

JET-REMPI-TOFMS DETECTION OF HAZARDOUS AIR POLLUTANTS USING A COMPACT TUNABLE UV LASER SOURCE

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Introduction

Jet-REMPI technology combines the principles of optical spectroscopy and mass spectrometry to provide a "two-dimensional" detection scheme. Simultaneous detection by both mass and optical wavelength yields extremely high chemical selectivity that is crucial for identifying one trace compound in the midst of many other similar species. The high selectivity and sensitivity of the technique allow real-time measurements to be obtained within seconds, without the need for pre-concentration or additional separation, as in GC-MS, for example.

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, GSF-Forschungszentrum für Umwelt und Gesundheit in Oberschleißheim, Germany, DLR (Deutsche Forschungsanstalt für Luft und Raumfahrt) in Stuttgart, Germany and SRI International in Menlo Park CA¹⁻⁵, have demonstrated instruments and their application or components of instruments based on REMPI and mass spectrometry.

The purpose of our research was to demonstrate that a compact tunable UV laser system could be used for the real-time detection of aromatic hydrocarbon hazardous air pollution vapors at sub-ppb levels using the Supersonic jet-REMPI technique. This technique has already been proven to be highly effective for the real-time measurement of complex mixtures of hydrocarbon vapors, but to date has required a large, complex and delicate high-resolution tunable UV laser system. By reducing the size and increasing the ruggedness of the tunable laser component, we have made the initial step towards taking this powerful technology from the lab and developing a field-portable instrument.

The primary task was assessing the effect of a laser with lower spectral resolution on chemical specificity and detection sensitivity. For this purpose we chose to focus on a small group of single-ring aromatics, including benzene, toluene, the xylenes, and chlorobenzene. Detection sensitivity measurements were then taken for pure compounds, samples with complex mixtures of non-isomers, and finally mixtures of isomers.

Materials and Methods

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. For REMPI of complex molecules, 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 the supersonic jet TOF-MS part of the instrument is given elsewhere⁶. 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 μ s sample pulses at a repetition rate of 10 Hz. Ions were mass analyzed by a reflectron type TOF-MS (R. M. Jordan) with a mass resolution of 1000, and recorded by a 500 MHz digitizer (Signatec DA500A). The jet-REMPI technique has already been proven to be highly effective for the real-time measurement of complex mixtures of hydrocarbon vapors in the laboratory, but to date has required a large, complex and delicate high-resolution tunable UV laser system.

The resolution of the laser system will affect the ability to distinguish between molecules, especially for isomers, where the mass resolution step cannot provide any distinction. Experiments were performed to confirm that unique spectral transitions could be isolated for several aromatic species, including isomers of the same compound.

The used laser system consists of a Nd:YAG pump laser, associated harmonic generation, optical parametric oscillator (OPO), UV extensions, and control electronics all on one rigid frame (OPOTEK, Inc., Vibrant). It is a compact all-in-one tunable laser system, which can generate tunable output from 210nm to 2.6 μ m at a 10Hz repetition rate and approximately 5 ns pulse length. Due to the all-solid state nature of this system, there is no need to circulate or change laser dyes that have typically been used to generate tunable light at these wavelengths. UV output was between 3.5 - 4.5mJ in the 250 - 280nm range using during these studies. The spectral linewidth of the system is 5 cm^{-1} .

Results and Discussion

In order to verify the applicability of the Vibrant laser, we have taken long Jet-REMPI scans over a broad spectral region for a select group of compounds, including a set of the three xylene isomers. These spectral features were used later for the detection limit and chemical specificity (mixture) tests described below. The selected group of compounds tested included benzene, toluene, the three xylene isomers and chlorobenzene. In each case, no change in spectral response was observed as shown in Figure 1 for p-xylene. We found that the broadband laser source has no influence on the spectral response for any of the compounds tested.

The excitation spectra were taken by measuring the ion signal at a fixed mass (that of the parent ion for a given compound) while scanning the laser over a 10nm range in the UV which shows strong $S_1 - S_0$ transitions for the individual compounds studied. The laser was scanned in 0.02 nm steps corresponding to the $\sim 5\text{cm}^{-1}$ linewidth of the laser system. The individual samples (including benzene and chlorobenzene) were prepared at 100 ppb concentration levels in a heated vessel. Individual xylene isomer samples were prepared by injecting measured volumes of liquid xylene diluted in acetone into a heated (150 C) 1-liter stainless steel flask. Other spectra, including xylene mixtures were measured using a calibrated mixture (Scott Specialty Gases) of several species at 100 ppb in N_2 carrier gas. We observed that the laser resolution is sufficient to access unique spectral features for each of the isomers of xylene (see Figure 2).

The broader spectral linewidth of the OPOTEK laser system also has a direct effect on the detection sensitivity of the Jet-REMPI process. If the linewidth of the laser is much broader than

the spectral features of the target molecules, much of the laser light will be wasted and the REMPI process will become less efficient.

Initial rough detection sensitivity data was taken for benzene and xylenes, varying the concentrations over a broad range in the ppb region. The extrapolated detection limit of the instrument for these compounds at a conservative S/N ratio of 3:1 is found to be approximately 300 ppt. Sensitivity is certainly in the range needed to make meaningful measurements in urban air where concentrations of these species can be in the 10ppb range.

Since a fieldable instrument is intended to analyze the complex vapor mixtures found in actual environments without the need for any prior chemical separation, assessing the performance with a simulated mixture is a critical task.

In the initial mixture tests, the concentration of a single component, benzene, was varied in a mixture of acetone (0.1%), toluene, o,p-xylene, and chlorobenzene (1 ppm each). The ion signal from benzene was found to vary linearly with concentration between 10 ppm and 1 ppb, with no offset at the origin due to contamination from

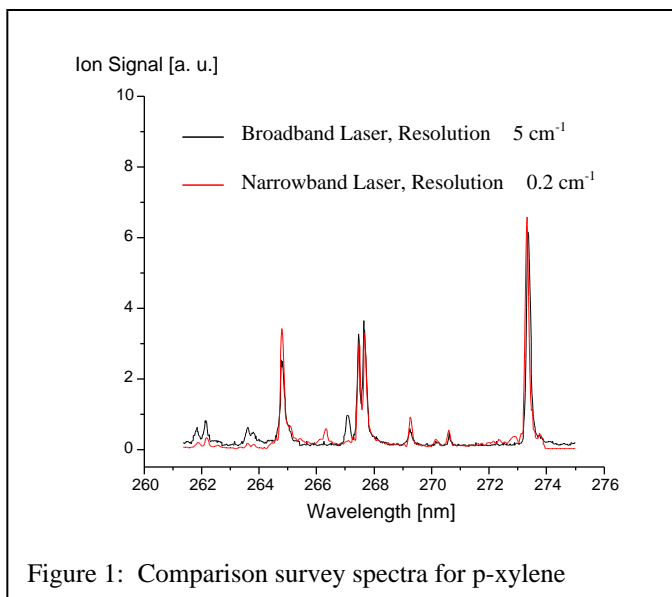


Figure 1: Comparison survey spectra for p-xylene

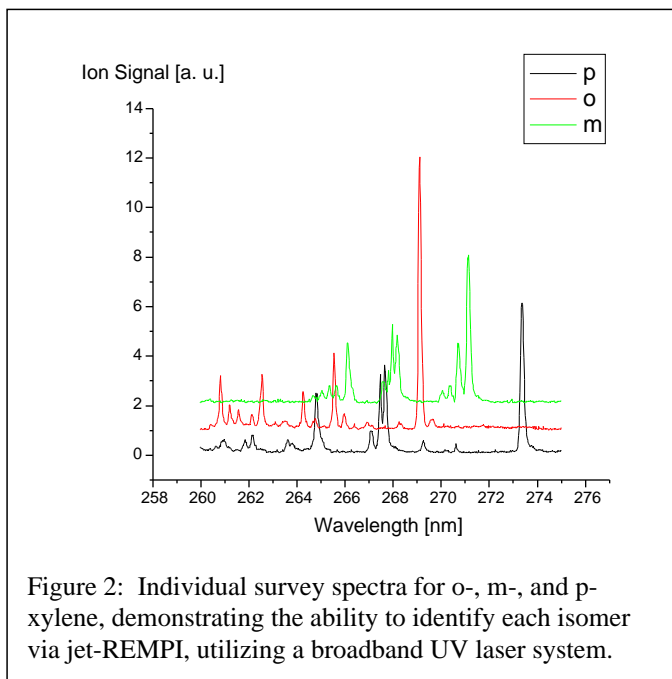


Figure 2: Individual survey spectra for o-, m-, and p-xylene, demonstrating the ability to identify each isomer via jet-REMPI, utilizing a broadband UV laser system.

other species in the mixture. Since the contaminant concentration was as much as a factor of 1000 higher than that of benzene, this test shows a significant chemical specificity performance that can be gained by the two-step combination of both mass-resolution and optical spectroscopy. By reducing the size and increasing the ruggedness of the laser component, we have made the initial step towards taking this powerful technology from the lab and developing a field-portable instrument. Our results are more than sufficient to provide accurate detection and quantification at real-world concentration levels in the ppb range. In addition, the chemical and isomer selectivity performance is quite good, with very high isomer selectivity in our initial tests. This provides a unique capability for real-time mass spectrometry detection that would otherwise require both lengthy pre-concentration and lengthy separation by additional means such as gas chromatography. These performance data s are very promising for the further development and miniaturization of the technology

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