

Initial Development Of Continuous Emissions Monitor Of Dioxin

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1. Introduction

The need for a continuous emissions monitor for the determination of dioxins and furans at realistic (ppt or sub-ppt) concentrations in real time (minutes) is widely recognized in the waste combustion community. The key issues are overall sensitivity, and selectivity among the many congeners found in real applications. At SRI International we are completing development of an instrument to meet these needs. Our instrument is based on supersonic jet expansion and cooling, followed by resonantly enhanced multiphoton ionization (REMPI) into a mass spectrometer. This furnishes the dual selectivity of tuned laser absorption and mass analysis.

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-REMPI.

2. Objective

Emission control strategies must ultimately rely upon a careful assessment of the link between health effects and ambient, human exposure levels to hazardous air pollutants (HAPs). Because polychlorinated organic compounds in general, and dioxins and furans in particular, are among the most toxic of HAPs, SRI International is developing a continuous emission monitor (CEM) for these species using the jet-REMPI technique under support from DOE. The unique capability for real-time detection and identification of these and other toxic HAPs directly in incinerator emissions using a CEM instrument is an essential component of emissions modeling, dispersion modeling, source apportionment, and ultimately, of human exposure modeling. Jet-REMPI is the only instrumental technique that can provide the speed, breadth, and sensitivity of measurement capabilities that are required in support of the development of a comprehensive strategy to monitor and control emissions of dioxins and furans from waste incinerators.

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. 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.

3. Approach and Technology Description

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.

The sample is introduced into the ionization chamber through a pulsed valve (General Valve series 9) that delivers 150 μ s 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, bandwidth = 1 GHz) and recorded by a 500 MHz digitizer (Signatec DA500A). Additional technical and experimental details are available in references 1 and 2.

4. Results

We have applied the jet-REMPI technique to the detection of a number of organic compounds, including lowly chlorinated dioxins and furans. For example, the wavelength dependence for 2-MCDF, which has never been examined by Jet-REMPI, was measured. The wavelength dependence, shown in Figure 1, has 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. In certain cases, using a second color is preferable or essential if the excited state lies at an energy less than half the ionization potential. For example, in tetrachlorinated dioxins (TCDD), the energy of the S_1 level is approximately half the ionization potential. 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.

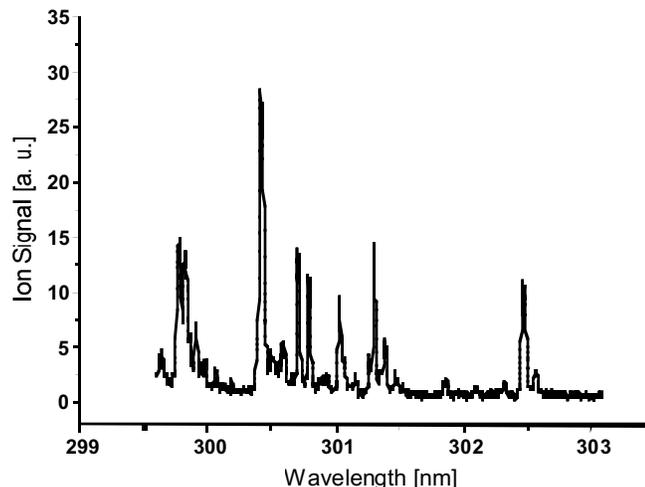


Figure 1. Wavelength dependence for the jet-REMPI detection of mono-chlorodibenzofuran using a one-color, two photon scheme. Mass 202 is monitored.

To test this possibility for 2-MCDF, we reexamined the REMPI signal corresponding to the m/z 202 parent ion under a variety of conditions. Our results, shown in Figure 2, appear to confirm the hypothesis that the two-photon, one-color scheme did not impart sufficient energy to achieve a high ionization probability, whereas the two-color scheme results in a significantly enhanced detection probability.

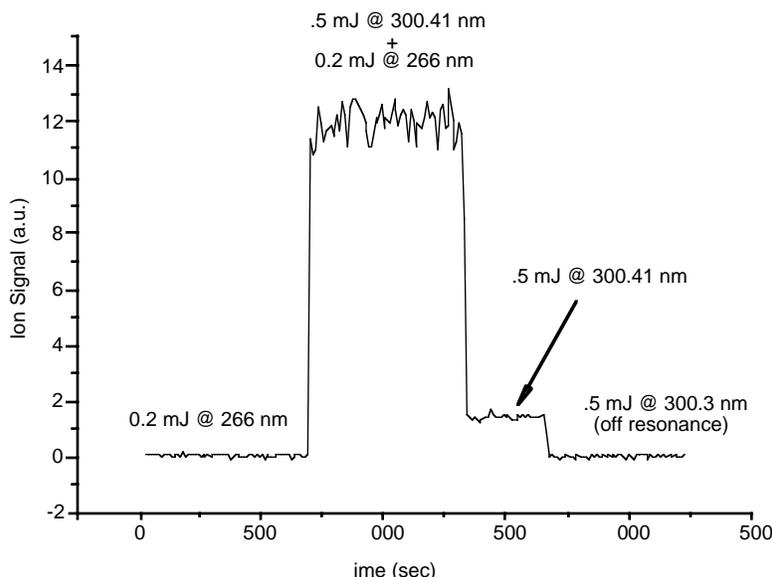


Figure 2. Dependence of mono-chlorodibenzofuran using signal on the REMPI scheme.

During the first ten minutes of detecting 2-MCDF, a one-color, two photon scheme was used with at a fixed frequency of 266 nm, and a pulse energy of 0.2 mJ. Note that no signal is

seen as 266 nm is off resonance for the S_0 to S_1 transition in 2-MCDF. During the next 10 minutes, a two-color scheme is used, combining one tunable photon at 300.41 nm (resonant with the S_0 to S_1 transition) with one fixed 266 nm photon. A very large ion signal at m/z 202 is observed. Without the 266 nm photon, the ion signal is still observed, but at a much lower intensity. Finally, when the laser is tuned off resonance to 300.3 nm, there is again no signal.

Recently, SRI performed a series of studies at EPA's RTP facility. These experiments represent quasi-field measurements since they were made at a pilot-scale combustion facility using an exact copy of our laboratory instrument that SRI built for EPA. During those studies, several interesting species were identified in a nominally clean methane flame. Benzene, phenol and aniline were all detected in the EPA reactor. For all species, the measured wavelength spectra were essentially identical to those recorded using a pure test gas mixture, and all were easily detected in the exhaust stream. Furthermore, their presence could be entirely attributed to the methane combustion chemistry as the background levels were not detectable in the absence of the flame.

Figure 3 shows the time dependence of the phenol signal at m/z 94 with the laser tuned to the primary resonance at 274.1 nm. The time resolution of this data was 1 second, corresponding to 10 laser shots per data point. Between $t = 0$ and 250 seconds, the background signal was measured with no reactant gases flowing. At 250 seconds, the methane and oxygen reactants were introduced but without igniting the flame.

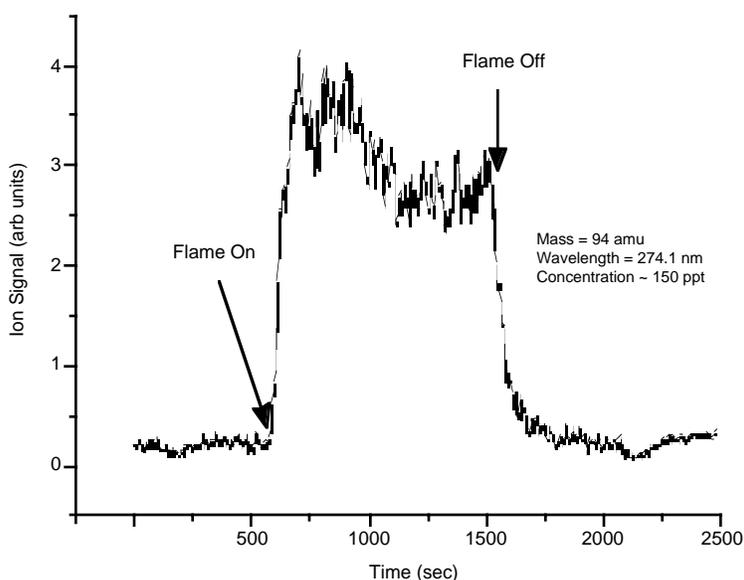


Figure 3. Time dependence of phenol measured in a lean methane flame at EPA.

Note that prior to flame ignition, the phenol signal was essentially absent. At the point indicated on the figure, the flame was ignited, and the phenol signal rose rapidly and remained more or less constant until the flame was extinguished. With the flame off, the phenol signal initially decreased rapidly followed by a slower decrease back to the baseline. The slower decay was likely due to residual phenol in the sampling line and pulsed valve. Increasing the temperature of these components would likely decrease the phenol clearance time. Under the REMPI conditions used to measure the data in Figure 3, we estimate the phenol concentration to be 150 ppt.

Figure 4 shows a similar time history recorded for the aniline signal at m/z 93 and a wavelength of 292.8 nm. In this measurement, the methane flame equivalence ratio was also 0.8. Again, the aniline signal was absent until the flame was ignited, at which point it rose rapidly and remained easily measurable until the flame was extinguished. No estimate has been made yet for the concentration of aniline in the exhaust gas stream.

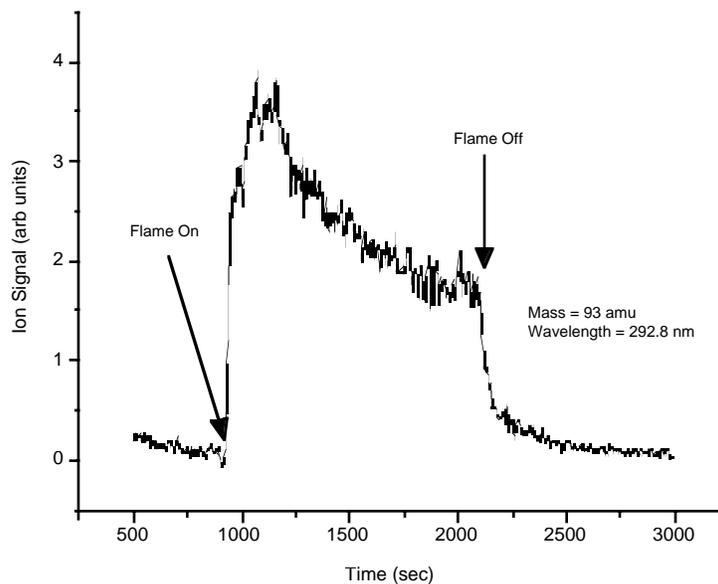


Figure 4. Time dependence of aniline measured in a lean methane flame at EPA.

5. Applications

There are at least two different applications for a dioxin CEM in connection with waste incineration. The first would be in support of pollution prevention at the source. For this application, on-line monitoring of suitable precursor compounds would be needed to control dioxin and furan formation and release. The requirements for this application include an instrumental sensitivity in the ppt range, and a thorough knowledge of formation chemistry within the incinerator.

A second application of a dioxin CEM is for compliance monitoring. In this application, on-line monitoring of stack emissions is required to determine the toxic equivalence (TEQ) value. This measurement requires instrumental sensitivity in the ppq range, below the detection limits of any current CEM. Possible approaches to achieve this sensitivity include development of fast preconcentration techniques and/or the use of indicator substances for the TEQ determination. Surrogate compounds might include chlorobenzenes or lowly chlorinated dioxin and furan congeners. The use of surrogates requires determination of the correlation between the TEQ and the levels of the indicator compounds. This correlation may be strongly dependent on the specifics of the incinerator, its operating conditions, and the feedstock.

For many environmental, process control, national security, and medical diagnostic applications, the extreme capabilities of the full scale jet-REMPI instrument used here are not required. Thus, a much simpler, more compact, and less expensive instrument can be developed that retains many of the inherent advantages of jet-REMPI. These new configurations greatly expand the range of uses for this analytical technique.

6. Future Activities

A number of improvements are being made in the instrument that will significantly increase its sensitivity. We are also developing additional instrumental configurations using fixed wavelength lasers, non-pulsed gas inlets, and direct sampling of organics in water. These new configurations use a smaller TOF-MS and simpler laser systems designed for field applications. These new instruments will greatly expand the range of analytical applications for Jet-REMPI.

For example, there are now commercially available time-of-flight mass spectrometers that fit in a standard 19 chassis rack, including all high vacuum pumps and control electronics. Similarly, there are commercial, 19 -based, fixed frequency (e.g. 193 nm, 246 nm, or 266 nm), solid-state laser systems. By combining these components with a suitable inlet, a field deployable system can be easily assembled for selected applications where fixed frequency REMPI is useful. Small, broadband, tunable solid-state laser systems are also available for applications where tunability is required to maintain chemical selectivity.

Likewise, a number of inlet configurations are under development, including improved pulsed valves, continuous flow capillary transfer lines, continuous flow aqueous samplers based on semipermeable membranes, and thermal desorption inlets for solid sample matrices.

7. Acknowledgements

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8. References

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