Title:

Real-Time Broad Spectrum Characterization of
Hazardous Waste by Membrane Introduction Mass
Spectrometry
Mid-Year Progress Report

Author(s):

Charles W. Wilkerson, Jr.

Submitted to:

<http://lib-www.lanl.gov/cgi-bin/getfile?00796875.pdf>

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

Mid-Year Progress Report

Charles W. Wilkerson, Jr.
Los Alamos National Laboratory

June 1, 1999

Goals of Project:

The goal of this project is to expand the range of chemical pollutants that can be detected by membrane introduction mass spectrometry to semivolatile organic compounds (SVOCs, e.g., polycyclic aromatic hydrocarbons, phenols, etc.) and to toxic heavy metals. This technology can be applied to a wide variety of environmental characterization and monitoring problems; in particular, the characterization of mixed hazardous wastes and heavy metal monitoring in incinerator effluents.

Technical Description of Work:

We are executing innovative research to develop and extend the capabilities of membrane introduction mass spectrometry (MIMS) to a broad range of organic and metal analytes. The driving force behind this project is the need for a rapid, sensitive, and broadly applicable tool for characterizing organic and metal-containing contaminants in a variety of waste streams. The Department of Energy currently has over one hundred waste sites, over 1400 different mixed waste streams, large volumes of contaminated water and soil, and anticipates significant additions to this burden. While simple *in situ* monitoring technologies are available for specific analytes in a few areas of application, our work will result in a more universal analytical tool. We are exploring key gaps in scientific knowledge and linkages in underdeveloped areas of MIMS that will lead to an instrument for the real-time characterization of organic and heavy metal contamination in hazardous or mixed wastes. Our technique will find application at the numerous DOE sites requiring waste stream characterization; effluent monitoring of waste treatment operations, including incineration; groundwater and soils cleanup; facility decontamination; and in ensuring overall environmental compliance. Real-time broad spectrum contaminant characterization by MIMS will be able to directly address hazardous waste management and characterization concerns of the DOE with respect to both legacy and future activities. This research will also improve our understanding of complex waste issues and serve to ameliorate public and private sector hazardous waste problems.

Background: The use of semipermeable membranes to enrich and introduce vapors to a mass spectrometer has been known for many years [1-3]. In the MIMS experiment, a polymer membrane, on the order of 100 microns thick, serves as the interface between the sample (often water or air) and the vacuum of the mass spectrometer. The membrane can take the form of a sheet across which the sample passes, or a capillary tube over which sample flows. We use a two stage pneumatically-assisted tubular membrane introduction system. [4] Transport of the analyte through the non-porous membrane occurs by the process of pervaporation. This is thought to involve three stages: absorption in the outer surface of the membrane, diffusion through the membrane, and evaporation from the inner membrane surface into vacuum. Membrane introduction mass spectrometry as developed to date has focused almost exclusively on volatile organic compounds (VOCs) in water or air; it offers relatively fast response times (about 0.5 - 5 min) with minimal operator intervention; and employs flow injection analysis techniques for sample handling to provide an on-line capability. Quantitation can be achieved using either internal or external standards. Most strikingly, detection limits for VOCs are in the low parts-per-trillion range. In fact, in favorable cases, the detection of parts-per-quadrillion levels of VOCs in water [5] and the detection of 20 parts-per-trillion by volume in air [6] have been demonstrated. Because the nonporous silicone membrane excludes particulates and ionic compounds, including the salts found in seawater, the technique offers a way to measure trace levels of organics in a complex aqueous matrix. [7]

There are several areas of research and development that we are engaged in to extend our current level of expertise to a broad analytical methodology: 1) novel ionization methods to enhance instrument reliability, and to increase specificity and selectivity for target analytes, 2) extension of MIMS to environmentally significant SVOCs (anilines, phenols, polycyclic aromatic hydrocarbons (PAHs), and polychlorinated benzenes) in air, water, and soil, and 3) methods development for heavy metals in air, water, and soil, including development of on-line complexation or derivatization reactions to increase volatility, or to increase the new metal-containing compound's solubility or diffusivity in the membrane. Each of these topics is briefly expanded upon below.

Novel ionization methods: Using the hybrid membrane configuration, a significant amount of oxygen is able to diffuse through the semipermeable barrier. The resulting high partial pressure of oxygen within the ion trap leads to rapid destruction (*ca.* 2 weeks) of the ionizing filament required in either the electron ionization or chemical ionization modes. This is unacceptable for a robust on-line diagnostic. Further, it is likely that solvent(s) and/or derivatizing agent(s) will be efficiently transported through the membrane. The introduction of these compounds to the mass spectrometer can lead to spectral interferences. To minimize the effect of these problems, we are developing a rare gas-supported microwave discharge for ionization. This source can be coupled to the ion trap via a linear radio-frequency quadrupole. By adjusting the DC and RF potentials on the linear quadrupole, we can select the ions of a particular mass-to-charge ratio (m/z) prior to their introduction to the ion trap [8]. In this fashion, we can reduce space charge effects, which will lead to improved mass spectral quality in terms of peak shape and mass measurement accuracy, [9] and mass selective storage will provide lower detection limits by allowing the selective accumulation of only those ions of analytical interest [10]. While mass selection of ions can be effected by applying broad-band waveforms to the ion trap to resonantly eject unwanted ions, it is our experience that external mass isolation leads to higher mass spectral quality than allowing all ions to enter the ion trap and then be ejected by resonant excitation methods.

Extension of MIMS to environmentally significant SVOCs: We have had good success in detecting certain semi-volatile organic compounds. However, other compounds, such as dimethyl methyl phosphonate, have long retention times in the hybrid membrane. Systematic studies of substituent effects will help us to understand the relationships among compound polarizability, dipole moment, boiling point and the compound's diffusivity and solubility in the membrane. Such studies will lead to a set of empirical rules to predict the transport behavior of a compound through a semi-permeable membrane. These studies will also provide important background data for the development of methods for MIMS of metal complexes. We must also study a representative number of compounds from each of the compound classes mentioned above. For example, chlorobenzene has a dipole moment, whereas hexachlorobenzene does not; and even though they are both chlorobenzenes, these two compounds might have very different transport properties through the membrane. These studies will focus on characterization of the MIMS methodology using hard analytical data: sensitivity, calibration linearity, limits-of-detection, and interferences and carry-over.

We are planning to investigate the utility of heating the membrane to improve the transport of less volatile species and other laboratories have observed some anomalous effects in the transit of SVOCs through the semi-permeable interface. These effects might be eliminated by appropriate heating of the membrane material, using electron beams [11], lasers, or pulsed radiant heaters to reduce response times. Alternative membranes may also provide an efficient and reliable interface for SVOC introduction. One possibility is the polypropylene microporous membrane. Microporous membranes do not reject the solvent and so they do not enrich the permeate in the analyte as do silicone and other amorphous membranes. They are, however, more suitable for larger and more polar compounds, and they may also have considerable advantages in terms of rapid response times and freedom from memory effects [12]. We will also investigate on-line extraction methods for SVOCs in soil. This may involve the use of a reverse-phase membrane approach for sensitive detection of targeted analytes. The microporous membrane allows a small amount of the organic solvent as well as the analyte to pass into the ion source. The vaporized solvent serves as a chemical ionization reagent gas to subsequently ionize the target analyte [13]. This approach can be further enhanced by affinity membrane mass spectrometry in which a chemically-modified membrane that selectively adsorbs and concentrates analytes is used to selectively transfer extracted SVOCs to the mass spectrometer [14].

Methods development for heavy metals in air and water: Airborne metal contaminants will be collected in a vortex or micromist sampler that entrains the contaminants in aqueous solution. The water

used in these collection methods can be pH adjusted as needed, or can contain organic solvents such as methanol. Some important metal compounds such as the mercury or lead alkyls might be directly analyzed with the existing MIMS instrument, just as we have done with ferrocene. This approach would provide a very simple and rapid tool to distinguish, *e.g.*, the various tetraalkyllead compounds. Because these compounds are present in trace concentrations in the biosphere, low detection limits are required. Detection limits for VOCs in water have been demonstrated to be as low as parts-per-quadrillion (femtograms per gram), [5] and it is quite possible that similar results can be achieved for the metal alkyls. If adequate detection limits cannot be demonstrated for direct analysis techniques, or if the matrix precludes direct analysis, simple sample preparation steps such as on-line complexation or derivatization reactions to increase volatility or to increase the new metal-containing compound's solubility or diffusivity in the membrane, can be implemented.

A novel route to on-line extraction and derivatization would be through affinity MIMS techniques. In this experiment, the membrane (generally a microporous membrane, although other membrane materials could be used) would itself be chemically derivatized or coated with a sorbent phase to entrain the metallic compounds. The adsorbed metal compounds would then be eluted from the membrane surface using the derivatizing agent for the metals. For the alkylmetals in water, a serial membrane system might be employed where a dimethyl silicone membrane first traps the organometals, which are eluted using an organic solvent system and introduced to the mass spectrometer through a microporous membrane. The affinity MIMS experiments will likely be done at Purdue University.

Our recent successes with the hybrid semi-permeable/microporous membrane lead us to believe that practically any organic-bearing compound can be detected by MIMS. The real issues in this work are (1) first stripping the target compound from its matrix, (2) then, for metal complexes, doing the right chemistry to attach the *appropriate* organic substituents to the metal which will act as carriers to transport the metal through the membrane via the pervaporation process. The organic substituents must be chosen to provide some volatility, and they must give the molecule the right combination of solubility and diffusivity for efficient transport through the membrane.

We feel that careful implementation and optimization of the membrane sampling system combined with external ionization capabilities will solve many problems related to the detection of SVOCs and metals. This instrumentation combined with some simple chemistry, either as an on-line sample preparation step or as a gas-phase ionic reaction, will provide the final analytical methodology.

Accomplishments to Date:

The vast majority of our efforts during FY99 have been directed towards the development and implementation of the microwave induced plasma (MIP)/MIMS interface. While initial experiments using rare gas analytes have been promising, our sensitivity for SVOCs and organometallic compounds has not been as good as initially anticipated. We suspect that there are a variety of reasons for this performance (see below). Flow injection measurements using analyte concentrations determined by the vapor pressure of the test compounds under study (aniline, ferrocene, triphenyltin) lead to noticeable changes in the color of the discharge. Molecular ions of both aniline and ferrocene have been observed, but not for the tin compound (only the phenyl ligand has been observed). Further, the increase in ion trap signal was not large compared to the amount of color change observed in the discharge.

We have been investigating a number of possible causes for the lack of strong ion signal in the MIP instrument. Initially, we believed that leaks in the sample manifold were resulting in a loss of analyte from the system. However, even after we modified, and significantly improved, the gas handling system for the MIMS/MIP interface, the ion signals were not markedly improved. It currently appears that poor ion transmission from the source to the mass spectrometer is the most likely culprit. The efficiency of the MIP source has been demonstrated in the literature, and our discharge appears to be working in both a normal and reproducible fashion, and thus it is not considered to be a problem area. We have been working for the last 3 months on a combined experimental and modeling effort to understand the behavior of the system. The complete ion optical system between the discharge and the ion trap mass spectrometer (but excluding the plasma itself) is shown in the following figure:

Figure 1 - MIMS/MIP Ion Optical System

At the far left, a three-element Einzel lens (a) is used as an “ion gate”, allowing ions to reach the mass spectrometer under experimental control. This lens also provides some ion focusing at the entrance to the next element, an RF/DC quadrupole lens (b), that is used to direct the ion beam to the ion trap mass spectrometer (ITMS, c). Experiments suggest that there is some ion loss, due to either poor coupling of elements or sub-optimal focusing, at the Einzel lens. Measurements are currently underway to assess the efficiency of the quadrupole lens. Detailed modeling of the system using the SIMION package is near completion. The tolerances on the various elements of the system are fairly tight, and a solution as simple as increasing apertures and tweaking focusing voltages may be sufficient to achieve the desired performance.

We have further developed our capabilities in simultaneous VOC/SVOC/organometallic detection, using MIMS with charge exchange (CE) ionization and ion trap mass spectrometric detection, as demonstrated in figures 2 and 3.

Figure 2 - Detection of Benzene, Naphthalene, and Ferrocene in Water

Figure 3 - Detection of MEK, Toluene, 1-Methylnaphthalene, and Ferrocene in Air

We have also investigated other metal-containing analytes, notably lead acetylacetonate (acac). All of these efforts have been undertaken using our standard hybrid membranes, and without using any derivatization chemistry to enhance permeation and/or ionization. In addition, we have successfully demonstrated the ability to detect methanol, a problematic analyte for GC techniques, using hybrid membrane MIMS.

Projections:

We anticipate completion of many SVOC/metals test experiments before the end of FY99, but because of the difficulties described above, and the reduced allocation (see below), the suite of experiments on the effect of molecular properties on membrane transport will probably not be completed.

For the remainder of FY99, we will concentrate on performing MIMS/EI(CE/CI) measurements on a variety of SVOC and organometallic test compounds, as well as completion of the MIPS/MIMS interface. We also plan on performing some preliminary experiments on polar VOC and SVOC analytes.

Funding:

Spending thus far in FY99 has run ahead of projections. This has been due to a variety of reasons, including not receiving the full FY99 allocation, unexpected equipment needs, and greater than anticipated travel costs to present our results at several national meetings. However, we expect to finish the year within budget. Further, expenditures will be reduced for FY00, since almost all hardware is now in hand. Because of the reduced FY99 allocation, collaborative work with Purdue University was not executed in FY99. We hope to resume this interaction in FY00.

Issues/Problems:

We have encountered more serious difficulties than originally expected in the development of the microwave plasma ionization source. As discussed above, we suspect that ion optical difficulties are the source of this problem. The experimental/modeling approach described above is expected to yield conclusive corrections to the design.

Corrective Actions:

We have engaged additional local expertise in microwave discharge ionization sources to assist us in determining the most efficient operating parameters for our system. We are also involved in a

collaboration (not funded by EMSP) with external university colleagues (Univ. of New Mexico and Purdue Univ.), and their input has been very helpful in identifying and correcting possible problems.

Additional Information:

During FY99, the following presentations have been made at national meetings based on results obtained under this project:

- 1) WM99 - "HLW, LLW, Mixed Wastes and Environmental Restoration – Working Towards a Cleaner Environment", Tucson, AZ, February 28 – March 4, 1999.
- 2) Workshop on Harsh Environment Mass Spectrometry, St. Petersburg, FL, February 22-23, 1999.
- 3) 1999 Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, Orlando, FL, March 7-12, 1999.

1. Hoch, G; Kok, B. *Arch. Biochem. Biophys.* **1963**, 101, 160.
2. LaPack, M.A.; Tou, J.C.; Enke, C.G. *Anal. Chem.* **1990**, 62, 1265.
3. Kotiaho, T.; Lauritsen, F.R.; Choudhury, T.K.; Cooks, R.G.; Tsao, G.T. *Anal. Chem.* **1991**, 63, 875A.
4. Dejarne, L.E.; Bauer, S.J.; Cooks, R.G.; Lauritsen, F.R.; Kotiaho, T.; Graf, T. *Rapid Commun. Mass Spectrom.* **1993**, 7, 935.
5. Soni, M.H.; Bauer, S.J.; Amy, J.W.; Wong, P.S.H.; Cooks, R.G. *Anal. Chem.* **1995**, 67, 1409.
6. Cisper, M.E.; Townsend, L.E.; Hemberger P.H. *Anal. Chem.* **1995**, 67, 1413.
7. Wong, P.S.; Cooks, R.G.; Cisper, M.E.; Hemberger P.H. *Environmental Science and Technology*. **1995**, 29, 215A.
8. Dawson, P.H. in *Quadrupole Mass Spectrometry*, Dawson, P.H. (Ed.) Elsevier Scientific Publishing Company, Amsterdam, The Netherlands. Chapter 1.
9. Cleven, C.D.; Cooks, R.G.; Garrett, A.W.; P.H. Hemberger. *J. Phys. Chem.* **1996**, 100, 40.
10. Garrett, A.W.; Cisper, M.E.; Nogar, N.S.; Hemberger P.H. *Rapid Commun. Mass Spectrom.* **1994**, 8, 174.
11. Leth, M; Lauritsen, F.R. *Rapid Commun. Mass Spectrom.* **1995**, 9(7), 591.
12. Lauritsen, F.R.; Kotiaho, T.; Choudhury, T.K.; Cooks, R.G. *Anal. Chem.* **1992**, 64(11), 1205.
13. Lauritsen, F.R.; Choudhury, L.E.; Dejarne, L.E.; Cooks, R.G. *Anal. Chin. Acta.* **1992**, 266, 1.
14. Xu, C.; Patrick, J.S.; Cooks, R.G. *Anal. Chem.* **1995**, 67, 724