the gas injected from the pulse valve is cooled sufficiently or not. If the gas is insufficiently cooled, its peak width is very broad and so the fragment ions and the parent ones are produced simultaneously. In contrast, if the gas is cooled sufficiently, the wavelength spectrum width becomes sharp and the fragment ions are mitigated. Sufficient cooling may not be the only condition for extending the excitation lifetime of the molecules. A nano-second laser is used for ionization of PCDDs/DFs in our experiment, not a pico-second or femto-second laser.

In order to demonstrate whether its excitation lifetime have a nano-second region or not, the two-color-two-photon ionization signal for 2,3,7,8-TeCDD have been observed as a function of the delay time between exciting and ionizing laser according to the experimental method shown by

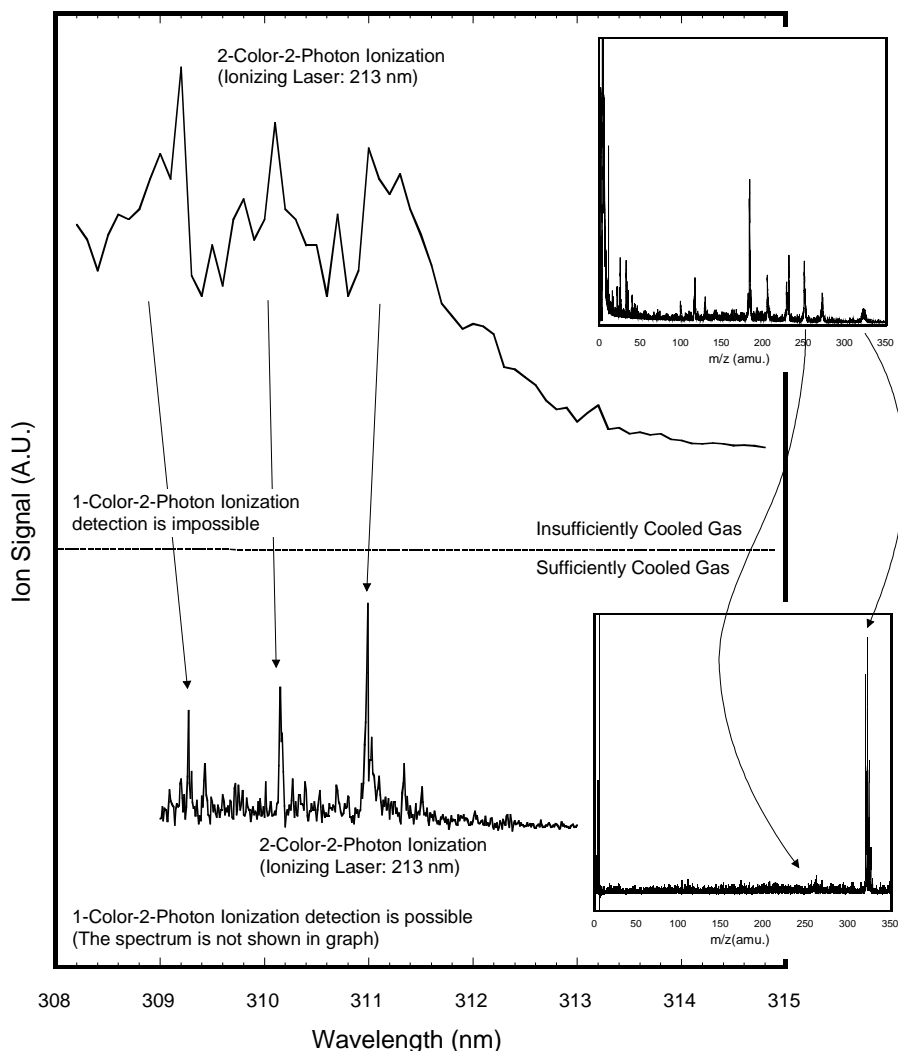


Fig.6 Wavelength spectra and mass spectra (inlet) of 2,3,7,8-TeCDD in cases of the sufficiently and insufficiently cooled gas.

reference [9]. In experiment, Nd:YAG (266 nm, 3 – 4 nano-second pulse width, 10 Hz repetition rate, 4 mJ maximum output energy) for ionizing excited molecules was used. Figure 7 shows the above-mentioned experimental results using 266 nm and 213 nm for ionizing excited molecules respectively. With 266 nm, an ionization signal is obtained when the excitation/ionization laser are overlapping in time only. With 213 nm, the ionization yield decrease slowly over a range of some hundred-nanosecond excitation/ionization laser delay time. This experimental results show that the excitation lifetime of 2,3,7,8-TeCDD molecules is the order of nano-second and that in triplet level  $T_1$ , the lifetime is about one microsecond.

From these result, we believe that our short pulse valve can produce not only extremely cooled gas but also high-density and no-collision gas flow, which is called "crystal flow". In the crystal flow, the gas flows uniformly and all particles have the same translation velocity. Namely, interaction and collision do not occur in the gas flow. This phenomenon appears in the short pulse operation of the valve, unlike with the long pulse valve used hitherto. The distance among molecules in the gas is fixed and the crossing between items of transition level does not occur, hence the lifetime of the excited level is extended. These results indicate that a new critical and optimum distance between the gas valve and the place to be irradiated by the laser light can be decided by this newly developed measuring method.

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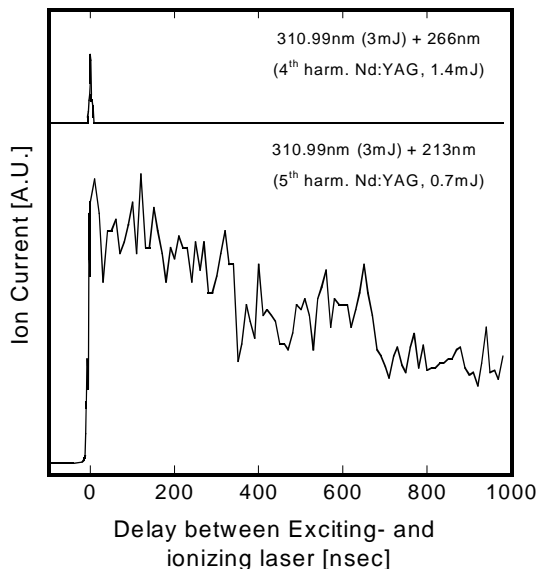


Fig.7 2-color-2-photon ionization yield for 2,3,7,8-TeCDD as a function of the delay time between exciting and ionizing laser

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