

Overview

Robust operation of field portable mass spectrometers in harsh environments necessitates the use of simple sampling interfaces. Membrane inlet systems fulfill this requirement for many portable mass spectrometer systems^{1,2}. Modest need for sample preparation, reduced gas loads on mass spectrometer vacuum pumps, and physical and chemical ruggedness are several benefits that result from the use of MIMS.

Experiments to characterize the membrane inlet system have illustrated that a change in membrane permeability occurs when sample hydrostatic pressure is increased. This change can be on the order of 50% and is believed to arise from compression of the polydimethylsiloxane (PDMS) membrane. Insight into this mechanism is obtained via observations of MS signal intensities created by abrupt changes in sample flow. This allows calculation of membrane permeability, diffusivity, and solubility.

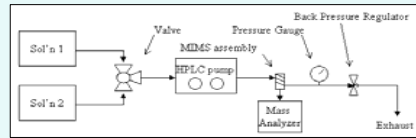


Figure 1. Schematic representation of the experimental setup for introduction of dissolved gasses. The solutions were gas-equilibrated at 25°C and were heated to 45°C in the MIMS assembly.

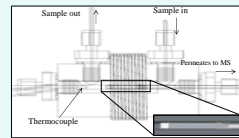


Figure 2. The membrane inlet assembly. The PDMS membrane is mounted on a sintered rod. The assembly can sustain pressures well in excess of 200 atm. Restrictive dimensions around the membrane generate high flow velocities at the membrane surface.

Instrumentation and Methods

Data were collected in the laboratory with an Inficon Transceptor 2.0 mass spectrometer with an open ion source. The flow-over hollow fiber polydimethylsiloxane (PDMS) (Dow Corning) membrane is supported by a 1/16" Φ , 10 μ m porosity Hastelloy C rod.

Experiments were performed using deionized water buffered to a pH of 3.7, and equilibrated with a gas standard containing 78% N₂, 21% O₂, 0.1%CO₂ and 0.1% CH₄. The experimental setup for the calibration experiments is shown in figure 1 and the MIMS assembly is depicted in figure 2.

All field data were collected with the 200 amu underwater mass spectrometer system. This system uses an Inficon Transceptor CPM (closed ion source) with a membrane inlet sampling interface and is described in previous work³.

Boundary Layer Considerations

Boundary layer conditions were characterized by varying the sample flow rate at hydrostatic pressures of 1 and 100 atm. This was to ensure that measured changes in signal intensity are a property of changing membrane permeability and not influenced by the boundary layer. Figure 3 shows the changes in signal intensity with respect to flow rate.

Additional experiments were designed to focus on membrane permeability. To facilitate this, flow rates were maintained at 8ml/min.

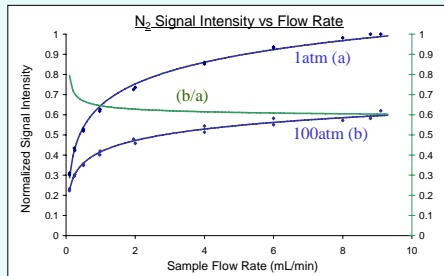


Figure 3. Signal intensities versus flow rate were compared at 1 atm (a) and 100 atm (b). At high sample flow rates the change in signal intensity is constant and at low sample flow rates the change in signal intensity shows a sharp increase in the boundary layer thickness with respect to pressure.

References

- C. Janfelt, H. Frandsen, F. Lauritsen. Characterization of a mini membrane inlet mass spectrometer for on-site detection of contaminants in both aqueous and liquid organic samples. *Rapid Communications in Mass Spectrometry*, 20(9), 2004, 1441-1446.
- P. Wong, G. Cooke, M. Cisner, P. Hemberger. Online, in situ analysis with membrane introduction MS. *Environmental Science and Technology*, 29(5), 1995, 215A-8A.
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Membrane Permeability vs. Pressure

Analyte signal intensity varies with respect to hydrostatic pressure due to changes in membrane permeability (figure 4). The effect varies between analytes, and is particularly strong for analytes with polar characteristics.

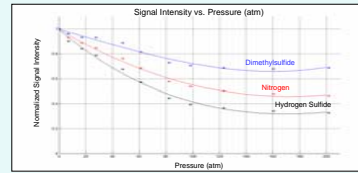


Figure 4. The influence of hydrostatic pressure varies between analytes.

Hysteresis

Observations of gas permeability show pressure dependant hysteresis (figure 5).

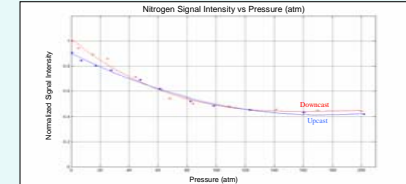


Figure 5. Plot of Nitrogen permeability vs. pressure. Membrane compression results in hysteresis of gas permeabilities. The magnitude of the hysteresis is also influenced by changes in gas concentrations.

Partition or Diffusion Coefficient? (figure 6)

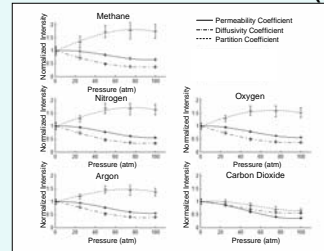


Figure 6. A concentration step function facilitates determination of the relative change in analyte diffusion and permeability coefficients with respect to pressure. The relative change in partition coefficient can thus be calculated.

Future Work

Absolute values for the permeability, diffusion, and partition coefficients will be investigated by degassing a known volume of sample at the membrane surface (figure 7).

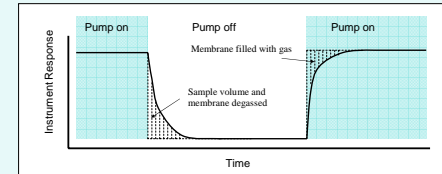


Figure 7. Flow step functions facilitate characterization of the MIMS membranes.

Application

The underwater mass spectrometer was deployed in the Gulf of Mexico in January, 2006. The mass spectrometer was deployed on a 500m tether, allowing real-time communications. The raw data were post processed using calibration coefficients determined in the laboratory. Results are presented in figure 8.



Figure 8. Concentration profiles of dissolved gases have been determined to approximately 500m depth.

Conclusions

Permeability, diffusion, and partition coefficients; boundary layer thickness; and hysteresis have been examined for insight into membrane transport phenomena. These characterizations are prerequisite to the determination of true concentrations of dissolved gases in deep marine environments.

Acknowledgements

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