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Real-Time Broad Spectrum Characterization of Hazardous Waste by Membrane Introduction Mass Spectrometry

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Research Objective

The objective of this project is to expand the capabilities of Membrane Introduction Mass Spectrometry (MIMS) to the pivotal problem of Mixed Hazardous Wastes, with secondary emphasis on monitoring incinerator stack gases for both organics and toxic metals. The methodologies developed in this proposal could also be applied to other environmental monitoring problems that require highly sensitive on-line detection of volatile and semi-volatile organic compounds, and heavy metals

Research Progress and Implications

As of May 1, 1998, we have designed and tested the rare gas ionization source and the associated ion optics. Ions are generated in a microwave plasma which can be supported by helium or argon from room air. A series of extraction and focusing lenses followed by a linear quadrupole serves to inject ions into the ion trap. Injection efficiency and favorable trapping of externally-generated ions are dependent on several parameters including lens potentials, quadrupole operation, buffer gas pressure, kinetic energy of the injected ions, and amplitude of the trapping potential. We have investigated rf-only operation of the linear quadrupole. RF/DC operation will be studied as a means for further reducing interferences. A publication on this work has been submitted to Int. J. Mass. Spectrom. Ion Proc.

To date we have used MIMS to detect 40 volatile and SVOCs without preconcentration, primarily from an air matrix. The 40 analytes range in boiling point from 21 to 279° C and include chlorinated and oxygenated solvents, chlorophenols, polyaromatic hydrocarbons, and substituted benzenes.

Using MIMS, we have demonstrated the direct, simultaneous detection of a volatile organic compound, a semi-volatile organic compound, and an organometallic compound with a single analytical technique in near real-time for two waste streams, air and water. To our knowledge, this is the first time this has been accomplished.

We have investigated the analysis of several organometallic compounds containing heavy metals by MIMS. These include lead and tin compounds. When these molecules are analyzed, organic fragment ions are observed. However, neither the intact molecular ion, nor the metal ion species are seen in the mass spectrum. These results are interesting because in the spectra of metal compounds most of the ion current is normally carried by metal-containing species [J. Charalambous, ed., Mass Spectrometry of Metal Compounds].

We speculate that it is oxygen, present either as a neutral or as an ionized species, that may be inhibiting the appearance of metal-containing fragment ions in certain cases. Oxygen is one of the predominating species in the ion trap environment in our experiment. Its high availability for secondary reactions as either a neutral or positively charged ion and the stability of possible products from these secondary processes may make the detection of metal-containing ions problematic in the current set-up. The formation of highly refractory neutral metal oxides, for example, would preclude the detection of metal-containing fragment ions.

We are investigating experimental means to test the questions that have been raised by these observations. Other ion trap instruments in our lab with additional capabilities to study ion/molecule chemistry may provide help in testing and resolving this issue.

Various researchers have investigated in situ ethylation using the reagent sodium tetraethylborate for the determination of heavy metals in environmental samples. In aqueous solution, sodium tetraethylborate will ethylate ionic lead, tin, and mercury species to produce volatile derivatives. We have reviewed the pertinent literature and are preparing a study incorporating MIMS and in situ ethylation of tin compounds, a number of which are toxic to marine life.

Planned Activities

For the remainder of FY98 we will focus on the detection of organic compounds using membrane introduction combined with the microwave source/ion trap mass spectrometer. In FY99, we will continue to focus on semi-volatile organic compounds and their ion chemistry in discharge ion sources, and in parallel, we will extend our preliminary investigations of MIMS of metal-containing compounds.

Other Access To Information

Although the following two papers appeared in print before this proposal was funded, they provide an introduction to the MIMS methodology and show its potential for the characterization of semi-volatile organic compounds and metals:

M.E. Cisper, P.H. Hemberger, *Rapid Commun. in Mass Spectrom.*, 1997, 11, 1449.

M.E. Cisper, P.H. Hemberger, *Rapid Commun. in Mass Spectrom.*, 1997, 11, 1454.

A publication arising from this work has been submitted. This paper describes the application of a combined microwave plasma source/ion trap mass spectrometer for atmospheric analysis of fixed gases and volatile organic compounds.