

Vacuum Ultraviolet Photon Ionization Mass Spectrometer for Detection of Dioxin Precursors

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Abstract: Waste incineration is considered as a main source of dioxins. During the generation of dioxins, dioxin precursors, such as polychlorinated benzenes (PCBz), polychlorinated phenols (PCPh), polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) etc. have been proved to be produced with much higher concentrations than dioxins, which are determined to be closely related to dioxin toxic equivalents. Therefore, online monitoring of these precursor compounds has been becoming one of the main research directions of dioxin detection. In this study, a novel method for online detection of these dioxin precursors in gas phase was developed by nanosecond vacuum ultraviolet single photon ionization technique, combined with time-of-flight mass spectrometer. This setup was evaluated by monitoring chlorobenzene, polychlorinated phenols and naphthalene in gas phase. The results show that there is a linear relation between the parent ion intensity and the chlorobenzene concentration ranged from 5 ppb to 100 ppb.

Key Words: Dioxin precursors, Time-of-flight mass spectrometer, Vacuum ultraviolet; Single photon ionization

1 Introduction

Dioxins are commonly regarded as highly toxic compounds, such as polychlorinated dibenzo-p-dioxins (PCDD) and polychlorinated dibenzo-p-dibenzofurans (PCDF). Due to its strong carcinogenicity and considerable impact on our environment and ecosystems, dioxins had aroused extensive concern in the international community. Municipal solid waste incinerator is one of the main sources of dibenzo-p-dioxins contribute to environmental pollution and cause serious social problems^[1,2]. Currently, the detection of production of dioxins in waste incineration are commonly completed by the off-line analysis methods, i.e., field collecting a certain amount of sample from the incinerator flue gas and analyzing the sample in specialized laboratories^[3]. For example, quantitative analysis of PCDD by gas chromatography interfaced with a mass spectrometer often takes more than one week due to complicated sampling and extracting processes. Continuous real-time online monitoring of the toxic components in the flue gas has attracted great attentions to enable feedback

control of incinerators.

Owing to its large molecular weights and huge family (more than 200 chemical byproducts), direct trace analysis of dioxins is technically difficult and expensive. Therefore, real-time analysis of surrogates of dioxin is a good alternative direction. The dioxin precursors, such as polychlorinated benzenes (PCBz), polychlorinated phenols (PCPh), polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) etc., were found to play important roles in the formation process of dioxin in the incinerator flue gas^[4-6]. Good correlation between international toxicity equivalents of dioxins (I-TEQ) and these precursors were reported^[7-10]. In the case of PCBz and PCPh, as two kinds of dioxin indicators in online monitoring of flue gas, for example, the linear correlation coefficient between the concentrations of PCBz and the dioxin toxic equivalency was up to 90%. Moreover, the concentrations of these precursors are generally over 1000 times larger than the density of PCDD, up to $\mu\text{g m}^{-3}$ (in the order of ppb, parts per billion). Therefore, a real-time measurement of PCBz and PCPh in the flue gas is one of the

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main directions of monitoring the dioxin-like toxics in the incinerator flue gas. Among various methods, the detection technique based on the time of flight mass spectrometers aroused great interests in past decades, for its unique ability of full mass analysis in tens microseconds^[8–17].

In 1997, Zimmermann *et al* developed a mobile resonance-enhanced multiphoton ionization (REMPI) time-of-flight mass spectrometry (TOF-MS) device for on-line analysis of aromatic pollutants in the flue gases^[13]. By using chlorobenzene as dioxin indicator, they demonstrated the feasibility of the REMPI approach for real-time on-line trace analysis of process gases and combustion flue gases. Further application of REMPI in monitoring the flue gas component was limited for its complicated skills involved in REMPI methods and its high molecular selectivity^[11–13]. In general, single photon ionization method (SPI) is a kind of soft ionization technique with less fragmentation. In SPI method, molecules are directly ionized from its ground state into ionic state, without any intermediate state involved, while in multiphoton ionization process, at least, one intermediate state must be excited which might result in fragmentation^[14–17]. To ionize the dioxin precursors by one photon, the photon energy must be higher than the ionization potentials of these precursors, i.e., over 9 eV, which means vacuum ultraviolet light (VUV). Current available VUV sources can be classified into three kinds, low-pressure inert gas discharge lamp^[14], laser frequency tripling^[16–18] and synchrotron radiation^[18]. Synchrotron radiation is seldom applied to on-line monitoring of flue gas, due to its huge dimension and complicated system^[19].

Given the VUV conversion efficiency in xenon medium was about 10^{-4} ^[15], each 355 nm nanosecond laser pulse would generate about 10^{12} VUV (118.4 nm) photons in several nanoseconds duration, which is 7–8 orders of magnitude higher than that of commercial low-pressure xenon lamp (about 10^{10} photons in one second)^[17]. Therefore, tripling generation of VUV from nanosecond laser is an ideal SPI source. There are few reports about this method^[9–16], while there some initial attempts on low-pressure inert gas lamp^[19] in China. It is essential to investigate the possibility of this technique applying in the real time monitoring of the dioxin precursors.

Obviously, on-line analytical techniques are useful for direct process control and optimization of the waste incineration process. In particular, it is important to real-time monitor the relevant hazardous pollutants or of reliable indicator compounds by mass spectrometer. There are a few successful attempts on the on-line mass spectrometer monitoring completed by several institutes in China^[19–23].

Among various dioxin precursors, mono chlorobenzene is an ideal indicator, which has the highest concentration and the good linear correlation-ship with the dioxin I-TEQ^[10]. In past years, online detection of mono chlorobenzene became one of

the main research directions^[7–12] and often was used for evaluating new online detection methods^[13,15,19]. In this study, a time-of-flight mass spectrometry coupled with vacuum ultraviolet single-photon ionization (VUV-SPI-TOF-MS) was used to detect mono chlorobenzene with a detection limit of 5 ppb.

2 Experiment

2.1 Instruments and experimental conditions

The experimental setup is illustrated in Fig.1. The 3rd harmonic output of a neodymium-doped yttrium aluminum garnet laser (YAG laser, Beamtech Optronics Co., SCR-10), 355 nm with a pulse duration of 8 ns operating at 10 Hz was focused by a fused silicon lens ($f = 350$ mm) through a quartz window into a 210-mm-long stainless steel cell for third harmonic generation. The tripling gas cell was filled with inert mixed noble gas (Xenon diluted in Argon). Phase-matching conditions for the tripling process of 355 nm could be optimized by changing the ratio of xenon to argon and total pressure of the mixed gas. The produced 118 nm radiation (vacuum ultra violet, VUV) was directly focused into the ionization region by a plain convex MgF₂ lens ($f = 50$ mm). The plain convex MgF₂ lens served as both seal plane between the gas cell and the vacuum system by fluororubber O-ring and a dispersion optical element. Due to the dispersion difference between 355 nm ($n = 1.39$) and 118 nm ($n = 1.68$), it was possible to keep the 118 nm light focusing into the time-of-flight mass spectrometer (TOF-MS) while the 355 nm light defocusing to avoid too strong multiphoton ionization and fragmentation process.

The sample gases were expanded from a pulsed valve (General Valve Series 9, 0.5 mm orifice diameter) with a stagnation pressure of 0.1 MPa and collimated by a skimmer with a 1.0 mm center hole. The molecular beams of sample gases were introduced into the center of three-electrode accelerating-extracting region of the home made orthogonal TOF-MS. The generated ions by the VUV light were accelerated and extracted perpendicularly towards a two-stage microchannel plate (MCP) detector. The field drift-free region was about 50 cm. The output of MCP detector was sampled, averaged and recorded by a four-channel virtual oscilloscope with 1 GHz sampling rate (Pico Technology, PICO6404), which was programmed in the graphic program language, LabVIEW. The time sequences among the YAG laser, the pulsed valve and the virtual oscilloscope were controlled by a digital delay generator (Stanford Research System, DG535). Each mass spectrum was the averaged result over 1000 laser shots to decrease the fluctuation effect between laser pulses. The TOF-MS accelerating-extracting chamber was kept below 1×10^{-4} Pa with the molecular beam on (with a stagnation pressure of 0.1 MPa).

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