Development of a Laser Ionization Mass Spectrometer for the Rapid Detection of Aromatic Hydrocarbons in Aqueous Samples

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Introduction

The ability to detect toxic compounds in real-time is important for ground water, drinking water, and surface water analysis, especially when identifying contamination products that can be harmful to the water supply.[1] Some compounds such as benzene, toluene, ethylbenzene, and xylene (BTEX) can be found in ground and drinking water. A major source of contamination is underground gasoline storage tanks. The BTEX group is found naturally in crude oil and thus gasoline; it forms the characteristic odor at a gas pump. Sometimes ethylbenzene is used as a fuel additive. All these compounds are also used as solvents in a variety of industrial processes. BTEX can leach from the storage tanks and make its way into ground water, where it dissolves. Water taken from this source through wells then contains the contaminants. Benzene has been identified as a carcinogen and the others likely have the same property. With long-term, low-level exposure, liver, kidney, and nervous system damage may also occur.

The detection of BTEX compounds in the gas phase has been examined in our laboratory through the use of jet-Resonantly Enhanced Multi-Photon Ionization Time-of-Flight Mass Spectrometry (jet-REMPI-ToF MS).[2] These BTEX compounds, as well as chlorobenzene, are well suited for detection via this method due to spectroscopic absorption properties of the aromatic ring. However, this method utilizes a supersonic jet expansion, which is not applicable to the direct detection of BTEX compounds in water.

In order to extend the REMPI-ToF approach to the detection of organics in water, a new type of inlet system must be coupled to the REMPI apparatus. By combining a membrane-based inlet system with a REMPI apparatus, the volatile organic compounds (VOCs) can be successfully introduced into the vacuum chamber without interference from the water solvent. Membrane Introduction Mass Spectrometry (MIMS) has been utilized for over 40 years,[3] but the coupling of a membrane inlet to REMPI ToF mass spectrometry is new.

A combination of MIMS and REMPI with time-of flight mass spectrometry, which allows for the direct analysis of water samples, has been developed in our laboratory. The application of

ToF MS offers some advantages such as high ion transmission, robustness, and the ability to record a full mass spectrum for each laser shot. The objective of this research was the detection of trace amounts of aromatic contaminants, particularly BETX and chlorobenzene, in aqueous solutions without interference or clogging of the inlet due to the vastly greater amount of water.

Materials and Methods

In order to evaluate and characterize the combination of membrane-based sample introduction and laser ionization ToF MS, water was spiked with known concentrations of molecules from the BTEX family and chlorobenzene.

The membrane introduction device was obtained commercially from MIMS Technology (Palm Bay, FL), consisting of a flow injection module and a membrane tip.[4] The sample is loaded into the flow injection module, which maintains a constant flow of water through the membrane tube. As the analyte solution passes across the inner surface of the membrane, the target molecules diffuse through the membrane and evaporate into the REMPI mass spectrometer chamber. The temperature of the membrane is controlled by varying the temperature of the water flow. As the temperature is increased, the analytes diffuse faster through the membrane, increasing the speed of the measurement. However, diffusion of organic compounds is hampered as the temperature reaches 100°C due to formation of air bubbles in the water. Experiments were performed initially with the temperature being varied between 25°C and 85°C in order to determine the shortest response time in combination with the most sensitive signal response.

The membrane probe is inserted into the inlet of the vacuum chamber forming a vacuum-tight seal. As the sample flows through the membrane, the VOCs evaporate into the vacuum chamber in a rapid and effusive flow. About 2 cm separates the exit of the membrane tip and the ionization region. Those VOC molecules that cross the laser beam path, which is perpendicular to the plane of Figure 1, are ionized. The ions are then extracted using specially designed ion optics, and their masses determined by the time-of-flight mass spectrometer.

A schematic of the laser photoionization process and mass spectrometer is shown in Figure 1. The laser system used for ionization is the fourth harmonic output (266 nm) of a Nd:YAG laser system (Continuum Powerlite Precision 9010). The laser operates at a 10 Hz repetition rate with output energy at 266 nm of approximately 7 mJ/pulse and a pulse width of 5 ns. A constant and defined ionization volume (~10 mm^3) was maintained throughout the experiments. The nascent ions were extracted and mass analyzed by a R. M. Jordan reflectron ToF-MS with a mass resolution of approximately 500. Two turbomolecular pumps (Varian Turbo V-250) maintain pressures in the ionization chamber and mass spectrometer regions of 10^{-5} Torr and 5 X 10^{-7} Torr, respectively. The ion signals were amplified by an Ortec 9306 preamplifier with a gain of 85 and a 1 GHz bandwidth, and recorded using a 500 MHz Signatec DA500A digitizer. Signals are typically averaged for time periods of 1 to 5 seconds.

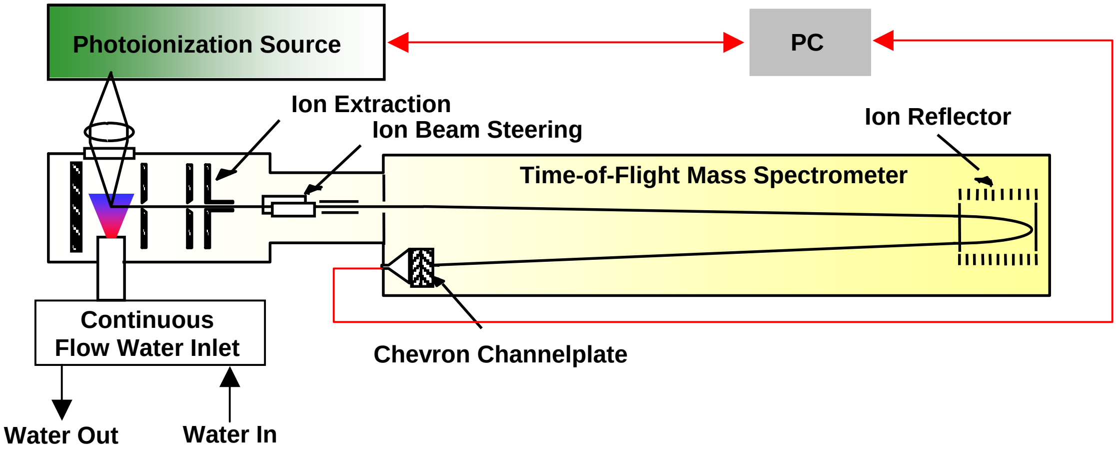

Figure 1. Schematic diagram of the continuous-flow inlet coupled to the photoionization-ToF mass spectrometer.

Results and Discussion

The goal of our initial experiments was to determine whether the MIMS-REMPI device could provide sensitive mass identification of the parent compounds with little or no fragmentation. Figure 2 shows the mass spectrum obtained from chlorobenzene in water. There is very little fragmentation of the parent compound, and the ratio of the mass signals at 112 amu and 114 amu reflect the 3:1 natural abundance of the chlorine isotopes. Figure 2 shows that the MIMS-REMPI system is capable of detecting the parent ion with a mass resolution similar to that observed in the gas phase measurements.

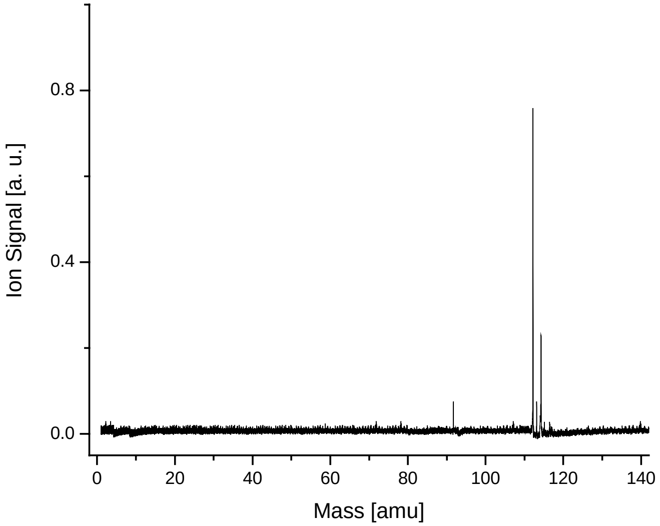

Figure 2. Mass spectrum of chlorobenzene in water using 266 nm photoionization obtained after its introduction into the ionization chamber through the membrane-based inlet system.

In order to examine the limits of detection (LOD) for various BETX molecules using the MIMS-REMPI system, sample concentrations between 0.001 and 10 ppb of benzene, chlorobenzene, and xylene were prepared by dilution in deionized water. All solutions were spiked with perdeuterobenzene in order to provide a constant reference calibration signal at m/z=84 amu throughout the measurements. Figures 3 and 4 show the plots of ion signal versus concentration for xylene and chlorobenzene, respectively. The signals were averaged for 5 seconds for these particular measurements. There is a high degree of linearity over four orders of magnitude in concentration. Based on these experiments, the LOD for xylene and chlorobenzene are estimated as 30 ppq and 1 ppt, respectively.

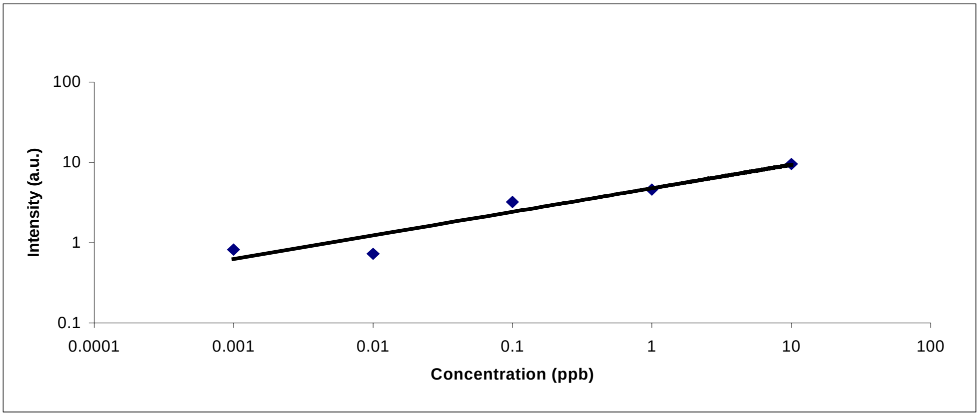

Figure 3. Ion signal versus concentration of xylene in water.

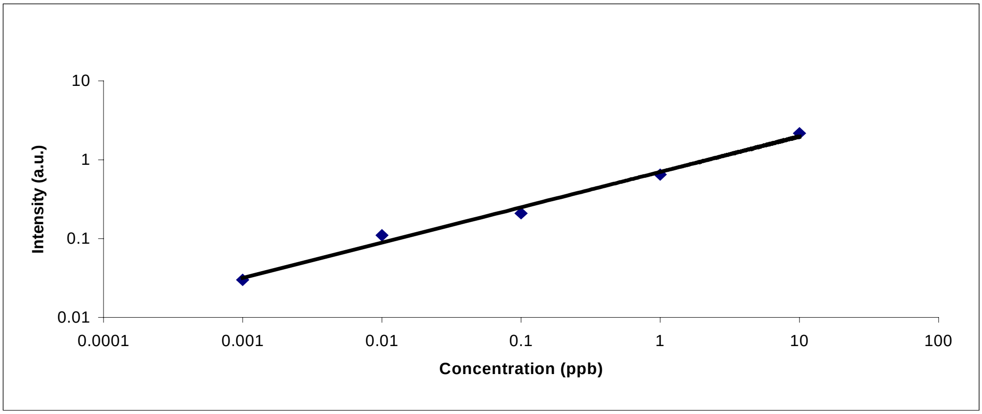

Figure 4. Ion signal versus concentration of chlorobenzene in water.

The determined limits of detection are already similar in magnitude to studies performed using a standard MIMS inlet system coupled with an EI ion trap mass spectrometer, although averaging times were not given in the reference.[5] It is anticipated that further optimization of the MIMS-REMPI system combined with longer averaging times will further reduce our limits of detection.

The advantages of laser photoionization detection as applied to organic pollutants found in water are speed and sensitivity. The laser photoionization method, which generally can be adjusted to limit photofragmentation, allows for parent mass identification. Laser photoionization offers the advantages of both sensitive and rapid analysis without preseparation, or sample preparation, and parent ion mass identification without deconvolution of multiple mass peaks.

Future work on this project will include the study of other environmentally important water-borne pollutants, as well as the development of a compact and rugged analytical instrument that has the sensitivity to detect these contaminants in real time.

Acknowledgements

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