

### DEVELOPMENT OF A REAL-TIME CONTINUOUS EMISSIONS MONITOR FOR HAZARDOUS AROMATIC AIR POLLUTANTS

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#### Introduction

Under the 1990 Clean Air Act (CAA) Amendments, the U.S. Environmental Protection Agency (EPA) was mandated to implement a research program providing the scientific foundation to develop a comprehensive national strategy. This strategy aim to control 90%, or more of the emissions of the 30 most hazardous toxic pollutants in urban areas. This control strategy must ultimately rely on a careful assessment of the link between health effects and ambient, human exposure levels to hazardous air pollutants (HAPs). Despite the need for such data, reliable ambient concentrations have been measured for fewer than 40% of the 189 HAPs.<sup>1</sup> Even these limited measurements provide no spatial or temporal information on HAPs levels, whose variation is inherent due to the sporadic, episodic nature of many combustion-related HAPs releases. This information cannot reliably be estimated or inferred by typical current method, like GC-MS. It must be acquired through actual field measurements under typical, time-varying, ambient human exposure conditions.

A powerful alternative to current HAPs monitoring methods is Jet-REMPI-ToF-MS. It combines resonance enhanced multiphoton ionization (REMPI), supersonic jet cooling, and time-of-flight mass spectrometry.

SRI International is developing a continuous emission monitor (CEM) for HAPs using the REMPI technique under support from the U. S. Department of Energy (DoE) and the U.S. Environmental Protection Agency (EPA).

Our instrument will provide real-time HAPs at ambient and toxicological concentrations, instead of the multi-hour or multi-day averages obtained using existing, conventional sampling and analysis methods. This instrument will provide the speed, breadth, and sensitivity of measurement capabilities required by EPA in support of its development of a comprehensive national strategy to control emissions of HAPs from urban sources.

#### Materials and Methods

Our approach to detecting toxic organic HAPs and HAP mixtures in urban areas at the required levels is to perform direct measurement of specific isomers using the Jet-REMPI method. Jet-REMPI is an ultra-sensitive analytical technique that can selectively identify and quantify vapor-phase constituents at parts-per-trillion levels or lower.

In recent years, many significant improvements have been made in the detection of hazardous, vapor-phase, organic compounds of environmental importance using Jet-REMPI. It has been demonstrated by several research groups, including SRI<sup>2,5</sup>, DLR<sup>6,7</sup>, and The Technical University of Munich, Germany<sup>8,9</sup> - under the condition of supersonic cooling, the two-dimensional detection scheme based on laser excitation spectrum plus mass spectra can provide a unique method of molecular identification and structural detection.

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 HAPs and even 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 pulsed gas valves also provide advantages over continuous gas inlets, such as reduced gas flow and hence smaller vacuum pumps and is compatible with the pulsed nature of REMPI.

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 does this without any sample pre-separation, such as by gas chromatography, for example, because of the inherent ability of the laser excitation step to readily distinguish among isomers.

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. The TOF mass analyzer uses a simple, linear flight path compatible with the short pulsed laser. 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.

A more detailed description of our laboratory Jet-REMPI ToF-MS instrument is given elsewhere<sup>10</sup>. Therefore we present here just a brief summary of our instrument.

The sample is introduced into the ionization chamber through a pulsed valve (General Valve series 9) that delivers 150  $\mu$ s sample pulses at a repetition rate of 10 Hz. 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-250 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  $0.2 \text{ cm}^{-1}$ .

An unfocused laser beam is used, with a beam area of about  $2 \text{ mm}^2$  and pulse energies of approximately 1 mJ. Ions were mass analyzed with a reflectron type ToF-MS (R. M. Jordan), amplified by an Ortec 9306 preamplifier (gain = 85, bandwidth = 1 GHz) and recorded by a 500 MHz digitizer (Signatec DA500A).

### Results and Discussion

The effective temperature of samples in the supersonic jet is important for sensitivity and selectivity using Jet-REMPI. Lower temperatures lead to narrower lines, which improves

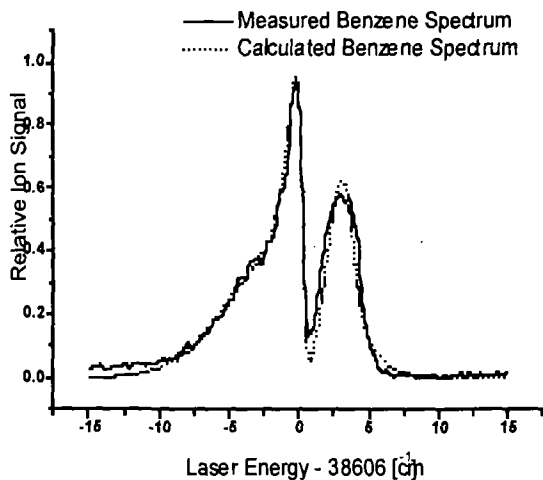


Fig. 1: Relative ion signal and spectroscopic fit for the benzene transition around 259 nm

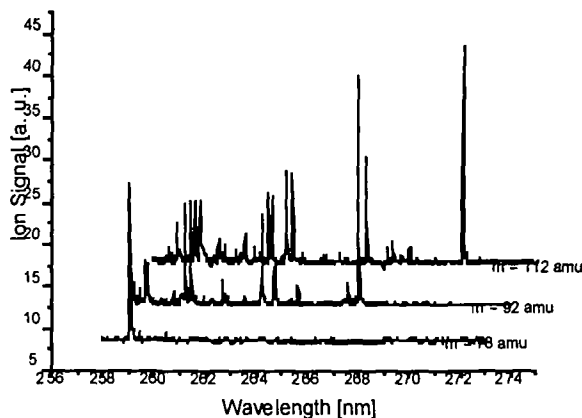


Fig. 2: Wavelength dependent REMPI spectra for Benzene (78 amu), Toluene (92 amu), and Chlorobenzene (112)

selectivity. In addition, there are fewer total lines, again improving both sensitivity and selectivity. To learn the operating conditions that achieve the lowest temperature in combination with the highest sensitivity from our pulsed nozzle/ion extraction arrangement, we have used benzene as a thermometric species. The spectroscopy of benzene is known quite well, allowing determination of the effective rotational temperature from measured spectra. Measurements of a single band are shown in Fig. 1. This spectrum was taken at a distance of about 2.7 cm from the nozzle. The band shown is part of the lowest singlet-singlet transition ( $S_1 \leftarrow S_0$ ) of benzene near 259 nm. The band shown corresponds to many overlapping rotational lines. From the overall contour of these overlapping lines, we can determine an effective rotational temperature of the benzene. We simulate the form of the main contour as a function of temperature. Rotational band calculation follow the method given by Callomon, et al.<sup>11</sup> The result is also shown in Fig 1. The best agreement of the general shape for the simulated band contour with the experimental result is given at a temperature of  $19 \pm 1$  °K. This indicates a high degree of internal relaxation. To demonstrate the two dimensional detection scheme based on wavelength and mass we used a mixture of benzene, toluene, and chlorobenzene as test substances.

These molecules are known HAPs and their REMPI spectra are defined<sup>12, 13</sup>. Due to soft ionization, only the parent peaks at their respective masses are recorded and no cross sensitivities

occur. The results in Fig. 2 show that we have good optical resolution for our measured spectra. This also indicate sufficient cooling.

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