

## DEVELOPMENT OF A REAL-TIME CONTINUOUS EMISSIONS MONITOR FOR DIOXINS AND OTHER CHLORINATED AROMATICS

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### INTRODUCTION

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 the U.S. Department of Energy (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.

Our technique will provide real-time dioxin and furan concentrations rather than the multi-hour or multi-day averages as in the case for existing, conventional sampling and analysis methods. This capability will allow a detailed investigation of the relationship between dioxin emissions and the incinerator operating parameters and waste feed characteristics. Such a study may reveal that "puffs" (transient pollutant emission events) account for a majority of the dioxin emissions, and hence only short-term control methods would be required to meet time-averaged regulatory emission limits. Such control strategies may be much more cost effective than full-time emission control approaches. Tailoring the emission control strategy in response to minute-by-minute changes in the emission of hazardous pollutants can only be accomplished if a suitable CEM is available, such as our Jet-REMPI based instrument.

### MATERIALS AND METHODS

Our approach to acquiring the dioxin and furan levels is to perform direct measurement of specific congeners using the Jet-REMPI method. Jet-REMPI is an ultra-sensitive analytical technique that can selectively identify and quantify vapor-phase constituents present at ppt levels in incinerator emissions without preconcentration or sample collection.

In recent years, many significant improvements have been made in the detection of hazardous, vapor-phase, organic compounds of environmental importance. Several research groups, including SRI, (1-4) DLR, (5,6) and The Technical University of Munich, Germany, (7,8), have demonstrated instruments or components of instruments based on REMPI and mass spectrometry.

Ions produced by resonance enhanced multiphoton ionization (REMPI) are often 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 extremely high chemical selectivity crucial to identifying one trace compound

in the midst of many other similar ones. Typical sensitivities of conventional REMPI TOF-MS systems that do not use sample molecule cooling are in the mg/dscm range and higher, which is totally insufficient either for a laboratory system or for regulatory monitoring of chlorinated aromatics in a waste treatment process such as an incinerator.

A major improvement in sensitivity without loss in selectivity can be achieved using a pulsed gas valve that produces a supersonic expansion. Pulsed gas valves provide a number of advantages over continuous gas inlets, including reduced gas flow and hence smaller vacuum pumps, higher local gas densities, well-defined spatial distribution, significantly reduced translational energy distribution orthogonal to the propagation direction, and reduced internal (vibrational and rotational) temperatures leading to greatly enhanced spectroscopic resolution.

REMPI is a highly sensitive, highly species-selective, gas-phase analysis technique that has been applied to numerous problems in molecular spectroscopy and combustion research. For REMPI of complex molecules, such as dioxins, the spectra can be simplified greatly by expansion through a nozzle. Adiabatic expansion results in low sample temperatures, which increases the electronic ground state population and narrows the resonance line widths through reduction in molecule velocities (reduced Doppler or temperature broadening) and through reduction in transition-perturbing collisions (reduced pressure broadening). These reduced linewidths lessen the ionization of other molecular species (interferences) - leading to improved selectivity - and make the peak absorption larger - leading to improved sensitivity. One or more lasers are used to ionize the cooled gas molecules by absorption of two or more photons, one of which must be resonant with an electronic transition in the target molecule.

Because different isomers of a given chemical composition may have very different toxicities, it is essential that a measurement instrument be capable of distinguishing among isomers. Our instrument is able to do this without any sample pre-separation, such as by gas chromatography, for example, because of the inherent ability of optical spectroscopy (REMPI in this case) to readily distinguish among isomers. The selectivity of the optical spectroscopy is vastly improved through the pulsed nozzle cooling effects, as discussed above.

The mass spectrometric capabilities of our system include an upper mass range typically up to 500 amu, limited only by the size of the mass spectral data files. Typical laser-based TOF mass analyzers use a simple, linear flight path combined with a short duration, pulsed laser, ionization source. Low signal levels that may result from the use of a very short ion formation pulse can be compensated for by signal averaging using multiple scans. To optimize this mode of operation, a high repetition rate ionization laser is used. Achieving good mass resolution ( $m/\Delta m$ ) with a TOF instrument is straightforward using a pulsed laser for ionization because of the narrow spatial, temporal, and energy spread of the nascent ions.

### RESULTS AND DISCUSSION

The laser system used in our preliminary experiments described below consists of a Continuum Powerlite Precision 9010 Nd:YAG and Sunlite EX OPO with a nominal tuning range in the visible between 445 and 710 nm, a 5 ns pulse width, and a repetition rate of 10 Hz. Frequency doubling is achieved using an Inrad autotracker II. The optical linewidth of the system is approximately  $0.1 \text{ cm}^{-1}$ .

The pulsed valve is an unmodified General Valve series 9 unit, with an orifice diameter of 0.5mm. The nominal opening time was 150  $\mu\text{s}$ , with a 2.5 cm separation between the exit of the valve and the ionization region. With the sample reservoir at atmospheric pressure, the two 250 l/s turbomolecular pumps (Varian Turbo V-250) maintain pressures in the ionization chamber and mass spectrometer regions of  $10^{-5}$  Torr, and  $5 \times 10^{-7}$  Torr, respectively.

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The ionization conditions used to acquire the preliminary data included a pulse energy of approximately 1mJ in a 1.5 mm diameter laser beam. Ion signals from the R. M. Jordan angular reflectron TOF-MS were amplified by a Comlinear preamplifier with a gain of 10 and a 350 MHz bandwidth. Signals were recorded by a 500 MHz, Signatec DA500A digitizer.

A sample of 1,2-dichlorobenzene was used for the initial instrument testing. To simplify these tests, a small quantity of liquid was injected into a stainless steel tube on the upstream side of the pulsed valve, and room air was used as a carrier gas. All components were at room temperature. 1,2-Dichlorobenzene is commonly used for testing because of its high vapor pressure at room temperature, and it may also be an important indicator species of total dioxin levels (9). Moreover, the REMPI excitation spectrum is well known, so that tuning the laser to resonance line at 261.2 nm produced the mass spectrum shown in Figure 1.

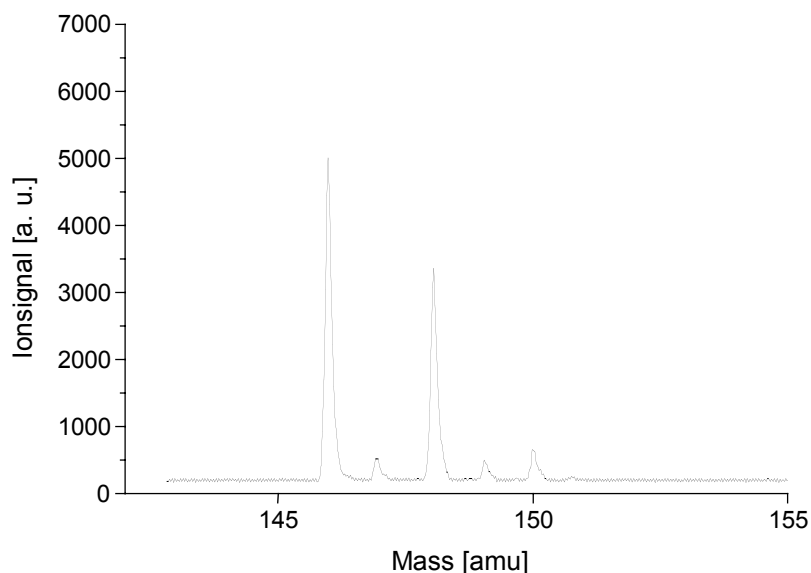


Figure 1. Jet-REMPI mass spectrum of 1,2-dichlorobenzene at a wavelength of 261.2 nm.

We also performed a rapid survey of the  $m/z$  146 ion signal strength as a function of laser wavelength to produce the REMPI excitation spectrum. That spectrum, shown in Figure 2, is in good agreement with previously reported results for the same molecule. Both the resonance locations and their peak heights are consistent with published REMPI spectra, indicating that our instrument is functioning correctly.

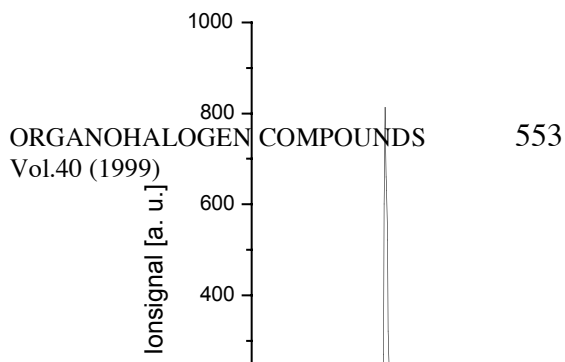


Figure 2. Wavelength dependence of the m/z 146 ion signal for 1,2-dichlorobenzene.

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