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Project Title: Real-Time Broad Spectrum Characterization of Hazardous Mixed Waste by
Membrane Introduction Mass Spectrometry
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Number of students involved in project: One postdoctoral researcher (LANL), 1 graduate student (Univ. of Texas, Arlington), and one undergraduate student (Univ. of North Dakota).

Research Objective: The goal of this project is to expand the range of chemical species that may be detected by membrane introduction mass spectrometry (MIMS) in environmental monitoring applications. The driving force is the need for a rapid, sensitive, and broadly applicable tool for characterizing organic and metal-containing contaminants in a variety of DOE (and other) waste streams.

Research Progress and Implications:
This section summarizes work completed over the first 30 months of the 3-year program. There are four areas of research and development that we have been engaged in to extend our current level of expertise to a broad analytical methodology: (1) novel ionization techniques, (2) extension of MIMS to environmentally significant volatile (VOC), semi-volatile (SVOC), and metal-containing compounds in air and water, (3) simultaneous detection of VOC, SVOC, and organometallic compounds in air or water matrices, and (4) application of tailored membranes for selective measurement of specific classes of hazardous chemicals.

Novel Ionization Methods. Charge exchange ionization in conjunction with MIMS provides a sensitive method for detecting compounds in air and/or water, and is simple to implement. While the polymer membrane acts as a semi-permeable barrier between a sample and the vacuum of the mass spectrometer, the overwhelming prevalence of oxygen and water in air and liquid matrices, respectively, leads inevitably to the permeation of these species through the membrane. We have turned this potential liability into a significant advantage by exploiting the ability of the ion trap mass spectrometer to perform controlled gas phase chemistry. The water or oxygen is used to generate chemical reagent ions that enhance analyte signals anywhere from 2 to 20 times over those obtained from more traditional electron impact ionization, with a concomitant reduction in detection limits. In the second year of the project, significant effort was directed towards the development of a microwave induced plasma (MIP) ionization source interfaced with MIMS. The motivation for this work was the fact that such discharge ionization techniques are often very efficient (up to 5%), which would further reduce the method detection limit. Initial measurements of rare gases using a directly coupled MIP/ion trap mass spectrometer system (i.e. with no membrane introduction) were promising, however sensitivity to environmentally important compounds was not as good as initially anticipated. Flow injection measurements using various analytes (ferrocene, triphenyltin chloride and aniline) showed distinct changes in the color of the plasma discharge, but little ion signal was observed in the mass spectrometer. Detailed modeling of the instrument using the SIMION ion optics simulation package and extensive experiments suggest that the lack of ion signal is due to poor ion transmission from the plasma discharge source to the ion trap mass spectrometer. Further work would be required to achieve the performance necessary for environmental characterization applications. We believe that chemical ionization (as described above) will provide outstanding detectability for our analytes of interest, and consequently there are no plans to pursue further MIP/MIMS experiments.

Environmentally Significant Compounds. The contamination of air and/or drinking and ground water by organic compounds and heavy metals is a major environmental problem and concern. Over the course of this project we have successfully demonstrated the real-time detection of (1) methanol, a problematic analyte for GC techniques (due to its high solubility in water), in air and water using MIMS; (2) several semi-volatile compounds (e.g. dimethyl methyl phosphonate, malathion, nitrobenzene, methyl salicylate, 2-chlorophenol, cyclohexanol, diethyl malonate, and naphthalene) in air; (3) metal-containing compounds (ferrocene, $(\eta^5\text{-}C_5H_5)_2$Fe, and molybdenum hexacarbonyl) in air; and (4) a wide variety of volatile organic

compounds in air. We have also investigated the transport of various substituted phenols through PDMS (polydimethylsiloxane) membranes in order to gain a better understanding about the mechanism of compound permeation (i.e. solubility and diffusivity) and detection. The time from sample introduction to both initial ion signal and steady-state response depends primarily on the membrane interaction with each compound, and secondarily on the ion trap mass spectrometer response (i.e. ionization efficiency) to each compound. Using oxygen charge exchange ionization, we have observed that flux is enhanced for phenols with electron donating (such as -CH_3) versus electron withdrawing (such as –Cl) substituents. For example, 2,4-dimethylphenol diffuses more readily (the initial response time is 1.5 times faster) through the membrane than 2,4-dichlorophenol. Further, other metal-containing compounds (in addition to the iron and molybdenum species mentioned above), such as lead acetylacetonate ($Pb(acac)_2$) and $Ni(acac)_2$, have also been investigated. Using either charge exchange or electron impact ionization, we were able to detect the acac ligand, but not the metal ion nor the intact molecular ion for these two species. To date, we have not used derivatization chemistry to enhance permeation and/or ionization, however, this is an area that needs further exploration.

Simultaneous Detection. We have further demonstrated the versatility of MIMS for the simultaneous detection of VOC, SVOC, and organometallic compounds in air and water using charge exchange (CE) ionization. As mentioned above, CE ionization produces enhanced molecular ion signal over electron impact ionization (EI). This is a result of the fact that more internal energy is deposited to the molecule in the EI process, leading to more fragmentation of the analyte than by CE with $O_2^{+?}$ or H_3O^+. When mixtures of compounds are analyzed, quantification may be more easily accomplished with CE ionization where fewer ions resulting from fragmentation are observed or only the molecular ion is detected. These results are promising for the eventual implementation of a near real-time method for mixed waste characterization at a number of the DOE sites that will can lead to substantial savings in time and costs.

Recent Results. During FY00 we have been conducting experiments aimed at tuning the selectivity of pervaporation membranes in order to optimize the measurement of specific classes of hazardous chemicals. Silicone (PDMS) membranes are well-suited for real-time analysis of non-polar and moderately polar volatile organic compounds. However, analyses of more polar and less volatile analytes are often more difficult with a silicone membrane, because of decreased solubility and diffusivity issues. In collaboration with R. B. Timmons (Dept. of Chemistry, University of Texas at Arlington), we are developing new membranes with tunable properties that will allow us to largely avoid such problems. Both the nature of the monomer (e.g. dimethylsiloxane, allyl alcohol, methylamine, etc.) and the conditions under which it is polymerized (pressure, plasma duty cycle, final film thickness) can be controlled to achieve desired membrane performance. Preliminary data show that, compared to a PDMS membrane, a particular plasma-deposited allyl alcohol membrane enhances the detection of polar organic compounds while simultaneously suppressing the detection of non-polar species. By simply changing the plasma duty cycle during polymerization, this same monomer produces a membrane with completely reversed MIMS properties (i.e. suppression of polar, and transmission of non-polar, analytes). We feel that exploitation of this new paradigm in MIMS will allow the development of a truly broad-spectrum technique.

Planned Activities: For the remainder of the FY, we will be performing experiments using a combination of tailored membranes and chemical ionization strategies to map the extent of analyte physicochemical properties accessible to this technique. We will also investigate the use of serial membranes with different pervaporation characteristics to provide chemical class separation (polar vs. non-polar species), resulting in additional selectivity at almost no cost to analysis time. We have applied for a renewal of this program in order to fully exploit the almost limitless possibilities available with chemically controlled membranes for environmental applications.

Information Access: Multiple presentations at universities and national meetings (ACS, ASMS, WM99, Pittcon, Arizona St. Univ., Univ. of Texas-Arlington, Univ. of North Dakota); four manuscripts to peer-reviewed publications and/or books (listed below).

1. "Real-time Analysis of Methanol in Air and Water by Membrane Introduction Mass Spectrometry." Allen, TM; Falconer, TM; Cisper, ME; and Wilkerson, CW. Submitted to Analytical Chemistry (JAN 2000).
2. "Membrane Introduction Mass Spectrometry: Trends and Applications." Johnson, RC; Cooks, RG; Allen, TM; Cisper, ME; and Hemberger, PH. Mass Spectrometry Reviews, 2000, 19, 1-37.
3. "Simultaneous Detection of VOCs, SVOCs, and Organometallic Compounds in Air and Water by Membrane Introduction Mass Spectrometry." Allen, TM; Cisper, ME; and Wilkerson, CW. In Preparation for Analytical Chemistry (MAR 2000).

4. "Environmental Monitoring" in Membrane Introduction Mass Spectrometry, Cisper, ME; Allen, TM; Kotiaho, T; Ketola, R.; Editors: R. Graham Cooks and Tapio Kotiaho, J. Wiley & Sons, Inc., Invited book chapter. In Preparation.