Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Chlorocarbon Permeabilities Of Several Polymeric Membranes Determined By Membrane Introduction Mass Spectrometry (Mims)

Mark L. Stone[a]; Linda A. Polson[a]
[a] Idaho National Engineering and Environmental Laboratory, Idaho Falls, Idaho, USA

Online publication date: 07 September 2003

To cite this Article Stone, Mark L. and Polson, Linda A.(2003) 'Chlorocarbon Permeabilities Of Several Polymeric Membranes Determined By Membrane Introduction Mass Spectrometry (Mims)', Separation Science and Technology, 38: 12, 3215 — 3223
To link to this Article: DOI: 10.1081/SS-120022594
URL: http://dx.doi.org/10.1081/SS-120022594

MARCEL DEKKER, INC. • 270 MADISON AVENUE • NEW YORK, NY 10016

SEPARATION SCIENCE AND TECHNOLOGY
Vol. 38, Nos. 12 & 13, pp. 3215–3223, 2003

Chlorocarbon Permeabilities of Several Polymeric Membranes Determined by Membrane Introduction Mass Spectrometry (MIMS)[#]

Mark L. Stone[*] and Linda A. Polson

Idaho National Engineering and Environmental Laboratory,
Idaho Falls, Idaho, USA

ABSTRACT

Membrane introduction mass spectrometry uses a semipermeable membrane to enhance the response of a mass spectrometer. The chemical composition of the membrane determines its permeation rates to various species. Careful selection of the membrane may make it possible to characterize more definitively close members of a chemical family. This article gives the results of an initial survey of the permeabilities, as determined by MIMS, of a variety of polymers to a family of

[#]The submitted manuscript has been authored by a contractor of the U.S. Government under contract No. DE-AC07-99ID13727. Accordingly, the U.S. Government retains a non-exclusive, royalty-free license to publish or reproduce the published form of this contribution, or allow others to do so, for U.S. Government purposes.

[*]Correspondence: Mark L. Stone, Idaho National Engineering and Environmental Laboratory, P.O. Box 1625, Idaho Falls, ID 83415-2208, USA; E-mail: mls2@inel.gov.

DOI: 10.1081/SS-120022594 0149-6395 (Print); 1520-5754 (Online)
Published by Marcel Dekker, Inc. www.dekker.com

MARCEL DEKKER, INC. • 270 MADISON AVENUE • NEW YORK, NY 10016

chlorocarbons that are often the major components of subsurface remediation concerns.

Key Words: Polymer membranes; Permeability; MIMS.

INTRODUCTION

One of the main classes of subsurface remediation contaminants is chlorocarbons. These materials were used in a wide variety of applications and then dumped at various sites in pits or buried in drums, some of which are now corroded and leaking. The movement of these compounds in the vadose zone poses a threat to underground aquifers that are sources of potable water for populations downstream from the contamination sites. New methods are needed to monitor and measure contaminant levels during remediation efforts.

Membrane introduction mass spectrometry is a technique that uses semipermeable membranes to preconcentrate or selectively transport materials for mass spectral analysis.[1–4] When a liquid feed stream is passed across the surface of the membrane, analytes are selectively dissolved into the polymer, transported across it, and then are volatilized directly into the mass spectrometer (known as pervaporation). MIMS can also be used directly for gas analysis as well. The combination of the membrane preconcentration of the analyte with the superior specificity and detection capabilities of a mass spectrometer, makes MIMS a powerful analytical tool.[5,6]

There are a number of design variables and experimental parameters that can be varied and optimized to improve the instrument's performance. These include injector design, flow rates, carrier fluids, temperature, and detector types (ion trap, quadupole, etc.). However, one of the most important components of the MIMS technique is that of the membrane itself. This article presents a survey of polymer membrane performance from testing of two commercially available, as well as in-house produced, membranes in a MIMS arrangement when exposed to four chlorocarbons.

EXPERIMENTAL

A Varian Saturn I ion trap mass spectrometer with the heated capillary interface removed was used for this research. The capillary interface was replaced with a MIMS Technology, Inc. (Palm Bay, FL) direct insertion probe inlet configured specifically for the Saturn I ion trap. A MIMS Technology, Inc. flow injection module (FIA-TC2) was used in conjunction with a sheet

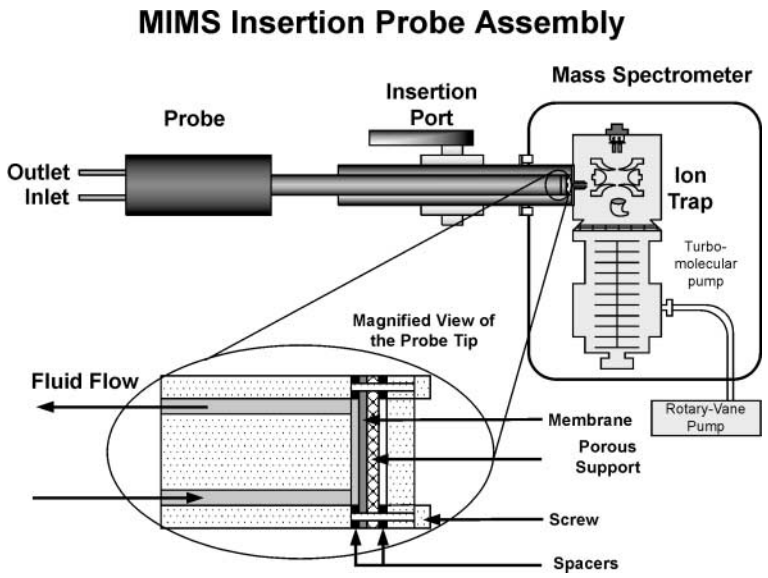

Figure 1. A schematic of the MIMS experimental set up.

membrane probe (model 1900-S1), which held the membrane (Fig. 1). All of the analyses were made at 1 mL/min flow with the probe held at 30°C. Deionized water that had passed through a Nanopure system (> 18 Mohms) was used as the solvent and feed transport fluid. All of the reagents were prepared immediately prior to each set of runs, and all dilutions were sealed in Teflon-lined septa capped vials. When making a run, 4 or 5 mL were passed through the sample loop to ensure good sample loading, then, a 1-mL portion of solution was injected via the injection port into the pumping system. Such a set up infers that the membrane was exposed for approximately 1 minute to the analyte. The mass ranges monitored were m/z 145 to 160 for carbon tetrachloride, m/z 115 to 125 for chloroform, m/z 80 to 90 for methylene chloride, and m/z 125 to 135 for trichloroethylene (TCE). In the acquisition method, the settings were seconds/scan = 1.00, acquire time = either 45 or 60 minutes, depending upon the sample such that three injections could be run, fil/mul delay = 0 seconds, peak threshold = 1 count, mass defect = 40 mmu/100 amu, and background mass = 39 amu.

In a typical run, the feed water was allowed to pass over the membrane for several minutes prior to sample injection. Upon injection of the 1-mL aqueous sample, the instrument response was monitored until the response returned to

the initial baseline. At that time, another sample was injected. At least three runs were made at each analyte concentration. Typically, a complete cycle lasted approximately 15 to 20 minutes per injection. Signals were considered valid if their peak heights were greater than the value obtained by taking three times the standard deviation of the baseline average and adding that to the baseline average value.

Polydimethylsiloxane was purchased from Specialty Manufacturing Incorporated (Saginaw, MI) as silicone sheeting. The material used in this study was 100- to 110-μm thick.

The polyphosphazenes were synthesized in-house.[7,8] The three were poly(bisphenoxy) phosphazene, poly(bis p-ethylphenoxy) phosphazene, and poly(40% sugar 60% trifluoroethoxy) phosphazene. The film thicknesses were determined to be 60 and 100 μm. The films were cast from tetrahydrofuran (3 to 5% solution) onto a glass plates, air dried, and then immersed in water to float it off the glass. Water was removed from the freestanding film by first air drying, followed by vacuum pumping until dry.

Ethylene propylene diene monomer (EPDM) rubber was cast from a solution of 10% Keltan 512 and 1% benzoyl peroxide in toluene onto a glass plate. It was air dried, then heated at 135°C for 10 minutes to ensure

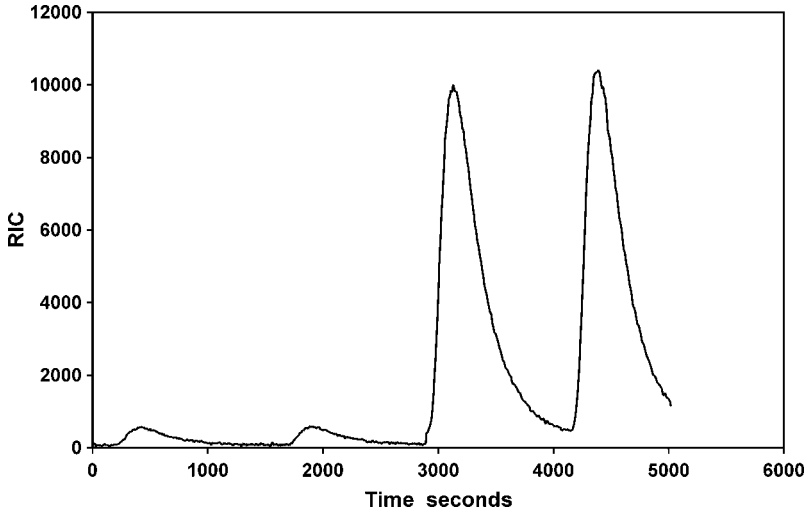

Figure 2. Typical MIMS response curves. Illustrated is the response of poly(bisphenoxy) phosphazene to injections of 20-ppm and 200-ppm methylene chloride in water.

crosslinking. The resulting 275-μm thick film was soaked off the glass plate in water and then air dried.

Membranes were prepared by placing them in a cutting die to make six small holes for the screws that connect the end cap on the probe. The membrane was then mounted on the probe tip, and any excess was trimmed off with a razor. No other pretreatments were administered. Membrane surface area in all cases was 23.2 mm^2.

Aqueous solutions of four chlorocarbons (methylene chloride, chloroform, carbon tetrachloride, and trichloroethylene) were used starting at 200 ppm and diluted by factors of 10 until undetectable. Three to five repetitions were made for each sample concentration. All of the analyses were made using a 1-mL injection into a feed carrier flow of 1 mL/min with the temperature of the probe held at 30°C. Figure 2 shows the typical peak shape and the peak-to-peak repeatability in MIMS spectra.

RESULTS AND DISCUSSION

The scope of this work was to make a survey of the permeabilities of readily available polymeric membrane materials for a series of similar chlorocarbons. The survey was to determine which materials were suitable for use with an ion trap based MIMS system. The two parameters that determine a materials usefulness is whether it allows any analyte to permeate and its ability to exclude water well enough to prevent the ion trap from being swamped. It shows how the species that pass through the membrane are injected directly into the ion trap for detection. Thus, the better the membrane is at permitting only the analytes through, the more suitable it is for this application.

Figure 2 shows the types of curves that are typical for MIMS analysis. Injections of 20 ppm followed by two injections of 200 ppm methylene chloride across a poly(bisphenoxy) phosphazene membrane were made. The repeatability and large dynamic range can be seen. A calibration curve can be easily generated by simply running a set of known concentrations.

Table 1 lists the results of testing the four chlorocarbons. All gave responses in the low ppm to ppb range, indicating that many polymers could be used for this applicaion. A number of interesting interactions and comparisons can be noted. Figure 3 gives the responses of two different phosphazene polymers to injections of 200-ppm TCE. Two differences between the polymers are very apparent. First, the overall amplitude for the bisphenoxy polymer was approximately four times that of the other membrane. The other noticeable difference is that the bisphenoxy polymer takes over seven times as long to return to the baseline. One explanation is that the TCE solubilizes much more

Table 1. Detection limits for the membrane materials exposed to the four chlorocarbons.

Polymer	Methylene chloride	Trichloroethylene	Carbon tetrachloride	Chloroform
Polybisphenoxy phosphazene	20 ppm	10 ppm	Not run	Not run
Polybis (p-ethylphenoxy) phosphazene	2 ppm	200 ppb	200 ppm	20 ppm
Polybis(40% sugar–60% trifluoroethoxy) phosphazene	20 ppm	2 ppm	200 ppm	20 ppm
Polydimethyl siloxane	200 ppb	2 ppb	Erratic	200 ppb
EPDM rubber	20 ppm	200 ppb	200 ppm	20 ppm

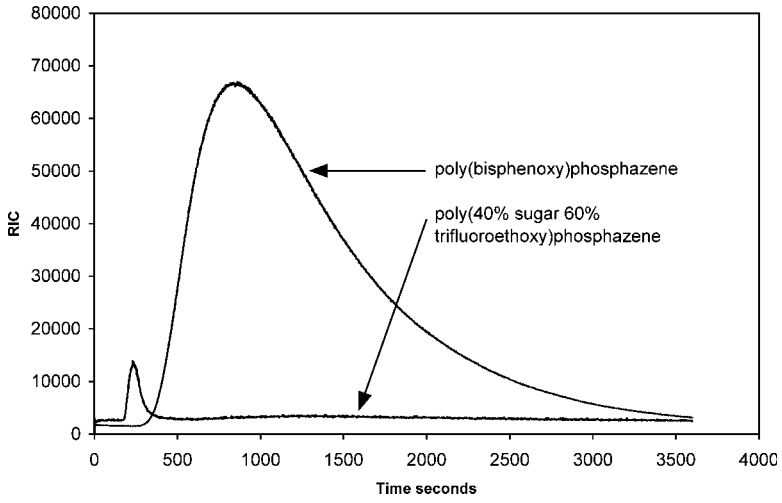

Figure 3. Comparison of the MIMS response to injections of 200-ppm TCE of two polymers.

readily into the bisphenoxy polymer. This would have the effect of filling up the membrane with the TCE that would then, over a period of time (nearly an hour), diffuse out and be detected. This long response time is fairly remarkable considering the membrane size and that it is only exposed for approximately 1 minute. The amount of TCE penetrating into the sugar/tfe polymer is much less and gives both a smaller peak and much shorter response time.

Another interesting observation is directly related to the purpose for which this study was conducted (i.e., to see if there are permeability and selectivity differences that can be observed within a family of related solvents to a single type of material). Figure 4 displays the results of 200-ppm injections of three different chlorocarbons against the sugar/tfe membrane. TCE is by far the more permeable, with the chloroform and methylene chloride nearly equal to each other but much less than that of the TCE.

The results also point to the excellent solvent characteristics of TCE. Practically all of the polymers showed some level of permeation, and, in most cases, its detection limit is at least an order of magnitude lower than that of the other chlorocarbons.

Polydimethylsiloxane (PDMS) had the best overall sensitivity to the most analytes. However, PDMS gave erratic results in the carbon tetrachloride runs.

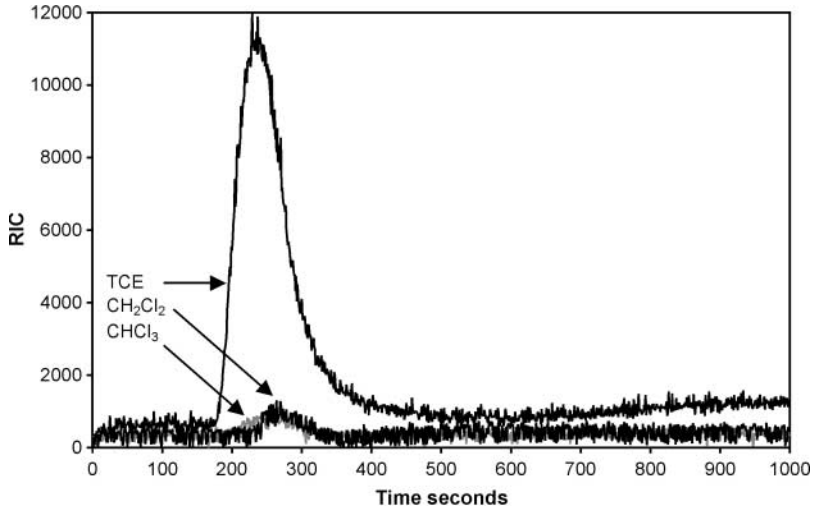

Figure 4. Comparative responses of poly(40% sugar 60% trifluoroethoxy) phosphazene to 200-ppm injections of three chlorocarbons.

CONCLUSION

MIMS is a powerful analytical tool used to measure analytes in a number of important applications. The membrane controls the selectivity, sensitivity, and flux of the analyte into the mass spectrometer.

A study was made of a number of materials, some that were commercially available as thin polymer films and others that were synthesized in-house. There was a wide variation in the responses obtained. Trichloroethylene showed a response in nearly all of the membranes.

The results obtained are very important from the point of view of developing an array of materials that can be used to distinguish between these closely related analytes. The objective was to see if membranes might be developed that, either individually or in use as an array, might be used either as preconcentrators or as barriers. The results showed that within a family of chlorocarbons, some materials were permeable to all analytes, some were unsuitable and erratic, and others could be used as barriers. It also appears that it might be possible to make some selective separations within the family of chlorocarbons. MIMS is well suited for this type of membrane characterization.

ACKNOWLEDGMENTS

The authors thankfully acknowledge the funding support of the Environmental Systems Research and Analysis Program, United States Department of Energy, contract number DE-AC-07-991D13727 BBWI.

REFERENCES

1. Johnson, R.C.; Cooks, R.G.; Allen, T.M.; Cisper, M.E.; Hemberger, P.H. Membrane introduction mass spectrometry: trends and applications. Mass Spectrom. Rev. **2000**, *19*, 1–37.
2. Cisper, M.E.; Hemberger, P.H. The direct analysis of semi-volatile organic compounds by membrane introduction mass spectrometry. Rapid Commun. Mass Spectrom. **1997**, *11*, 1449–1453.
3. Srinivasan, N.; Johnson, R.C.; Kasthuridrishnan, N.; Wong, P.; Cooks, R.G. Membrane introduction mass spectrometry. Anal. Chim. Acta **1997**, *350*, 257–271.
4. Bauer, S. Membrane introduction mass spectrometry; an old method that is gaining new interest through recent technological advances. Trends Anal. Chem. **1995**, *14* (5), 202–213.

5. Ketola, R.A.; Virkki, V.; Ojala, M.; Komppa, V.; Kotiaho, T. Comparison of different methods for the determination of volatile organic compounds in water samples. Talanta **1997**, *44*, 373–382.
6. Billings, C.H. New technique for monitoring VOCs (membrane introduction mass spectrometry; volatile organic compounds). Public Works **1995**, *126* (2), 86–93.
7. Stewart, F.F.; Harrup, M.K.; Peterson, E.S.; Stone, M.L.; Orme, C.J.; Polson, L.A. Chemically tailored phosphazene polymers for water separations applications: synthesis, characterization, and membrane formation. Proc. Am. Chem. Soc. Div. Polym. Mater.: Sci. Eng. **1999**, *81*, 539.
8. Stone, M.L.; Peterson, E.S.; Stewart, F.F.; Tsang, M.N.; Orme, C.J.; Polson, L.A. Polyphophazene membranes: Part 1. Isopropanol/dye separations. Sep. Sci. Technol. **1999**, *34* (6 & 7), 1243–1251.