An Experimental Challenge of RIMMPA for On-site, Dioxin-direct and Rapid Monitoring of the PCDDs/Fs Exhausted from Incinerators

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Abstract

We tried to analyze the highly (4 to 8) chlorinated PCDDs/Fs on the exhausted gas from EPA/ETV boiler with our newly developed equipment RIMMPA, which is composed of 2 lasers for excitation and ionization, MMS (Multi-Mirror system), HTPD (High Temperature Pulsed-gas Device) and TOF-MS. MMS and HTPD are the key technologies which have brought the selective soft ionization of PCDD/F isomers. For sampling the exhausted gas, we inserted an accumulation column of the adsorbing/desorbing material between the sampling nozzle and RIMMPA.

In the experiment, the accumulation column did not work well. Though a few dioxins were identified by isotope ratio of chlorination from signals obtained with TOF-MS, most signals were masked by unexpected intense noise originated from dense polychlorinated polycyclic aromatics which were used for production of dioxins in the boiler.

Introduction

We have succeeded in the development of RIMMPA (Resonance Ionization with the Multi-Mirror system Photon Accumulation-TOF-MS). We have achieved the 2 color 2 photon resonance ionization of the highly (4 to 8) chlorinated PCDDs/Fs. The selective soft ionization of PCDD/F isomers has also been achieved[1,2,3].

The analytical principle with RIMMPA is as follows:

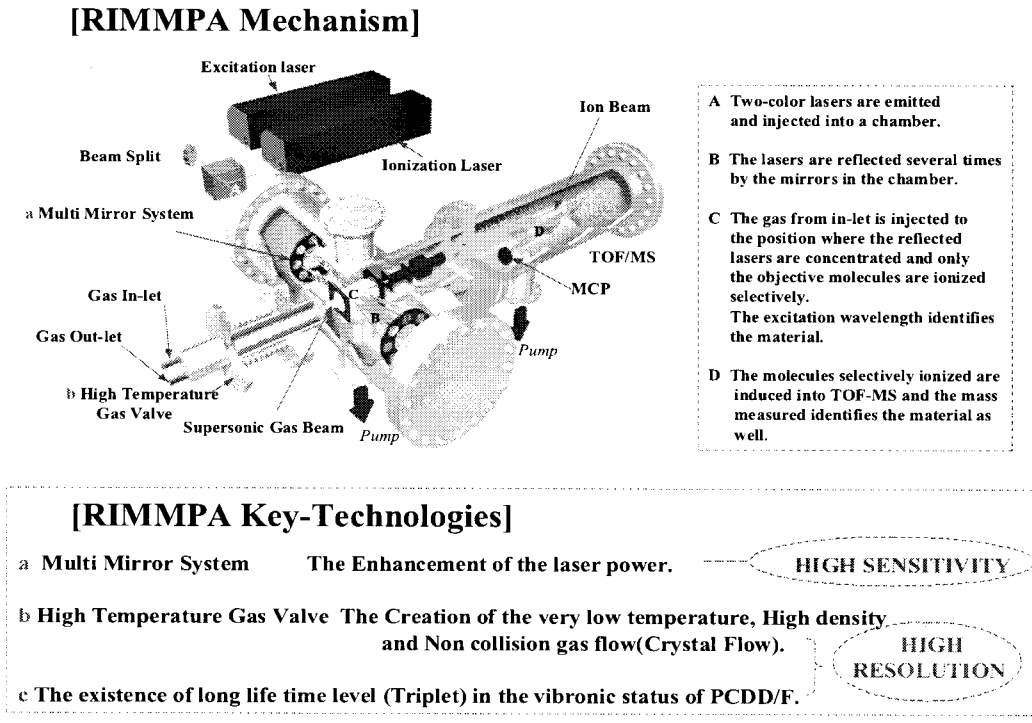

Fig.1 RIMMPA mechanism and the Key technologies

In this system, we use two lasers of nanosecond pulse duration: one is a dye laser of which the wavelength is tunable in the ultraviolet range for excitation and the other is a fixed wavelength laser of the YAG 5th 213nm for ionization of molecules. The molecules are selected by excitation wavelength. This scanning operation is defined as isomer mode.

The typical experimental data are shown in Figs. 2 and 3. The same mass spectrum of 2 isomers 2,3,4,7,8-PeCDF and 1,2,3,7,8-PeCDF obtained from TOF-MS are shown in Fig. 2 where the soft ionization is successfully carried out and only parent ion signal appears without any fragmentation. The wavelength spectra of 2 isomers are shown in Fig. 3 with the resonant wavelength for excitation.

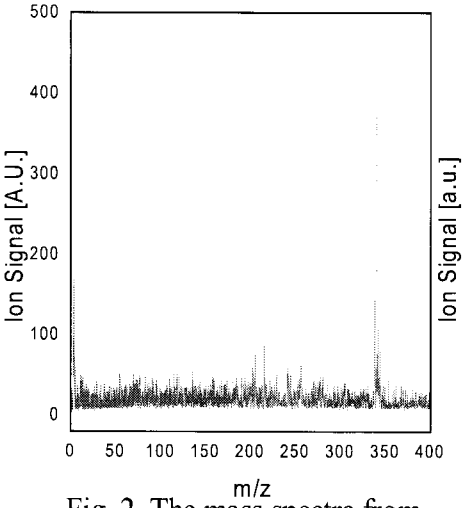

Fig. 2 The mass spectra from TOFMS and its soft ionization

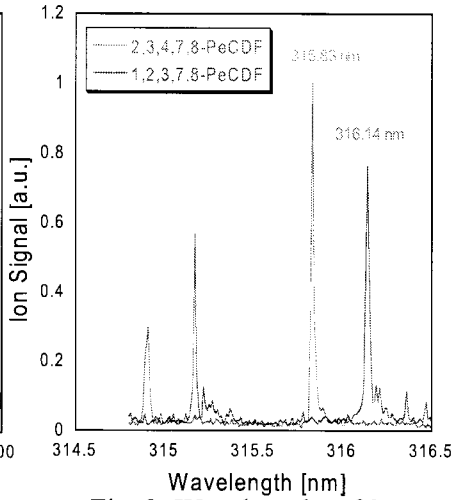

Fig. 3 Wavelengths of 2 isomers of PeCDF

The results of experimental analysis of PCDDs/Fs are concluded in Figs. 4 and 5. The all detection points for PCDD/F isomers are dotted on the frame of excitation wavelength and mass number in Fig. 4. The wavelength dependence of excitation spectra for PCDDs and PCDFs are different each other: For PCDF isomers, a series of sharp isolated resonant spectra appear in the longer wavelength region and broad band spectra appear in the shorter wavelength region. On the contrary, for PCDD isomers except 2,3,7,8 PeCDD, only broad band spectra appear so that wavelength separation for isomers is not easy. The broad band spectra regions for each congeners, however, are illustrated by vertical 10 lines in Fig. 4 and the wavelength commonly crossing all the broad band regions is noted with a horizontal line by "a" in the figure. The laser of wavelength on the horizontal line can excite all congeners in one time and ionized by 213 nm laser. The operation mode is defined as congener mode. The detection limit for 2,3,4,7,8-PeCDF is achieved to 0.41 ppt as shown in Fig. 5.

These data mentioned above were obtained from the standard samples of dioxins at the laboratory not at the field work. So, we participated EPA (the U.S. Environmental Agency) /ETV (the Environmental Technology Verification) Program. And we challenged to analyze the exhausted real gas from the EPA boiler.

Materials and Methods

For on-site and rapid monitoring of PCDDs/Fs exhausted from incinerators, however, there are two technical issues to be solved. The first is to use the He gas as carrier gas instead of air gas in order to keep the high sensitivity, the second is that as the minimum detectable limit is not so low as 0.4 ppt (400ppq or 4.4ng/Nm^3) that is 44 times larger than the Japanese environmental regulated value, the concentration has to be

enhanced. Adopting an accumulation column composed of adsorbing/desorbing material could be expected the concentration effect and the filtering performance on the disturbance impurities.

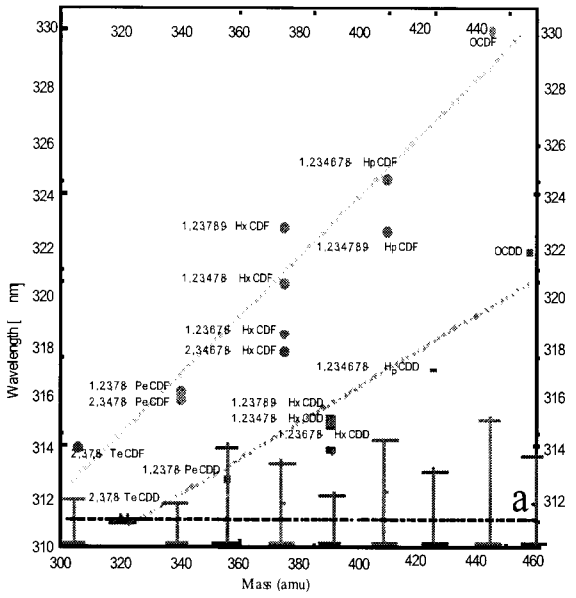

Fig.4 The wavelength and mass mapping of PCDD/F isomers and the wavelength of all congeners excitation is shown by a dotted line.

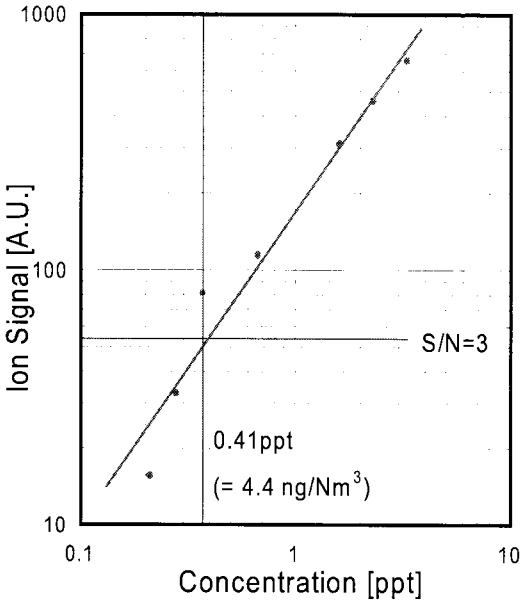

Fig.5 The detectable lowest limit for 2,3,4,7,8 PeCDF for S/N = 3.

Conceptual scheme of the sampling system is shown in Fig. 6. After the exhausting gas is filtered, it is adsorbed at 120° C and accumulated into a TENAX condenser (Adsorption step). The matter such as PCDDs/Fs then is desorbed with the specifically controlled temperature around 300° C (Heat Desorption step) and then to remove nitrogen, oxygen and organic compounds of low boiling point, helium gas of 120°C is substituted (Helium substitution step). During this injection of sample gas to RIMMPA, the operational temperature of HTPD was kept at 200°C.

In the experiment, we tried to select most effective accumulating material among TENAX, artificially-produce silica gel, glass fiber as the fittest material. By using this accumulation column and helium carrier gas method, RIMMPA could be redeemed a lack of sensitivity and the rapid monitoring method could be esteemed "semi-real time monitoring" as far as PCDDs/Fs could be measured during the shorter time than the variation time of the incineration burning.

Results and Analysis

The experiment was carried out during two weeks of 9/12/2005 to 9/22/2005. Nine test runs were carried out during this term. And the samples were collected for 42% of the duration.

However, this sampling system didn't work well and TENAX was not effective. We could not adjust the performance during this short term. Though a few dioxin were identified by isotope ratio of chlorination from signals obtained from TOF-MS, most signals were masked by unexpected intense noises from dense originated plychlorinated polycyclic aromatics which were used for production of dioxins in the boiler. We tried to analyze the several typical isomers with isomers mode and congeners with congener mode but any successful results about total TEQ of the sample gas could not be obtained.

Discussion and conclusions

We were obliged to challenge on the direct monitoring of the real gas without rehearsal because we could not find beforehand any domestic incinerator cooperating with us for the preliminary test. The operations of sampling system were not stable from beginning to end in the test circumstances. Extensive experiences of operation and maintenance were required. In conclusion, we realized the toughness in the real gas analysis and we learned many things. From these experiences we will be able to develop the new rapid monitoring methods and the new application of RIMMPA in near future.

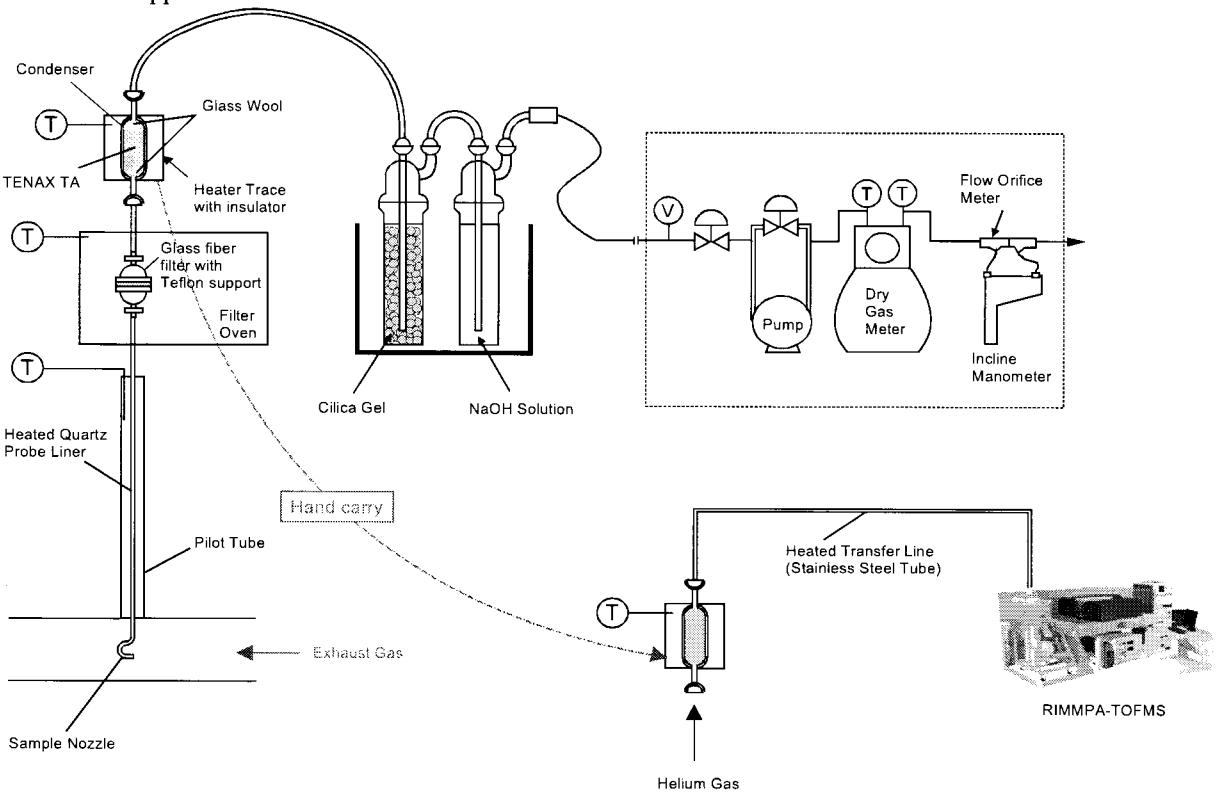

Fig. 6 Accumulation concept for adsorbing/desorbing the sampling matter

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