DIOXIN AND FURAN LABORATORY MEASUREMENTS USING JET-REMPI

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Introduction

On-line monitoring of stack emissions to determine TEQ values requires at the minimum, sensitivities at the ppq level, which is far below the detection limit of any current continuous emission monitor. An alternative approach is the real-time measurement of indicator substances, like lowly chlorinated DD/DF isomers, by jet-cooled, resonantly enhanced multi-photon ionization (Jet-REMPI).

The use of Jet-REMPI as an indirect real time TEQ monitor requires identification of sufficiently abundant lowly chlorinated isomers that correlate well with the TEQ values. Recent statistical analysis studies of TEQ values and concentrations for a subset of the mono- to tri-chlorinated PCDD/F congeners show promising correlations, suggesting that these compounds can act as TEQ indicators[1, 2]. The on-line nature of Jet-REMPI provides also a valuable tool for the mechanistic understanding of PCDD/F formation. This understanding may support finding process control methods to reduce or even prevent their formation.

Under support from the U. S. Department of Energy (DoE) and the U. S. Environmental Protection Agency (EPA), SRI International has developed a continuous emission monitor (CEM) for PCDD/F detection using the Jet-REMPI method. In an initial step, the focus of the research was to measure Jet-REMPI spectra for lowly chlorinated PCDD/F isomers, investigate mixtures of these compounds, and apply a more advanced ionization scheme, namely the two color, two photon ionization scheme, to increase the number of REMPI accessible PCDD/F isomers.

Materials and Methods

Jet-REMPI is an ultra-sensitive, highly selective, analytical technique that can identify and quantify vapor-phase constituents at parts-per-trillion levels. In recent years successful applications in on-line monitoring of hazardous air pollutants produced in waste incineration have been reported by two research groups[3, 4], and many significant improvements have been made in the detection of hazardous, vapor-phase, organic compounds of environmental importance using Jet-REMPI.

In the REMPI process, one or two laser wavelengths are used to ionize gas molecules by absorption of two photons, one of which must be resonant with an electronic transition in the target molecule. This optical resonance with the molecular quantum state provides part of the selectivity for Jet-REMPI. Ions produced by REMPI are detected using a time-of-flight mass spectrometer (TOF-MS) that takes advantage of the pulsed nature and well-defined temporal character of laser ionization. The simultaneous detection by mass and wavelength yields the extremely high chemical selectivity crucial to identifying one trace compound in the midst of many other similar ones.

For REMPI of complex molecules, such as dioxins, the spectrum can be simplified dramatically by expansion of the sample through a narrow orifice. The supersonic cooling step results in low sample temperatures, increasing the electronic ground state population and narrowing the resonance line widths through reduction in molecular velocities and through reduction in transition-perturbing collisions. These reduced linewidths eliminate the ionization of other molecular species (interferences) - leading to improved selectivity - and make the peak absorption larger - leading to improved sensitivity.

A more detailed description of our laboratory Jet-REMPI TOF-MS instrument is given elsewhere[5]. Therefore just a brief summary of is presented here. The sample is introduced into the ionization chamber through a pulsed valve (General Valve series 9) that delivers 150 µs sample pulses at a repetition rate of 10 Hz, which results in the advantage of a reduced gas flow and hence smaller vacuum pumps and is compatible with the pulsed nature of REMPI. Residual gas pressures of 10^{-5} Torr in the ionization chamber and 10^{-7} Torr in the mass spectrometer are achieved by the combination of sufficiently large pumps (Varian V-550 and Seiko Seki 301), the short gas injection time, a 0.5 mm orifice of the pulsed valve, and gas samples at atmospheric pressure. The laser system consists of a Continuum Powerlite Precision 9010 Nd:YAG and Sunlite EX OPO including frequency doubling with a nominal tuning range in the UV between 225 and 400 nm, a 5 ns pulse width, and a repetition rate of 10 Hz. The optical linewidth of the system is approximately 0.1 cm^{-1}. For the two color excitation scheme a combination of tunable UV from the OPO and 266 nm produced by the quadrupling of the fundamental wavelength of the Nd:YAG pump laser was used. The two laser beams were unfocused, with a beam area of about 2 mm^2 and pulse energies of approximately 1 mJ for the OPO output and 0.1 mJ of the 4th harmonic were used. Ions were mass analyzed by a reflectron type TOF-MS (R. M. Jordan) with a mass resolution of 1000, amplified by an Ortec 9306 preamplifier (gain = 85, bandwith = 1 GHz) and recorded by a 500 MHz digitizer (Signatec DA500A).

Results and Discussion

The on-line detection of lowly chlorinated DD/DF isomers is of particular interest for investigation of the formation chemistry of toxic PCDD/F, and indirect determination of TEQ values[1, 2]. For this purpose, we investigate the Jet-REMPI spectroscopy of 2,7- and 2,8-DCDD and 2-MCDF which are proposed as potential TEQ-indicators.

Despite the fact that Jet-REMPI for the two DCDD is already known[6], it has not been proven yet if Jet-REMPI is a valuable tool to discriminate these isomers. Therefore we conducted experiments by using a sample consisting of a mixture of equal amounts of 2,7- DCDD and 2,8-DCDD, desolved in acetone. To simplify these tests, a small quantity of the liquid mixture was injected into a stainless steel sample flask on the upstream side of the pulsed valve, and room air was used as a carrier gas to simulate semi realistic conditions. We estimate that the concentration of each isomer in the sampled gas stream was approximately 1 ppb. All components in the sample stream, including the nozzle, were heated to 150°C to prevent condensation. Figure 1 shows the ion signal recorded at mass 252, corresponding to the parent ion of both isomers, as a function of wavelength. Several individual absorption features are labeled to show which isomer gave rise to the ion signal.

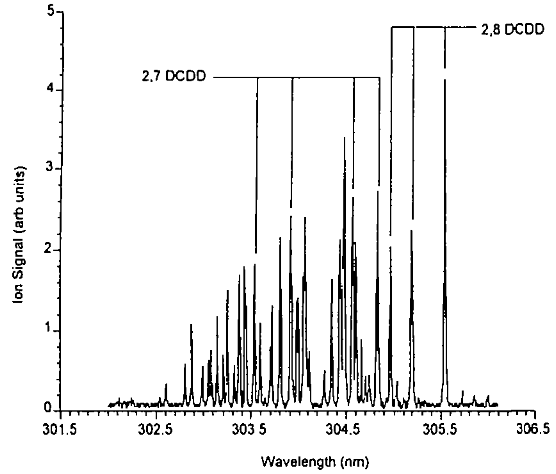

Figure 1: Wavelength dependence of the m/z 252 ion signal for jet-REMPI detection of an equimolar mixture of 2,7- and 2,8-dichlorodibenzodioxin

Assignment of these absorption features was made by measuring the Jet-REMPI spectra for each isomer separately and by comparison with the results of Weickardt et al.[6]. From an estimated signal-to-noise ratio of 20, we calculated a current detection limit of 50 ppt for both DCDD isomers.

The wavelength dependence for 2-MCDF, which has never been examined by Jet-REMPI, is shown in Figure 2. The wavelength dependence shows a number of clearly resolved peaks, however, the overall ion signal strength was less than for similar dioxin molecules. One common cause of low ionization probability occurs when the two photons do not excite the neutral molecule appreciably above its ionization threshold. One major consideration for improving REMPI sensitivity is the use of a different wavelength (color) for the ionization step, although one color for both the excitation and ionization steps is certainly simpler to implement.

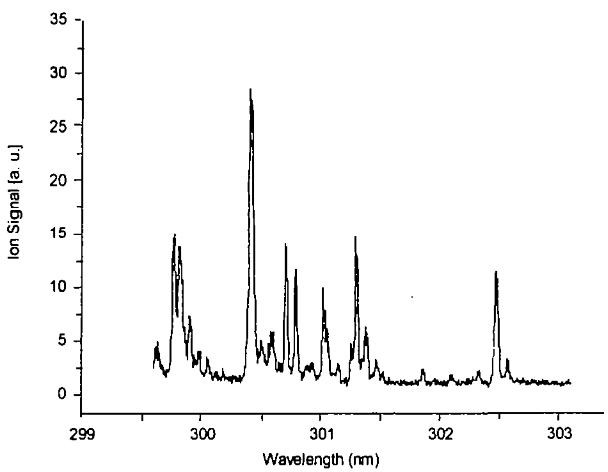

Fig. 2: Wavelength dependence of the m/z 202 ion signal for jet-REMPI detection of 2-monochlorodibenzofuran.

However, in certain cases, using a second color is preferable or essential. Specifically, if the excited state lies at an energy less than half the ionization potential then a second photon of the same wavelength will not have enough energy to ionize the molecule. For example, in tetrachlorinated dioxins (TCDD), the energy of the S_1 level is approximately half the ionization potential[7]. Thus, single-color REMPI may or may not be effective for TCDD. Two-color REMPI using a second, higher energy laser beam may be a much more efficient technique for TCDD detection. The second beam would not require an additional laser. When using a Nd:YAG pumped OPO, the

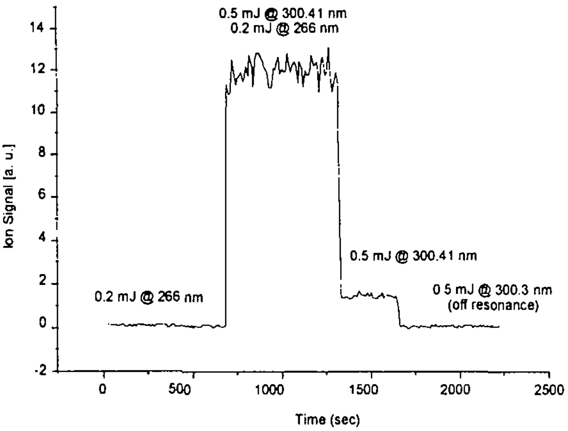

Figure 3: Measured m/z 202 ion signal for jet-REMPI detection of 2-mono-chlorodibenzofuran using various one- and two-color schemes.

second color can be the fourth harmonic at 266 nm or the fifth harmonic at 213 nm, of the Nd:YAG *fundamental* wavelength produced using nonlinear crystals.

To test this possibility, we reexamined the REMPI signal corresponding to the m/z 202 parent ion under a variety of conditions. The result is shown in Figure 3. With only the fixed wavelength (266 nm) light, the signal is at baseline. With the addition of light at 300.41 nm corresponding to the $S_0 \rightarrow S_1$ resonant transition of 2-monochlorofuran, the two-color REMPI signal appeared and remained constant. Turning off the 266 nm light caused the ion signal, due now only to the two-photon, one-color REMPI process, to drop by a factor of approximately 8. Detuning the laser off resonance to 300.3 nm resulted in the signal level again measuring zero. These results appear to confirm the hypothesis that the two-photon, one-color scheme did not impart sufficient energy to achieve a high ionization probability.

Acknowledgments

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