

REAL-TIME BROAD SPECTRUM CHARACTERIZATION OF WASTE BY MEMBRANE INTRODUCTION MASS SPECTROMETRY: PRELIMINARY RESULTS

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ABSTRACT

We present results for the direct on-line detection of volatile organic compounds, semi-volatile organic compounds, and organometallic compounds in air and water using membrane introduction ion trap mass spectrometry. The results that we have obtained are promising for the eventual implementation of a near real-time method for mixed waste characterization at a number of the DOE sites. We demonstrate the simultaneous detection of volatile (660 ppb methyl ethyl ketone and 7 ppb toluene), semi-volatile (316 ppb 1-methylnaphthalene), and organometallic (700 ppb ferrocene) compounds in air by using charge exchange ionization employing oxygen from air as the reagent gas. The charge exchange ionization method produces enhanced molecular ion signal over electron impact ionization. We also demonstrate simultaneous and direct analysis of volatile, semi-volatile, and organometallic compounds in aqueous solution, using the same membrane as used for air sample analysis, by the detection of 870 ppb benzene, 150 ppb naphthalene, and 180 ppb ferrocene with both electron impact ionization and proton transfer chemical ionization.

INTRODUCTION

Many of the mixed hazardous wastes at DOE sites are complex mixtures containing volatile and semi-volatile organic solvents (VOCs and SVOCs, respectively), heavy metals, and radionuclides. Characterization of mixed wastes is necessary in order to develop and assess remediation strategies. We have developed membrane introduction mass spectrometry (MIMS) for the on-line, near real-time analysis of volatile organic compounds in air and water. We report on recent efforts to expand MIMS to the analysis of SVOCs and metal containing compounds with potential application to mixed waste characterization.

The advantages of MIMS as an analytical tool are numerous but several in particular are quite relevant to mixed waste analysis: 1) the sample is returned to the waste stream, i.e. no new waste is created; 2) the mass spectrometer remains free of radioactive contamination in the analysis of organics in a mixed waste; 3) no sample preparation is required for organics and minimal sample preparation is expected for heavy metals, thus minimizing operator exposure and reducing risks; and 4) the time needed for analysis is minimal (seconds to minutes).

APPLICATIONS OF MIMS

Real-time broad spectrum characterization of wastes by MIMS promises to directly address hazardous waste management and characterization concerns of the DOE with respect to both legacy and future activities. Development of MIMS as a field screening method could reduce problems associated with sample handling and sample transport of air and water wastes by minimizing the need for time-intensive laboratory methods such as GC/MS. The MIMS

technology can be applied to the characterization of mixed hazardous wastes; heavy metal monitoring in incinerator effluents; groundwater and soils cleanup; facility decontamination; and in ensuring overall environmental compliance. Many DOE sites would benefit from the implementation of MIMS as a near real-time, on-line analytical method for addressing the problem of mixed hazardous waste.

Preliminary studies have established the viability of the MIMS methodology for detection and identification of several environmentally significant VOCs, SVOCs, and organometallic compounds in air and water. We have also demonstrated simultaneous detection of VOC, SVOC, and organometallic compounds by MIMS in both air and water samples. We are seeking input on relevant compounds pertinent to current mixed waste problems. Our current research will improve our understanding of complex waste issues and serve to rectify public and private sector hazardous waste problems.

A large fraction of mixed hazardous wastes at the DOE facilities/sites, such as INEEL, ORNL, Stanford University, Nevada Test Site, and LBNL, is present as complex mixtures containing a wide variety of volatile and semi-volatile organic solvents, water, heavy metals, and radionuclides. Characterization of mixed waste is necessary for developing suitable remediation strategies (i.e. storage, treatment, and disposal). MIMS is currently well-developed for the on-line analysis of VOCs and SVOCs in air and water. Development of the MIMS methodology for near real-time, on-line monitoring of a broad range of organic compounds and heavy metal contaminants in a variety of matrices and effluents is necessary for addressing the problem of mixed hazardous wastes at these and many other DOE sites.

Table I. Potential application of MIMS to current DOE sites

Potential Site of MIMS Application	Problem
INEEL	Characterization and direct analysis of contents of mixed waste
Nevada Test Site	Long term monitoring of pipes, wells, and effluent streams
ORNL	Long term monitoring of spring and well water at Chestnut Ridge Security Pits
Stanford University	Complex mixtures containing radionuclides, heavy metals, fuels, oils, organic solvents, and organic metal complexing agents
LBNL	Contaminants in gas/water interfaces include Pb^{2+} , CrO_4^{2-} , Cs^+ , and Sr^{2+}

EXPERIMENTAL

The membrane/jet separator assembly has been described in detail in previous work (1). A composite hollow fiber membrane manufactured by NeoMecs Inc. (Eden Prairie, MN, USA) is used in the pneumatically assisted transport mode (2). The membrane consists of a polypropylene microporous support fiber (240 μm i.d. x 300 μm o.d.) coated with an ultra-thin (approximately 0.5 μm) highly crosslinked plasma polymerized polydimethylsiloxane layer. This

hydrophobic silicone membrane is selective for organic compounds. Two parallel strands of the membrane fiber are sealed, using an epoxy adhesive, within the ends of two Swagelok tees joined by a short piece of ¼ inch o.d. Silcosteel tubing. Experimentally, we have found that two strands of the fiber maximize analyte signals while minimizing the amount of water vapor that may diffuse through the membrane. Excess water affects the tuning and the sensitivity of the ion trap mass spectrometer.

The total length of the fibers is approximately 10 cm. Ultrapure helium is flowed through the interior of the fibers, and serves as both the sample transport gas and the ion trap buffer gas. Sample air flows over the exterior of the fibers countercurrent to the helium flow (3). For most experiments sample flow is set at 45-200 mL/min. The Silcosteel tubing enclosing the membrane fibers is heated to 100 °C. The heated metal jet separator (1) is used for sample enrichment following membrane introduction.

Analytes of interest are detected using both charge exchange (CE) ionization and electron impact ionization (EI) in a modified Finnigan Model 800 Ion Trap Detector (San Jose, CA). The spectra obtained using oxygen CE were compared to EI spectra to determine relative sensitivities.

Air samples are prepared using VICI Metronics Dynacalibrator (Model 340-24-Y, Santa Clara, CA). Diffusion vials are used to generate known concentrations of the various analytes in air. Different concentrations of aqueous samples are prepared from stock solutions of the various analytes.

MIMS RESULTS

The versatility of the MIMS technique is demonstrated by the ability to detect several classes of volatile, semi-volatile, and organometallic compounds. To date, we have used MIMS to detect 40 volatile and semi-volatile organic compounds (see the Table II) without preconcentration, primarily from an air matrix. The 40 analytes range in boiling point from 21 to 464 degrees C and include chlorinated and oxygenated solvents, chlorophenols, polyaromatic hydrocarbons, and substituted benzenes. Many of the compounds listed in Table II are identified as hazardous environmental contaminants by the Environmental Protection Agency (EPA).

We have investigated the analysis of several organometallic compounds containing heavy metals by MIMS (see Table II). These include lead and tin compounds. When these compounds are analyzed using MIMS, organic fragment ions are observed. However, for many of the organometallic compounds neither the intact molecular ion nor the metal ion species are observed in the mass spectrum. Both ferrocene and molybdenum hexacarbonyl are readily detected in air following membrane exposure to headspace vapor from the solid. The molecular ions, m/z 186 and 266, respectively, are the most abundant ions observed with charge exchange ionization (4). Less than 5% iron (Fe^+) and less than 5% molybdenum (Mo^+), respectively, is observed under charge exchange conditions. Oxygen, as an ionized species (O_2^+), is one of the predominating species in the ion trap in our experiment and may be inhibiting the appearance of metal-containing fragment ions in certain cases. The high availability of O_2^+ for secondary reactions and the stability of the products from these secondary processes may make the detection of metal-containing ions problematic. We are currently investigating experimental means to test the questions that have been raised by these observations.

Table II. Compounds Detected by MIMS ^a

	Compound Detected by MIMS	Boiling Point (°C)	Vapor Pressure (torr) ^b	Molecular Weight
VOCs	Acetaldehyde	21	750	44
	Acetone	56	180	58
	Benzene	80	75	78
	Carbon tetrachloride	77	91.3	154
	Chlorobenzene	132	8.8	113
	Hydroxy acetone	131	10 (39.7°C)	74
	1-Hydroxy-2-butanone	164	1 (25.5°C)	88
	Isopropyl alcohol	82	40	60
	Methyl ethyl ketone	80	100	72
	Methyl isobutyl ketone	117	16	100
	3-Pentanone	102	27	86
	Propanal	49	300	58
	Toluene	111	22	92
	Trichloroethane	74	100	133
	Trichloroethylene	87	61	131
SVOCs	Acenaphthene	283	10 (131°C)	154
	Acetophenone	203	1 (15°C)	120
	Aniline	184	0.6	93
	2-chlorophenol	175	1 (12.1°C)	129
	3-chlorophenol	214	1 (44.2°C)	129
	Cyclohexanol	161	1 (21°C)	100
	1,3-Dichlorobenzene	173	1.9 (25°C)	151
	1,4-Dichlorobenzene	174	0.6	147
	2,4-dichlorophenol	210	1 (53°C)	163
	2-(diethylamino) ethanol	162	1	117
	Diethyl malonate	199	1 (40°C)	160
	Diisopropyl aminoethanol	187	0.1	145
	Dimethyl methyl-phosphonate	181	<0.1 (10°C)	124
	2,4-Dimethylphenol	210	1 (51.8°C)	125
	Dimethyl sulfoxide	189	0.4	78
	4-Hydroxy-4-methyl-2-pentanone	164	1.1	116
	Malathion	157	0.7 (157°C)	330
	Methyl salicylate	223	1 (54°C)	152
	1-Methyl-naphthalene	245	NA ^c	142
	Naphthalene	218	0.5	128
	Nitrobenzene	211	0.3	123
	Phenol	40	0.4 (25°C)	94
	Pyruvic acid	165 ^d	1 (21.4°C)	88
	1,2,4-trichloro-benzene	214	1 (38.4°C)	181
Organometallics	Ferrocene	249	2.6 (100°C)	186
	Molybdenum hexacarbonyl	156	0.1 (25°C)	266
	Lead acetylacetonate	NA	NA	405
	Nickel acetylacetonate	220 ^d	11 (220°C)	257
	Triphenyl tin chloride	464	<1	385

a) Boiling points, vapor pressure data, and molecular weights were taken from the Material Safety Data Sheets (MSDS).

b) Vapor pressure data at sea level is reported at 20°C, unless indicated otherwise.

c) NA: Not Available on MSDS form.

d) Decomposition temperature.

The reliability of an analytical method depends upon, among other things, its linearity, dynamic range, and reproducibility. Figure 1 shows a linear calibration curve for charge exchange (CE) ionization of 2-chlorophenol (b.p. 175 C) from 10 to 125 ppb in air taken over a 2 day period. Each point represents the average peak area measurement obtained by sampling each concentration 4 times each for 40 seconds. Relative standard deviations of the peak area measurements for the concentrations sampled range from 2.3 to 16.2%. At 10ppb, the CE response for 2-chlorophenol was an order of magnitude greater than the EI response (i.e. the ratio of charge exchange response to electron ionization response was 32). Although not shown here, we have demonstrated calibration curves for benzene in air obtained with MIMS that span nearly four orders of magnitude in concentration with high reproducibility (5).

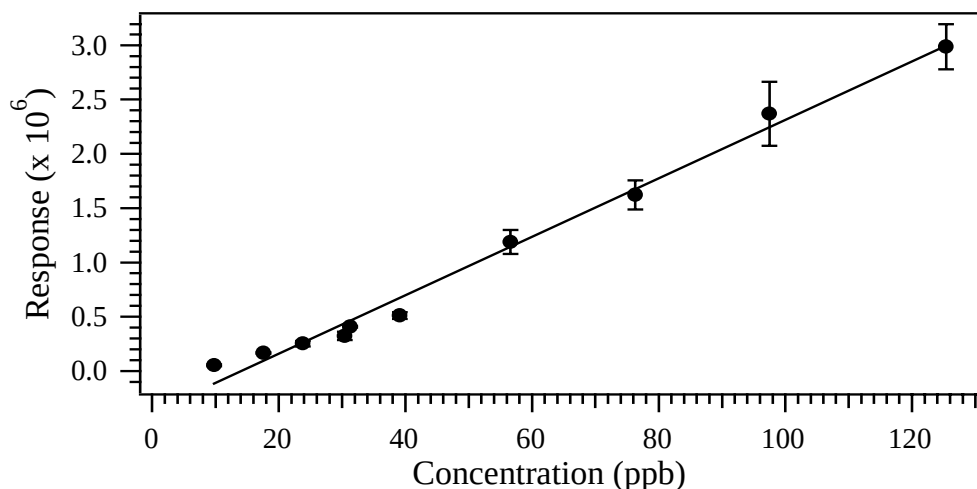


Figure 1. Linear calibration curve for charge exchange ionization of 2-chlorophenol in air obtained with membrane introduction mass spectrometry.

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, water and air (see Figures 2 and 3, respectively). To our knowledge, this is the first time this has been accomplished.

Figure 2 shows the simultaneous detection of (a) benzene (VOC), (b) naphthalene (SVOC), and (c) ferrocene (organometallic compound) in aqueous solution that was obtained with charge exchange ionization with H_3O^+ as the reagent ion. The sample flow rate was 16 mL/min. The membrane was exposed to an aqueous sample containing the analytes for a period of 30 seconds (starting at 60 seconds and ending at 90 seconds). This was sufficient to detect 870 ppb benzene, 150 ppb naphthalene, and 180 ppb ferrocene in water, as is illustrated by the ion chromatograms of each molecular ion, 78, 128, and 186, respectively. The benzene signal shows a sharp rise beginning at 120 seconds followed by a sharp decrease from 155 seconds to 180 seconds. Naphthalene (x2.5) and ferrocene (x4), on the other hand, show more gradual increases and decreases in ion signals, indicative of the longer diffusion times required for the less volatile compounds (than benzene) to pass through the membrane into the carrier gas. Permeation of the analyte through the membrane is governed directly by the diffusivity and solubility constants with diffusion being the rate-limiting step for species with similar solubility.

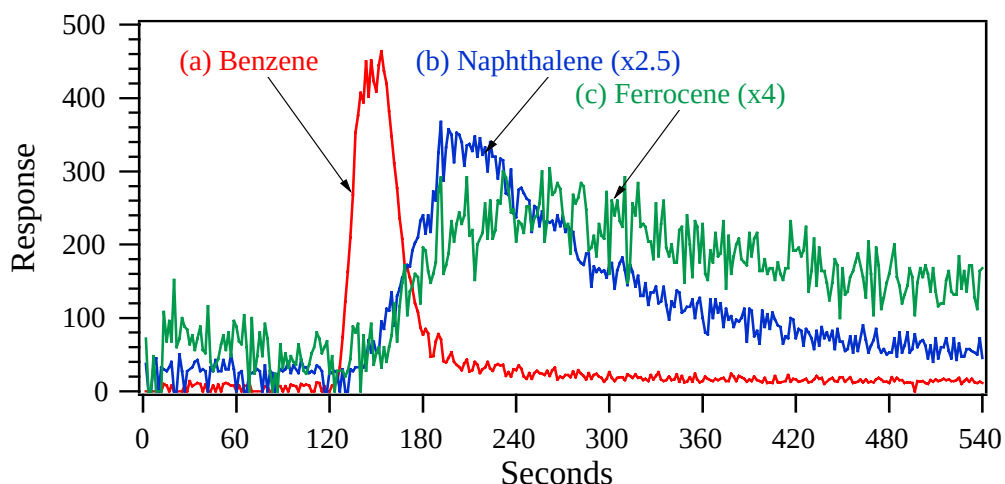


Figure 2. Simultaneous detection of 870 ppb benzene, 150 ppb naphthalene, and 180 ppb ferrocene in aqueous solution using membrane introduction mass spectrometry.

The same membrane assembly used for aqueous solutions (shown above in Figure 2) is also suitable for detection of VOCs, SVOCs, and organometallic compounds in air (shown below in Figure 3). Figure 3 illustrates the simultaneous detection of (a) 660 ppb methyl ethyl ketone (VOC), (b) 7 ppb toluene (VOC), (c) 316 ppb 1-methylnaphthalene (SVOC), and (d) 700 ppb ferrocene (organometallic compound) in air, and was obtained with charge exchange ionization with O_2^{+} from air as the reagent ion. A sampling period of 2 minutes is indicated by the dashed line at the top of Figure 3 beginning at 85 seconds (scan #35) and ending at 205 seconds (scan #85). Twenty five scans is equivalent to one minute. The response profile of the more volatile compounds, methyl ethyl ketone (MEK) and toluene, matches the sampling time period of 2 minutes. The ion chromatograms of MEK and toluene are depicted by a very sharp increase in the molecular ion signals at scan #40 followed by a sharp decrease at scan #90. Slower compound diffusivity is observed for the less volatile compounds of 1-methylnaphthalene (MNAP) and ferrocene. The response time lag of the membrane to MNAP is 70 seconds after sample release from the Dynacalibrator. The total sample time (ion chromatogram) of MNAP, illustrated in Figure 3 by the gradual decrease in the molecular ion signal, extends beyond the 2 minute sample exposure time by greater than one minute. The ion chromatogram of ferrocene shows a weaker response than MEK, toluene, and MNAP. The ferrocene response time lag is approximately 60 seconds.

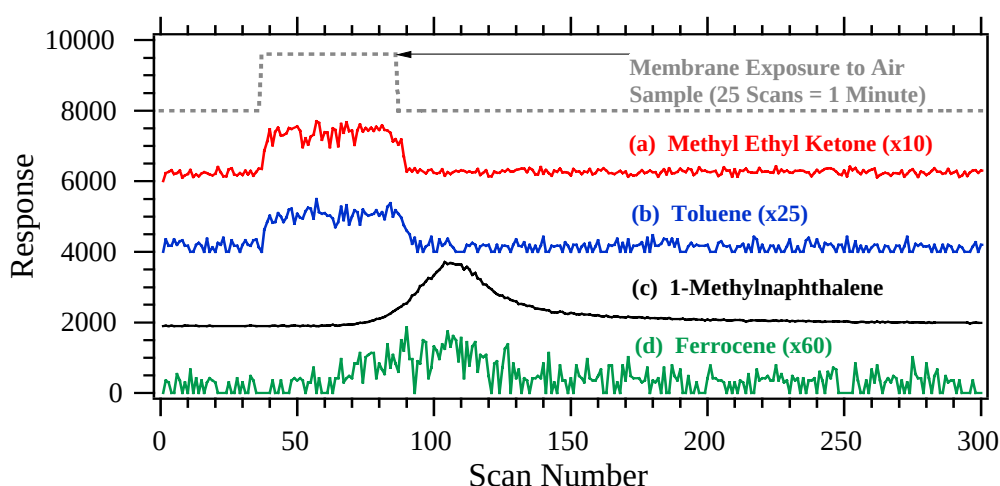


Figure 3. The top trace depicts a 2 minute time period of membrane exposure to the air sample. Simultaneous detection of (a) 660 ppb methyl ethyl ketone (VOC), (b) 7 ppb toluene (VOC), (c) 316 ppb 1-methylnaphthalene (SVOC), and (d) 700 ppb ferrocene (organometallic) in air using membrane introduction mass spectrometry.

DISCUSSION

Membrane introduction mass spectrometry functions as near real-time monitor: there is no sample preparation and sample analysis time is seconds to minutes. MIMS can be implemented as a flow injection technique, where samples, standards, and method blanks can be sequentially analyzed in a continuous fashion. The MIMS method operates as a closed-loop system. For example, the sample is returned directly to the waste stream, thus mitigating the creation of further waste during the analysis. The membrane acts as an interface between the sample (often water or air) and the vacuum of the mass spectrometer. Transport of the analyte through the membrane occurs by the process of pervaporation, which includes absorption to the outer surface of the membrane, diffusion through the membrane, and evaporation from the inner membrane surface into vacuum. Selective pervaporation of the analyte through the membrane results in its enrichment, and thus can result in low detection limits. Detection limits for VOCs are in the low parts-per-trillion range, whereas detection limits for SVOCs and organometallic compounds are in the mid to high parts-per-trillion range.

Membrane introduction mass spectrometry has been demonstrated with a wide variety of volatile, semi-volatile, and organometallic compounds. The MIMS technique is highly versatile in that the same membrane introduction system may be used without modification for detecting VOCs, SVOC, and organometallic compounds in water and air. The technique can be rapidly switched between air and water samples. Relatively fast response times (~0.5 to 5.0 minutes) with minimal operator intervention are achieved with MIMS. Background interferences due to atmospheric gases or to water vapor in air and/or water are reduced by the selectivity of the membrane for organic compounds, allowing for analyte enrichment without preconcentration. Quantitative measurements of several classes of compounds, including chlorinated and oxygenated solvents as well as phenols and chlorophenol compounds, demonstrate the sensitivity and reliability of MIMS for on-line, near real-time monitoring of liquid and air waste streams.

Charge exchange (CE) ionization yields more intense molecular ions than electron ionization (EI). Both ionization modes lead to the formation of odd-electron molecular ions, but the internal energy deposited to the molecule is dependent on the mode of ionization. More energy is transferred to the analyte in the EI process, leading to more fragmentation of the analyte, than by charge exchange with O_2^{+} or H_3O^+ . When mixtures of compounds are analyzed, quantification may be more easily accomplished with charge exchange ionization where fewer ions resulting from fragmentation are observed or only the molecular ion is detected.

The analysis of complex mixtures with MIMS has been demonstrated with the simultaneous detection of volatile, semi-volatile, and organometallic compounds in water and air. The relatively low vapor pressure of organometallic compounds, combined with differences in solubility and diffusivity in the membrane between organometallic compounds and VOCs and SVOCs, make the detection and analysis of organometallic compounds in air and water a challenging problem. Alternative membranes (other than polydimethylsiloxane) may be more suitable for improving the sensitivity and selectivity of MIMS to organometallic compounds. A chemically modified membrane which selectively binds and releases analytes could be used. Further investigation needs to be done to examine and compare analyte (i.e. organometallic compounds) solution flow rate across the membrane, membrane temperature, compound solubility in the membrane, and ionization techniques.

CONCLUSION

Membrane introduction mass spectrometry has been investigated for the on-line, near real-time analysis of volatile, semi-volatile, and organometallic compounds in air and water. The simultaneous diffusion of volatile, semi-volatile and organometallic compounds through the polydimethylsiloxane membrane in MIMS is one of the method's strengths in that all of the analytical information is obtained in a relatively short time, i.e. on the order of seconds to minutes. The versatility of membrane introduction ion trap mass spectrometry has been demonstrated by the simultaneous detection and analysis of volatile, semi-volatile, and organometallic compounds in both air and water matrices. Implementation of the MIMS technique to the problem of real-time, on-line monitoring of mixed hazardous waste at the DOE sites can lead to substantial savings in time and costs.

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