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Development of novel nano-composite membranes as introduction systems for mass spectrometers: Contrasting nano-composite membranes and conventional inlet systems

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Development of novel nano-composite membranes as introduction systems for mass spectrometers: Contrasting nano-composite membranes and conventional inlet systems

by

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A dissertation submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy
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Keywords: membrane inlet mass spectrometry, nano-composite membranes, polydimethylsiloxane, pervaporation, gas measurements, Setschenow coefficients

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Dedication

I dedicate this dissertation to my family.

Esta disertación se la dedico a mi familia.
Acknowledgment

I express my appreciation to my major academic advisor, Robert H. Byrne. His patience, confidence and support in me allowed me express my creativity during my academic development as I lead developments on novel nano-composite membranes for inlet systems of mass spectrometers.

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Abstract

This dissertation presents the development of novel nano-composite membranes as introduction systems for mass spectrometers. These nano-composite membranes incorporate anodic aluminum oxide (AAO) membranes as templates that can be used by themselves or modified by a variety of chemical deposition processes. Two types of nano-composite membranes are presented. The first nano-composite membrane has carbon deposited within the pores of an AAO membrane. The second nano-composite membrane is made by coating an AAO membrane with a thin polymer film. The following chapters describe the transmission properties these nano-composite membranes and compare them to conventional mass spectrometry introduction systems. The nano-composite membranes were finally coupled to the inlet system of an underwater mass spectrometer revealing their utility in field deployments.
Chapter 1

Introduction

Development of the membrane inlet mass spectrometer

Detection and quantification of chemical substances in large bodies of water can be a daunting task. Conventional analytical methods for chemical analysis of aquatic ecosystems typically require collection of samples and transport to a laboratory. Such methods can be subject to systematic errors including introduction of contaminants and/or loss of reactive or volatile chemical species. In addition, conventional sampling methods severely limit both spatial and temporal sampling densities. This can present a problem when, for example, investigators are faced with chemical discharges at sea. The manpower and cost of research vessels required for diagnostic pollution monitoring using conventional sampling methods can become overwhelming. Furthermore, conventional sampling can lengthen the time required to locate the source of a toxic chemical plume, increasing the possibility of wildlife and public-health endangerment. Prompt sampling and analysis is preferred for studies of vast aquatic environments including lakes, rivers or the sea.

Mass spectrometers are versatile sensors capable of analyzing complex mixtures of chemicals. Membrane inlet mass spectrometry (MIMS) is an analytical technique whereby analytes are introduced into a mass spectrometer without the need of sample preparation. In situ MIMS instruments can eliminate issues surrounding sample handling.
and storage, while greatly enhancing temporal and spatial resolution of changing chemical distributions in the environment. MIMS measurements of analytes in aqueous solutions are appropriate for low molecular weight or membrane-soluble compounds. Because MIMS can help detect and quantify dissolved gases and volatile organic compounds (VOCs) in aquatic environments, MIMS is important for studies of marine science, and is likely to be increasingly used by regulatory agencies for investigations such as for the Deepwater Horizon oil spill in the Gulf of Mexico.

The MIMS method introduces analytes into the mass spectrometer via a semi-permeable membrane in a process known as pervaporation. During pervaporation, analytes in solution are selectively sorbed on the feed (solution) side of the membrane, and then diffuse through the membrane and desorb into a vapor phase on the permeate side. Permeate analytes are ionized after entering the vacuum chamber of the mass spectrometer. Ionized species are dispersed according to their mass-to-charge ($m/z$) ratio by some combination of electric and magnetic fields. The electric and magnetic fields act as a mass filter sending selected ions to a detector. The detector then records the intensity of the selected $m/z$ ions as ion current or count rate. The user then identifies chemical compounds based on their mass spectra and quantifies them according to the intensity of their ion current signals. Over the past ~15 years, MIMS has been adapted to in situ underwater mass spectrometry measurements. The sections below describe some of the history and challenges surrounding the development of underwater mass spectrometry.
Underwater mass spectrometry

In the late 1990’s, the Center for Ocean Technology (COT) within the College of Marine Science (CMS) at the University of South Florida (USF) developed underwater mass spectrometers for in situ chemical analysis of aqueous environments (Short et al., 1999). Underwater mass spectrometers are small mass spectrometers confined inside a submersible pressure vessel. These instruments were designed for deployment on a variety of platforms, including moorings, cabled sensor nodes, ROVs, AUVs, and manned submersibles. The instruments are mobile and capable of simultaneous measurement of a variety of volatile constituents in the water column.

The Center for Ocean Technology research group, which lead the underwater mass spectrometry project, developed underwater mass spectrometers using commercially available quadrupole and ion-trap mass analyzers. Field deployment of underwater mass spectrometers have shown that these sensors are highly effective for measurements of dissolved gases and VOCs in a wide variety of aquatic environments (Short et al., 2000; Short et al., 2001; Kibelka et al., 2004; Short et al., 2006; Wenner et al., 2004; Bell et al., 2007).

Underwater mass spectrometers are designed to operate in harsh environments. However, researchers had to overcome some modular design challenges in order to allow sustained underwater operations. The underwater quadrupole mass spectrometer, shown in Figure 1.1, like most other underwater mass spectrometers, is comprised of a mass analyzer, detector, ion source, vacuum system, membrane inlet module, and power supply within a pressure vessel. The following sections describe some of the design challenges faced during the development of underwater mass spectrometry.
Figure 1.1. Components of a conventional underwater quadrupole mass spectrometer.

Mass analyzer

Quadrupole mass spectrometers with unit mass resolution are quite common and relatively inexpensive. A quadrupole mass analyzer, as shown in Figure 1.2, is composed of four parallel hyperbolic or cylindric-shaped rod electrodes. Direct current (DC) and radio frequency (RF) voltages are applied to the electrodes, creating stable trajectories, distinct for each \( m/z \) ratio, along which positive ions are typically delivered to either a high-gain electron multiplier or Faraday-cup detector. The mass fractionation of the analyzer occurs at very low pressure to maximize the mean free paths of ions traveling through the quadrupole.
Figure 1.2 Schematic of the MIMS mass fractionation process using a quadrupole mass spectrometer.

Ion source

Analytes permeating through the membrane are ionized by an ion source inside the vacuum chamber. Although there are several means of ionizing chemicals inside a mass spectrometer, the most common method is electron-impact ionization. This form of ionization relies on electron emission by a thermally heated filament. For MIMS analysis of aqueous solutions, water is the major constituent permeating through membranes. Accordingly, filaments are subjected to oxidation by permeating water, shortening their lifetime. Oxidation-resistant Yttrium-coated Tungsten and Thoria-coated Iridium are recommended for extending the length of underwater mass spectrometry operations.

Vacuum system

As noted previously, mass spectrometers operate at low pressure. The most common vacuum system used for mass spectrometry is comprised of a turbo-molecular pump (or turbo pump) in combination with a roughing pump. Pumping systems normally vent vapors from the vacuum chamber into the atmosphere. This is not possible in underwater operations as the mass spectrometer is submerged in a sealed pressure vessel. Since vapors are necessarily pumped into a closed vessel, the partial pressures of gases
increase through time, eventually limiting the duration of deployment. This problem is addressed by exhausting gases to a separate chamber within the pressure vessel and, occasionally, by using a getter pump within the exhaust-chamber.

**Mass spectrometer design and packaging**

Mass spectrometers are typically large laboratory instruments. In the last few decades, however, improvements in technology have made some mass spectrometers smaller and even portable. These small-format mass spectrometers have size, weight and power characteristics that make them suitable for packaging in small cylindrical vessels. Current mass spectrometry research is directed towards further reductions in size and power requirements.

**Membrane introduction systems**

In MIMS systems, introduction of analytes to the mass spectrometer is mediated by a semi-permeable membrane interface. Mass spectrometry measurements are therefore directly influenced by membrane solution-diffusion properties (Johnson et al., 2000). Underwater mass spectrometers have employed a variety of membrane module designs (Short et al., 1999, Wenner et al., 2004, Bell et al., 2007). Most underwater mass spectrometers use polydimethylsiloxane (PDMS) as the membrane material of choice. The research group at SRI International, in collaboration with the USF-CMS Center for Ocean Technology, has developed a variety of membrane modules for underwater mass spectrometry. The first membrane module used for underwater mass spectrometry was a PDMS tube connected to two concentric stainless steel tubes, Figure 1.3a (Short et al.,
Water was streamed through the PDMS tube using a peristaltic pump, while the outside of the PDMS tube was exposed to the vacuum of the mass spectrometer. This design was strongly susceptible to hydrostatic pressure, where the PDMS tube would typically expand and burst when the mass spectrometer was submerged below 30 meters. In light of the hydrostatic pressure limitations on the first membrane module, further modifications were made to support the PDMS membrane. The second membrane module, as shown in Figure 1.3b, had a stainless steel spring inserted within a cylindrical PDMS membrane (Wenner et al., 2004), and the pressure gradient was reversed. As before, the PDMS tube was connected between two steel tubes but water was streamed on the outside of the PDMS tube using a magnetic piston pump and a vacuum was applied inside the PDMS membrane. The spring provided support for PDMS tube against high hydrostatic pressures external to the tube. This design allowed the underwater mass spectrometer to reach depths as great as 250 meters. The need to study chemical distribution at greater depths in the environment further pushed membrane module designs to make them more resistant to hydrostatic pressure. Figure 1.3c shows another membrane module design used for underwater mass spectrometry. Following a concept similar to that shown in Figure 1.3b, the PDMS tube in Figure 1.3c is supported by a stainless steel sintered rod (Bell et al., 2007). This support rod allows the underwater mass spectrometer to reach depths of 2000 meters or more without membrane rupture.

The permeation properties of a membrane (e.g. PDMS) are subject to influences from hydrodynamics, temperature, sample composition and hydrostatic pressure. Sample hydrodynamics is very important for MIMS measurements. Analytes in the liquid phase are in direct contact with the surface of the MIMS membrane.
Figure 1.3. a) PDMS tube connected to two tubes where water is streamed inside the tube and the outside is exposed to the vacuum of the mass spectrometer. b) A spring support inside the PDMS tube prevents collapse from the hydrostatic pressure of streaming ambient water outside the tube. c) A sintered rod supports the PDMS tube allowing vapors to diffuse through the PDMS membrane and sintered tube, and subsequently into the vacuum chamber.

If the liquid sample is motionless, an analyte-depleted boundary layer will be formed in the solution at the surface of the membrane. To replenish the depleted layer, the liquid sample has to be streamed over the surface of the membrane. Figure 1.4 shows an example of how the intensity of a mass spectrometer’s ion current is affected by sample flow rates. Faster flow rates reduce the thickness of the boundary layer and generally produce higher signals until a plateau is reached at high flow rates. Consequently, MIMS measurements of analytes in solution are ordinarily performed not only at constant flow rates, but at rates sufficient to reduce the sensitivity of ion currents to hydrodynamic flow.
Baseline-normalized ion currents \( I_{BN} \) vs. flow rate for a PDMS membrane coupled to the inlet system of a mass spectrometer. Baseline-normalized ion currents \( I_{BN} \) were calculated using the following equation: 

\[
I_{BN} = \frac{\Phi_G - \Phi_{G(\text{baseline})}}{\Phi_{G(\text{baseline})}},
\]

where \( \Phi_{G(\text{baseline})} \) is a baseline current for a given gas, \( G \), and \( \Phi_G \) is the ion current for gas \( G \) measured at any point in time.

Analyte-permeation is strongly influenced by sample/membrane temperatures. An increase in the temperature of a membrane-introduction system will increase permeation rates of analytes. Ambient environmental temperatures can vary by as much as 5°C or more over only a few meters of water depth. Consequently, MIMS measurements are performed at a constant temperature. The sample stream entering the membrane module is thermally equilibrated with a heater. Sample composition is another factor that affects the permeability of analytes through membrane materials. Membrane swelling or competitive sorption of chemicals within the membrane can influence the permeation of analytes through a membrane.

The thickness of PDMS membranes previously used for underwater mass spectrometry was approximately 120μm (Short et al., 1999, Bell et al., 2007). In the previous membrane module design of Bell et al. (2007) (Figure 1.3c), a sintered rod helped support the PDMS tube from collapse. However, as seen in Figure 1.5, PDMS material can be deformed and compressed against the sintered rod with increasing hydrostatic pressure. When the PDMS membrane is compressed, the flow of gas
permeating through the membrane decreases. In addition, the PDMS membrane exhibits hysteresis when the hydrostatic pressure is decreased.

![Cross section of the boundary between the PDMS tube and the sintered rod in a MIMS system.](image)

**Figure 1.5.** Cross section of the boundary between the PDMS tube and the sintered rod in a MIMS system. Hydrostatic pressure deforms or compresses the PDMS membrane material. Gas permeation through a PDMS membrane decreases with increasing hydrostatic pressure.

Compressional and hysteresis effects increase the complexity of MIMS calibrations for PDMS membranes. Ideally a membrane inlet system for mass spectrometers should be able to provide responses that are unaffected by variable hydrostatic pressure. To address these hydrostatic pressure effects the USF College of Marine Science and Center for Ocean Technology, in collaboration with SRI International, has been developing novel nano-composite membranes as introduction systems for mass spectrometers.

This dissertation presents the development of novel nano-composite membranes for use in MIMS systems at high pressure. These nano-composite membranes incorporate anodic aluminum oxide (AAO) membranes as templates that can be used by themselves or modified by a variety of chemical deposition processes. Descriptions of nano-composite membrane developments have been published in the *Journal of Membrane*
Science in Miranda et al. (2009 and 2011). More recent work has also been submitted for peer-review. This dissertation describes studies of the transmission properties of two types of nano-composite membranes, and comparisons of these nano-composite membranes with conventional MIMS introduction systems.

The dissertation is divided into five chapters; this introduction is Chapter 1. Chapter 2 presents the study of a nano-composite membrane produced by carbon deposited within the pores of an AAO membrane. The properties of this membrane are compared with the gas-transmission properties of a capillary tube. Chapter 3 presents a study of a nano-composite membrane created by coating an AAO membrane with a thin polymer film designed to increase membrane tolerance and limit pressure-induced hysteresis effects. The gas-transmission properties of this membrane are compared to those of a conventional PDMS membrane. Chapter 4 compares the transmission properties of polymer coated nano-composite membranes and a conventional PDMS membrane for membranes in contact with dissolved gases in sodium chloride solutions. Chapters 3 and 4 demonstrate that nano-composite membranes have a variety of advantageous properties compared to the characteristics of PDMS membranes. Finally, Chapter 5 describes use of the novel nano-composite membranes as introduction devices for in situ underwater mass spectrometry measurements of dissolved gases at sea.
Chapter 2

Direct coupling of a carbon nanotube membrane to a mass spectrometer:
Contrasting nanotube and capillary tube introduction systems*

Abstract

A carbon nanotube membrane was directly coupled to the inlet system of a mass spectrometer to evaluate its use as a novel, potentially tunable, membrane inlet system. Carbon nanotubes for the membrane were synthesized using the template method. Chemical vapor deposition of a hydrocarbon precursor produced nearly graphitic carbon nanotubes within the pores of an anodic aluminum oxide membrane. The selectivity of the carbon nanotube membrane was compared to that of a capillary tube. Relative to the capillary tube, the carbon nanotube membrane was preferentially transmissive to methane. Conductance of gas mixtures exhibited different dependencies on total pressure in carbon nanotube and capillary tube introduction systems. In carbon nanotubes, conductance decreased with increasing total pressure, and the extent of the decrease became progressively smaller between methane and carbon dioxide (CH₄ > N₂ > O₂ > Ar > CO₂). In the capillary tube introduction system, conductance decreased substantially only for nitrogen. The capillary tube conductance for methane was nearly independent of total pressure, and conductance increased progressively between O₂, Ar and CO₂.

*This chapter was published in the Journal of Membrane Science; Miranda et al. (2009)
**Introduction**

Mass spectrometers are powerful analytical instruments that can detect and quantify a variety of analytes in complex matrices (Bauer and Solyom, 1994). Introduction of volatile analytes to the mass spectrometer (MS) has been commonly accomplished by capillary tubes, and other orifices, or by the use of thin polymer films, such as polydimethylsiloxane (PDMS) membranes, using the technique called membrane inlet (or introduction) mass spectrometry (MIMS) (Dheandhanoo et al., 2000; Johnson et al., 2000; Keil et al., 2007). Since its development in 1963 (Hoch and Kok, 1963), MIMS has been tested using new membrane materials and technologies, such as zeolite membranes (Bennett et al., 1999) and microporous hollow fibers (Ferreira et al., 2000), or using alternative polymer membranes (Johnson et al., 2000). The MIMS technique has employed a variety of membrane modules, where a gas or liquid sample flows through the membrane inlet system and analytes diffuse through the membrane material or pores into the MS.

Nanotechnology is one of the newest tools to generate novel membranes. The ability to control molecular geometries on a nanometer scale provides substantial control of membrane physical/chemical properties. In particular, it is expected that nanotechnology can be used to generate membranes that are preferentially transmissive to a variety of molecular analytes. This paper introduces the use of carbon nanotube (CNT) membranes as an integral part of MIMS. The CNT membrane used in this work was created using chemical vapor deposition to produce nearly graphitic nanotubes within the pores of an oxide film template.
The template approach (Parthasarathy et al., 1995) allows control over CNT aspect ratios (Kyotani et al., 1996) within the pores of an anodic aluminum oxide (AAO) membrane. Previous investigations of the gas transport properties of CNT membranes indicated that membranes exhibit fast mass-transport properties (Cooper et al., 2004; Newsome and Sholl, 2006; Kim et al., 2007; Noy et al., 2007) and remarkable selectivity (Holt et al., 2006). In this work we performed baseline measurements with a novel CNT/AAO membrane gas introduction system for mass spectrometry, and compared these measurements with those obtained with a conventional capillary tube (CT) sample introduction system. Specifically, a membrane generated using the template method was directly coupled to a MS, and gas transport properties of the CNT/AAO inlet system were then compared to the properties of a CT introduction system. MS analysis of gas mixtures allowed comparison of the CNT/AAO membrane and CT introduction characteristics. Selectivity between the CT membrane and the CNT/AAO membrane (hereafter referenced simply as a CNT membrane) was then assessed in terms of ion current ratios for different gases in gas mixtures. To the authors’ knowledge, this study constitutes the first assessment of a CNT membrane as part of a mass spectrometer membrane inlet system.

**Experimental methods**

**Anodic aluminum oxide membrane**

An aluminum strip (0.5mm thick, purity 99.999%) was degreased in acetone and partly covered with electroplating tape. Exposed aluminum was electropolished and anodized using the two-step process of Masuda and Satoh (1996). The initial aluminum anodization step was conducted at 40V in 0.3M oxalic acid at 10°C. After 17 hours the
oxide layer was removed using a mixture of phosphoric acid (6 wt%) and chromic acid (1.8 wt%) over a period of 1 hour at 60°C. The aluminum anodization was then repeated for 10 hours. A protective polymer coat was applied to the oxide surface, and the remaining aluminum was removed using a saturated mercuric chloride solution. The aluminum oxide membrane was subsequently etched in 5% phosphoric acid (45 minutes at 30°C). Mechanical removal of the polymer coating produced a freestanding AAO membrane. The AAO membrane was then heated in air between two quartz plates (30 minutes at 900°C) (Che et al., 1999) causing a phase transition from amorphous to gamma alumina (Mardilovich et al., 1995).

**Carbon nanotube synthesis**

In the first stage of carbon nanotube synthesis, the AAO membrane was placed in a quartz tube furnace, edge-up in a quartz boat. The furnace-tube was purged with argon and the temperature was raised to 750°C. After thermal stabilization, the argon flow was maintained at 10.5 mL/min and ethylene was added to the gas stream at 0.35 mL/min. Carbon deposition was allowed for 16 hours, after which the flow of ethylene was terminated and the furnace was cooled to room temperature with a continuing flow of argon.

**Preparation of the CNT membrane**

The chemical vapor deposition process generated carbon nanotubes within the pores of the AAO membrane and deposited a thin carbon film on the surface of the membrane. The carbon film was removed (ion milled, GATAN 691) from both sides of
the membrane, producing a smooth surface. The open pores of the CNT membrane produced in this process are shown in Figure 2.1.

![Figure 2.1](image)

**Figure 2.1.** Scanning electron microscope (Hitachi S-4800 Field Emission) image of the CNT membrane surface after ion milling. The dark areas in the image are open pores, the light rim around the pore is the CNT and the remainder substrate is the aluminum oxide film.

A membrane module was then created using vacuum epoxy to mount the membrane on a stainless steel frit (Figure 2.2). To demonstrate that the vacuum epoxy could eliminate leaks around the edge of the membrane, an extensive carbon deposition process was used to seal the pores of an AAO membrane with a thick carbon film. Mass spectrometry results showed insignificant gas introduction around the blocked membrane, ensuring that ion currents obtained with the CNT membrane would be attributable to diffusion through the CNT pores (results not shown).
Mass spectrometry experiments

The selectivity of the CNT membrane was examined using two Airgas certified gas mixtures: Gas Mixture A was composed of 0.50% methane (CH$_4$), 1.50% argon (Ar), 0.20% carbon dioxide (CO$_2$), 10.00% oxygen (O$_2$) and 87.80% nitrogen (N$_2$). Gas Mixture B was composed of 1.01% CH$_4$, 2.04% Ar, 2.03% CO$_2$, 14.96% O$_2$, and 79.96% N$_2$. Mass spectrometry experiments were conducted using the system shown in Figure 2.3. The two-position stage rotary valve (Valco Instruments Co. Inc.) in the center of Figure 2.3 had four connections whereby the inlet of the MS (Inficon, Transpector 2.0 Gas Analyzer System) could be connected directly to the CNT membrane module or the CT (Restek, Hydrogard FS, 0.1mmID) without breaking vacuum. A fourth valve connection provided coupling to a diaphragm pump. This diaphragm pump was used to reduce the pressure within the CNT membrane module and the CT when these inlets were not in use. This precluded sudden increases in MS vacuum chamber pressure when the valve was switched to either inlet. Experiments were begun after a steady baseline signal was observed. Gases were analyzed by their mass-to-charge (m/z) ratio. The m/z signals of CH$_4$, N$_2$, O$_2$, Ar, and CO$_2$ were analyzed at 15, 28, 32, 40, and 44, respectively, using a
Faraday cup detector. Gas mixtures were delivered to either the CNT membrane or the CT through a series of Swagelok valves. For direct comparison of the CNT membrane and the CT introduction systems, inlet flow rates were matched. This created similar total pressures inside the MS ionization region and, thereby, similar ionization conditions. The gas exhaust of both the CNT membrane module and the CT setup was connected to a single exhaust line where flow rate and pressure could be observed and controlled. Experimental runs were performed at a steady flow rate over a range of pressures. Total pressure inside the ionization region was measured using the pressure-reading software of the Transpector, and ranged between $3.3 \times 10^{-3}$ and $6.7 \times 10^{-3}$ Pa.

Figure 2.3. Schematic drawing of the mass spectrometry experimental setup.

Results and discussion

CNT membrane

The two-step anodization process developed by Masuda and Satoh (1996) creates a uniform and monodisperse array of pores. The AAO membrane produced in this work was 70μm thick and had channels 50nm in diameter. The ethylene gas pyrolyzed into a graphitic structure on the alumina surface (Kyotani et al., 1996). CNTs within the
membrane had an average wall thickness of 5nm, and outside diameters and lengths identical to those of the AAO pores. Slow flow rates of ethylene at concentrations less than 3.5%, and lengthy periods of deposition at 750°C, produced uniform growth of CNT walls. In contrast, rapid carbon deposition thickens the surface film of carbon and obstructs CNT wall growth.

The AAO membrane has remarkable strength properties (Choi et al., 2007), and AAO membrane strength can be improved by controlling pore-cell dimension and crystalline structure through calcination (Arrowsmith et al., 1986; Mardilovich et al., 1995). In addition, support by a stainless steel frit in the membrane module reduced stress on the membrane and increased membrane tolerance to high pressure differentials between the sample and the mass spectrometer vacuum.

Raman spectrum of the CNT membrane

Raman spectra of carbon allotropes revealed the characteristic crystal structure of the nanotubes. The extent of sp² and sp³ bonding on CNTs produces a unique Raman fingerprint (Hiura et al., 1993). Figure 2.4a shows a Raman spectrum for the synthesized CNTs. All spectra showed first-order Raman bands at ~1350cm⁻¹ (D band) and ~1580cm⁻¹ (G band). The D band to G band intensity ratio (I_D/I_G) is linearly related to the degree of CNT crystallinity (Lee et al., 2002). The I_D/I_G value of 0.80 shown in Figure 2.4a indicates a low degree of crystallinity compared to highly oriented pyrolytic graphite. Raman spectra and transmission electron microscope (TEM, Hitachi 7100) imagery (Figure 2.4b) of our CNTs confirmed a turbostratic structure (Holden et al., 1994; Eswaramoorthi and Hwang, 2006; Welz et al., 2006).
Figure 2.4. Results from analysis of CNT membrane: (a) Raman spectrum of the CNT membrane and (b) TEM image of a CNT.

Mass spectrometry

Figure 2.5 shows MS ion currents produced by methane ($\Phi_{\text{CH}_4}$) using (a) capillary tube introduction and (b) CNT membrane introduction. Each horizontal section in Figure 2.5 was produced during steady state flow at constant pressure. The different section heights in Figure 2.5 were produced by successive pressure increases in the system. Observations of the ion currents ($\Phi_{G}$) produced by each gas ($G$) were obtained in triplicate.
Figure 2.5. Ion currents produced by CH$_4$ using (a) capillary tube and (b) CNT membrane introduction systems.

Gases that passed through the inlet systems were constantly evacuated by the pumps achieving a steady state condition and thus constant pressure inside the vacuum chamber. $\Phi_G$ is proportional to the partial pressure ($P_G$) of each gas in the MS vacuum chamber via the relationship $\Phi_G = S \cdot P_G$, where $S$ is the MS sensitivity factor. Then $\Phi_G$ is proportional to the quantity of a gas that passes through the inlet plane in a known amount of time. Therefore, throughput ($Q_G$) of the inlet system is proportional to $\Phi_G$ times a proportionality factor $k$, $Q_G = k \cdot \Phi_G$. The properties of each gas and each introduction system were examined by averaging the measured values of $\Phi_G$. The conductance ($C_G$) of each gas was measured using the following equation: $C_G = Q_G/\Delta P$ where $\Delta P$ is the total pressure gradient. $C_G$ was normalized by the mole fraction ($\chi$) of each gas via the relationship $C_\chi = C_G/\chi$. The normalized conductance ($C_\chi$) was then
plotted against the total pressure on the inlet system (Figure 2.6). The results in Figure 2.6 show distinct differences in the transmission characteristics of the two introduction systems and distinct differences for different gases.
Figure 2.6. Normalized conductance ($C_\chi$) against total pressure for Gas Mixtures A and B using capillary tube and CNT membrane introduction system.

$C_\chi$ values in the CNT introduction system uniformly decrease with increasing total pressure. The extent of this decrease is greatest for CH$_4$ and becomes progressively smaller in the order CH$_4$ > N$_2$ > O$_2$ > Ar > CO$_2$. The influence of total pressure on transmission of CO$_2$ in the CNT system is quite small. In contrast, $C_\chi$ in the CT system generally has an inverse order. Pressure effects are smallest for CH$_4$ and, for the remaining gases, the pressure dependent slopes are progressively less negative (N$_2$ to O$_2$) and then increasingly positive (Ar to CO$_2$).

Graph b of Figure 2.6 shows that N$_2$ from Gas Mixture B has a somewhat less negative slope than the corresponding N$_2$ signal of Gas Mixture A. This is due to the increased concentration of CO$_2$ in the gas mixture, thus contributing CO$^+$ fragment ions.
to the $m/z$ 28 ion current signal. Nonetheless, the CNT and CT conductance trend for $N_2$ is real as this gas has the highest concentration in both gas mixtures.

Figure 2.6 shows, for each component gas, that CNT membranes have relatively simple flux characteristics. Increasing total pressure decreases the conductance of each gas. This simple behavior is not observed in the CT introduction system, in which gas conductance both decreases ($N_2$) and increases ($O_2$, Ar and $CO_2$) with increasing pressure. In each plot the dependence of normalized conductance on pressure is the same for Gas Mixtures A and B. However, in each case, normalized conductances are slightly higher for Gas Mixture A. This offset arises because the ion currents ($\Phi_G$) used to calculate normalized conductance for each gas were not background corrected for contributions of residual gas in the vacuum housing. The experiments for each gas mixture were performed on different days and thus a slight difference in the partial pressure of each residual gas led to the observed offsets.

In Figure 2.7 CNT and CT gas transmission characteristics as a function of pressure are compared in the following form: $C_A(CNT)/C_A(CT)$. Figure 2.7 shows that, relative to the CT system, the CNT membrane is selectively transmissive to $CH_4$ over a range of conditions. In the case of $N_2$, the CNT and CT introduction systems are generally comparable ($C_A(CNT)/C_A(CT)\sim 1$) over a range of pressures. For the remaining gases, $O_2$, Ar and $CO_2$, the CNT membrane is less conductive than the CT system, and the magnitudes of the differences in transmission become larger with increasing pressure. The results shown in Figure 2.7 are in general agreement with previous comparisons of CNT gas transmission properties obtained through analysis of discrete samples (Holt et al., 2006).
Figure 2.7. CNT membrane and capillary tube conductance ratios over the total pressure.

The synthesized CNT membranes have a low degree of crystallinity (Figure 2.4b), a high surface area, and thereby a high propensity for adsorption (Kim et al., 2005). The adsorption of gases to the surfaces of nanotube-channels causes a temperature-dependent (Arora and Sandler, 2005; Skoulidas et al., 2006) and pressure-dependent interfacial resistance to flow. The pressure dependence of the resistance ($R$) to transport caused by interaction of gas with the CNT can be expressed in terms of gas flux ($J$) and the $\Delta P$ via the relationship $R_G = \Delta P/J_G$. Since gas flux ($J_G$) is directly proportional to the ion flux via the relationship $J_G = K_G \cdot \Phi_G$, the proportionality factor, $K_G$, is then eliminated by normalizing the flux data to the flux at one atmosphere total pressure. As such, $R_{G(\text{normalized})} = \Delta P/\Phi_G$. 
Figure 2.8 shows $R_G$ for the CNT membrane normalized to $R_G$ at 1 atmosphere total pressure. The data shown in Figure 2.8 were obtained over a wider range of pressures than the studies which compared CNT and CT transmission characteristics.

![Figure 2.8. CNT normalized transport resistance of each component gas with increasing pressure.](image)

Figure 2.8 shows that flux resistance in the CNT introduction system increases with increasing pressure in the order $\text{N}_2 > \text{CH}_4 > \text{O}_2 > \text{Ar} > \text{CO}_2$. This effect is consistent with gas interactions with CNT walls becoming increasingly important at higher pressures. The pore geometry of our CNTs is characterized by a Knudsen number greater than 1, where the flow regime is dominated by particle–surface collisions rather than particle–particle collisions. The adsorption of gas molecules into the CNT channel walls at increased pressures has been shown by others (Holt et al., 2006; Skoulidas et al., 2006; Kim et al., 2007; Noy et al., 2007) to lead to a deviation from pure Knudsen behavior and is hypothesized to be the cause of decreased conductance with increasing pressure.
Conclusions

The template method was used to fabricate CNT membranes. Carbon was deposited within the pores of an AAO membrane using the chemical vapor deposition process. The properties of a CNT/AAO membrane directly coupled to the inlet system of a mass spectrometer were compared to those of a conventional MS introduction system, a direct-feed capillary tube (CT). The CNT membrane exhibited fast mass-transport properties and enhanced transmission of CH$_4$. In the case of N$_2$, the transmission properties of the CNT and CT introduction systems were broadly comparable. From the work of other groups (Holt et al., 2006; Skoulidas et al., 2006; Kim et al., 2007; Noy et al., 2007), it is reasonable to conclude that interfacial resistance – interactions of gas molecules with CNT walls – caused the conductance of the CNT membrane to decrease with increasing pressure, progressively favoring the transmission of heavier molecules. However, since gas conductance through the CT introduction increases with pressure in the order CO$_2$ > Ar > O$_2$ > CH$_4$ > N$_2$, comparison of CNT vs. CT gas transmission always showed the following order (CNT/CT): CH$_4$ > N$_2$ > O$_2$ > Ar > CO$_2$.

This work demonstrates that CNT membranes can be viable introduction systems for mass spectrometers. Since CNT membranes can be internally (Kyotani et al., 2002) and externally (Lau et al., 2003) functionalized, CNTs have considerable promise for providing membrane systems with a wide range of transmission characteristics. Future work will focus on functionalized CNT membranes and their selective transmission properties for various analytes in solution.
Chapter 3

The influence of hydrostatic pressure on gas diffusion in polymer and nano-composite membranes: Application to membrane inlet mass spectrometry*

Abstract

A nano-composite membrane, created by coating a thin polysiloxane film to the surface of an anodic aluminum oxide (AAO) membrane, was directly coupled to the inlet system of a mass spectrometer. The gas-permeation properties of the polysiloxane nano-composite (PNC) membrane were compared to those of a conventional polydimethylsiloxane (PDMS) membrane over a range of hydrostatic pressures. Permeation of gases through the conventional PDMS membrane was reduced at high pressure by compression of the siloxane matrix. The PNC membrane had a much higher mechanical strength than the PDMS membrane, and exhibited little deviation in gas permeation at elevated hydrostatic pressure. Consistent with this difference in behavior, whereas the PDMS membrane exhibited hysteresis throughout cycles of increasing and decreasing hydrostatic pressure, hysteresis effects were substantially limited for the PNC membrane. The time required to attain steady-state diffusion through the PNC membrane was substantially reduced relative to the PDMS membrane.

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Introduction

Mass spectrometer (MS) inlet systems have included capillary tubes, a variety of orifice-types, inorganic and organic membranes, and composite membranes (Stassen et al., 1995; Cisper et al., 1997; Alberici et al., 1999; Dheandhanoo et al., 2000; Johnson et al., 2000; Keil et al., 2007; Hasegawa et al., 2008). The diversity of MS introduction systems allows customization for particular analytes and specific applications. Membrane introduction (or inlet) mass spectrometry (MIMS) has been used as a chemical sensing technique since 1963 for a variety of applications (Hoch and Kok, 1963). Since its development, MIMS technology has primarily been used to monitor dynamic chemical systems (Johnson et al., 2000). Membrane introduction is created by streaming a solution over the surface of a semi-permeable membrane. Analytes in the solution that are sufficiently volatile and membrane-soluble pass through the inlet membrane and desorb into the evacuated chamber of the MS. Gaseous analytes are then ionized by various means and analyzed over a predetermined mass range. MIMS analyses provide simplicity, speed and sensitivity, and are suitable for measurements of complex matrices (Bauer and Solyom, 1994).

MIMS is a valuable technique for analysis of volatile solution species, and is particularly useful for in situ or on-line applications. MIMS has been used to detect analytes at concentrations as low as parts-per-trillion (Bauer and Solyom, 1994). Due to the versatility of MIMS it has found diverse applications in a wide variety of scientific, governmental and commercial applications (Srinivasan et al., 1997; Johnson et al., 2000).

Polydimethylsiloxane (PDMS) is currently the most frequently selected membrane for MIMS analysis of volatile, relatively nonpolar analytes in aqueous
solutions. Commercially available PDMS membranes have thicknesses on the order of hundreds of micrometers (microns), making them easy to mount without mechanical tearing. Under normal laboratory conditions, membrane inlet systems are generally used at atmospheric pressure. However, in some applications, including in situ measurements of dissolved volatile components of seawater and monitoring of analytes in bioreactors (Futó and Degn, 1994; Bell et al., 2007), membrane inlets are exposed to variable hydrostatic pressure. In such cases, compression of the PDMS silicone matrix affects its permeability. For conventional micron-thickness PDMS membranes, hysteresis is encountered, resulting in inconsistent membrane permeability when membranes are compressed and decompressed (Futó and Degn, 1994; Bell et al., 2007).

Polymer films have been reported to exhibit higher hardness than their bulk polymer counterparts when film thickness decreases (Jiang et al., 2007; Liu et al., 2009; O’Connell and McKenna, 2009; Li et al., 2011). In addition, thin polymer films have been reported to exhibit little or no pressure-induced hysteresis (Thangawng et al., 2007). A Young’s modulus assessment of the influence of compression on polymer film permeation properties suggests that thin films may exhibit the necessary mechanical strength (if properly supported) to minimize film compression and reduce hysteresis effects.

To characterize the permeation properties of thin films with respect to variable hydrostatic pressure, we have fabricated and tested nano-composite membranes for MIMS analysis of dissolved gases in aqueous solutions. The nano-composite membrane was composed of an anodic aluminum oxide (AAO)-membrane substrate coated with a thin polysiloxane film. MS ion currents produced using polysiloxane nano-composite
(PNC) membranes and conventional PDMS membranes were used to assess the gas permeabilities of each type of membrane over a range of hydrostatic pressures. To the authors’ knowledge this manuscript provides the first observations of the effects of hydrostatic pressure on a PNC membrane that have been obtained using membrane introduction mass spectrometry.

**Experimental methods**

**Polysiloxane nano-composite (PNC) membrane**

A membrane module was created using vacuum epoxy to mount an AAO membrane (Whatman) on a stainless steel frit. Previous results demonstrated that the vacuum epoxy eliminates leaks around the edge of the oxide membrane (Miranda et al., 2009), ensuring that ion currents obtained with the nano-composite membrane would be attributable solely to diffusion through the PNC membrane. AAO membranes have remarkable strength (Arrowsmith et al., 1986; Choi et al., 2007). Further, support by a stainless steel frit in the membrane module can reduce stress on the PNC membrane and increase membrane tolerance to large pressure differences between sample solutions and the MS vacuum. The thin polysiloxane films were made using a room-temperature-vulcanizing silicon rubber (736 Heat Resistant Sealant, Dow Corning). A small amount of silicon rubber was mechanically spread over the exposed surface of the AAO membrane. Silicon rubber was then immediately applied to the AAO membrane a second time and was evenly spread using compressed air. Four membranes produced in this manner were mounted in series on a custom-made manifold membrane module (Figure 3.1a). The PDMS membrane module was purchased from MIMS Technology Inc. and
was modified to incorporate a stainless steel frit that provided mechanical support for the membrane. The assembly for support of the PDMS membrane is shown in Figure 3.1b.

Membrane characteristics

The AAO membranes used in this work had a uniform and monodispersed arrangement of pores (Figure 3.2a). The AAO membranes were 60μm thick and had channels (pores) with an average diameter of 200nm. The polysiloxane films were uniformly deposited across the upper surface of the AAO membranes and, on average, were 11μm thick (Figure 3.2b). Scanning electron microscope (SEM) analysis showed polymer material to depths of 400nm within the AAO pores (image not shown). The cumulative area of the four PNC membranes was ∼8mm². The PDMS membrane (Diversified Silicon Products, Inc.) was 304μm thick and had a total area of 18mm² (Figure 3.2c).

Mass spectrometry experiments

Mass spectrometry measurements were conducted using the system shown in Figure 3.3. The membrane module was connected directly to a quadrupole MS (Inficon, Transpector 2.0 Gas Analyzer System). The PNC and PDMS membrane modules were connected and disconnected from the MS via a Swagelok fitting. An HPLC pump (Shimadzu) transported experimental solutions from the sample reservoir (d, Figure 3.3) into the membrane module. The membrane modules had a built-in heater block for regulation of sample temperature at the membrane–water interface. A backpressure regulator (Swagelok) was used to control the hydrostatic pressure within the membrane module. Hydrostatic pressure was monitored with a digital pressure gauge (Cecomp
Electronics Inc.). Sample flow rates were monitored using a rotameter (Omega) at the exit end of the backpressure regulator. Exiting fluid was returned to the sample reservoir. Gas-diffusion experiments, described in the mass spectrometer response to gas permeation section, were performed using a peristaltic pump on the retentate side of the membrane modules.

Experimental solutions were created by equilibrating deionized (DI) water with a gas mixture (Airgas) in a volumetric flask. The gas mixture consisted of 1% methane (CH$_4$), 2% argon (Ar), 2% carbon dioxide (CO$_2$), 15% oxygen (O$_2$) and 80% nitrogen (N$_2$). Before entering the volumetric flask the gas stream was hydrated by bubbling through another flask that contained DI water. Solutions were equilibrated at atmospheric pressure within a constant temperature bath (28°C). The DI water was acidified to a pH $\approx$ 2 with concentrated HCl to eliminate HCO$_3^-$ and CO$_3^{2-}$ that would otherwise form in the presence of dissolved CO$_2$.

Measurements were made using a Faraday cup detector. The ion currents produced by diffusion of CH$_4$, N$_2$, O$_2$, Ar, and CO$_2$ through the PDMS and PNC membranes were analyzed at $m/z$ ratios of 15, 28, 32, 40, and 44. Background values were measured by stopping the flow of the sample and allowing the solution to degas through the inlet membrane. For direct comparison of the PNC and PDMS membrane introduction systems, overall inlet permeability rates were empirically matched, whereby the total pressure inside the vacuum chamber created similar ionization conditions. Experimental runs were performed at a steady flow rate over a range of hydrostatic pressures. The temperatures of the aqueous solutions that entered and passed through the membrane module were regulated at 30°C for the PNC and PDMS membrane. Total
pressure inside the ionization region was measured using the pressure-reading software of the Transpector mass analyzer, and ranged between $2.4 \times 10^{-4}$ and $6.9 \times 10^{-4}$ Pa.

Figure 3.1. (a) Diagram of the PNC membrane module. (b) Diagram of the PDMS membrane module.
Figure 3.2. a) Scanning electron microscope (SEM) (Hitachi S-3500N) image of the AAO membrane surface. b) Cross sectional SEM image of the PNC membrane. c) Cross sectional SEM image of the PDMS membrane.
Figure 3.3. Schematic drawing of the mass spectrometry experimental setup: (a) gas mixture cylinder, (b) gas hydrating bubbler, (c) sample reservoir, (d) constant temperature bath, (e) HPLC pump, (f) membrane module with built-in heater block, (g) vacuum chamber, (h) mass analyzer, (i) turbo pump, (j) roughing pump, (k) pressure gauge, (l) backpressure regulator, (m) rotameter and (n) computer for data acquisition and display.

Permeating gases achieve a steady state gas flow \( F_G \) into the MS vacuum system that is directly proportional to the concentration of a gas \([G]\) or, ideally (Bell et al., 2011), the fugacity \(f_G\) of each gas in solution. This relationship can be expressed as \( F_G = f_G \cdot b_G \), where the proportionality constant, \( b_G \), for each gas is dependent on the intrinsic properties of the membrane. The ion current \( \Phi_G \) measured by the MS is directly proportional to \([G]\) or \(f_G\) via the relationship \( \Phi_G = f_G \cdot c_G \), where \(c_G\) is a proportionality factor that is influenced by both membrane characteristics and the sensitivity of the MS itself. These relationships can be combined to yield the relationship between gas flow and ion currents, \( F_G = \Phi_G \cdot S_G \), where the sensitivity factor, \( S_G \), is equal to \( b_G/c_G \).

MS signal responses \( \Phi_G \) for transmitted gases, corresponding to their flows through the membranes, were determined at \( m/z \) ratios of 15, 28, 32, 40, and 44. The permeability properties of the PDMS and PNC membranes were observed at various hydrostatic pressures in the following manner. Observed ion currents produced by gas
flow through the membrane were allowed to attain steady state at a hydrostatic pressure of ≈ 1 bar. Once $\Phi_G$ signals were steady, the external hydrostatic pressure on the membrane module was increased, in steps, to approximately 41 bars for the PNC membrane and 14 bars for the PDMS membrane (the lower pressure limit for the PDMS membrane was caused by limitations of the membrane assembly). External hydrostatic pressure was then returned to 1 bar in a series of steps.

Results and discussion

Mass spectrometer response to gas permeation

Baseline or background levels were attained after stopping the pump and allowing the sample to degas through the membrane (Figure 3.4). Baseline (background) values were taken as observed steady state values in the absence of dissolved gases. After the background signals reached a steady state, the pump was restarted. Ion currents were then measured as the system approached and attained steady state.

Figure 3.4. Determination of baseline ion currents; 1) Flow of a gas equilibrated sample across the introduction membrane was stopped. 2) Sample in contact with the membrane then degassed through the membrane.
Baseline normalized ion currents ($I_{BN}$) were calculated (Equation 3.1) as a means of comparing the transmission properties for both types of membrane.

$$I_{BN} = \frac{\Phi_G - \Phi_{G(baseline)}}{\Phi_{G(baseline)}}$$  \hspace{1cm} (3.1)

where $\Phi_{G(baseline)}$ is a baseline current for a given gas, $G$, and $\Phi_G$ is the ion current for gas $G$ measured at any point in time. Figure 3.5 shows a comparison of background-normalized ion currents ($I_{BN}$) for each gas permeating through the PDMS and PNC membranes.
Figure 3.5 shows that gases permeating through the PNC membrane attain steady-state considerably sooner than is the case for permeation through the PDMS membrane. Diffusion properties for most non-porous membranes have been estimated by a time-lag technique (Ziegel et al., 1969; LaPack et al., 1990). Diffusion coefficients for the PDMS and PNC membranes are presented in Table 3.1 and were calculated using the following equation (Ziegel et al., 1969):

\[ D_G = \frac{L^2}{6 t_{1/2}} \]  

(3.2)

where \( D_G \) is the diffusion coefficient, \( L \) is the membrane thickness and \( t_{1/2} \) is the time required to achieve 50\% of the final steady state permeation. Diffusion coefficients for
the PNC membranes were calculated using the average thickness (11µm) of the thin polymer films. An apparent diffusion coefficient, “\(D_G\)”, for the PNC membrane was also calculated using the total thickness of the polymer film plus AAO membrane (11µm + 60µm).

**Table 3.1.** Diffusivity coefficients were determined using Equation (3.2): Units for diffusivity are cm²/s. Units for half-time (\(t_{1/2}\)) are seconds. “\(D_G\)” is the apparent or average diffusion coefficient for the combined polymer film plus AAO membrane. “\(D_G\)” was calculated using Equation (3.2) with \(L\) taken as the sum thickness of the polymer film and AAO membrane. The thickness of the PDMS membrane was 304µm.

<table>
<thead>
<tr>
<th>Gas</th>
<th>PNC membrane (t_{1/2}) (µs)</th>
<th>PNC membrane (D_G) (µm²/s)</th>
<th>PNC membrane “(D_G)” (µm²/s)</th>
<th>PDMS membrane (t_{1/2}) (µs)</th>
<th>PDMS membrane (D_G) (µm²/s)</th>
<th>(t_{1/2}) (PDMS)/(t_{1/2}) (PNC)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₄</td>
<td>2.52</td>
<td>8.00 x 10⁻⁸</td>
<td>3.33 x 10⁻⁸</td>
<td>20.65</td>
<td>7.49 x 10⁻⁶</td>
<td>8.19</td>
</tr>
<tr>
<td>N₂</td>
<td>1.47</td>
<td>1.36 x 10⁻⁷</td>
<td>5.70 x 10⁻⁸</td>
<td>15.6</td>
<td>9.92 x 10⁻⁶</td>
<td>10.61</td>
</tr>
<tr>
<td>O₂</td>
<td>1.42</td>
<td>1.41 x 10⁻⁷</td>
<td>5.88 x 10⁻⁸</td>
<td>13.92</td>
<td>1.11 x 10⁻⁵</td>
<td>9.80</td>
</tr>
<tr>
<td>Ar</td>
<td>0.76</td>
<td>2.64 x 10⁻⁷</td>
<td>1.10 x 10⁻⁵</td>
<td>14.1</td>
<td>1.09 x 10⁻⁵</td>
<td>18.55</td>
</tr>
<tr>
<td>CO₂</td>
<td>1.04</td>
<td>1.92 x 10⁻⁷</td>
<td>8.02 x 10⁻⁸</td>
<td>13.8</td>
<td>1.12 x 10⁻⁵</td>
<td>13.26</td>
</tr>
</tbody>
</table>

Table 3.1 shows that \(t_{1/2}\) (PDMS)/\(t_{1/2}\) (PNC) ranges from 8.2 to 18.6 for gases permeating through the PNC membranes. Thus, the time required to attain steady state diffusion is approximately an order of magnitude smaller than is the case for the PDMS membrane. This attribute can be very useful for *in situ* monitoring of dissolved volatile species in aqueous environments. Diffusion coefficients for the PNC membrane, measured using the thin polymer film thickness, are approximately two orders of magnitude lower than those measured for the PDMS membrane. In contrast, apparent diffusion coefficients, “\(D_G\)” calculated using overall (combined) membrane thickness are roughly comparable to those calculated for the PDMS membrane. Notably, in spite of the much greater thickness of the PDMS membrane, the observed ion currents obtained with this membrane are uniformly greater than those obtained with the PNC membrane.
The PNC membranes consist of a thin polymer film and a nano-porous support substrate. Transport through the thin polymer film can be described by Fick’s law (Johnson et al., 2000). Gas flow through the nano-pores of the substrate is described by Knudsen flow (Mulder, 1996), where gas molecules rarely collide with each other but frequently interact with the walls of the pore. As such, adsorption on pore walls (Paul and Kemp, 1973; Rosynek, 1975; Kruczek et al., 2005; Lee et al., 2005; Li et al., 2009) can strongly influence the flow of gas molecules through the AAO membrane. Although Knudsen flow is associated with no resistance to gas transport (Kruczek et al., 2005), sorption of gas molecules on the oxide substrate can explain the relatively lower diffusivity of gases through the PNC membrane.

When exposed to aqueous solutions, thin-film membranes exhibit high water permeation rates (Alberici et al., 1999). Decomposition of water produces O$_2$ species and increases the background of oxygen. This can in turn decrease the reliability of oxygen measurements (Ørsnes et al., 1997; Tortell, 2005).

The signal intensity of a gas is proportional to the rate of each gas permeating through the membrane. Both membrane systems produced similar pressures inside the vacuum chamber of the MS and, thereby, similar ionization conditions. An “enrichment factor” for each gas can be determined (at approximately identical ionization conditions) by measuring the ratio between the background-normalized ion currents ($I_{BN}$) observed for the PDMS membrane and the PNC membrane. The observed PDMS/ PNC enrichment ratios for each gas at steady state were: 1.28 for CH$_4$, 3.24 for N$_2$, 5.19 for O$_2$, 3.59 for Ar, 1.92 for CO$_2$, and 0.043 for H$_2$O ($m/z$ 18). Thus the PNC membrane had
enrichment ratios that were roughly a factor of three lower than the PDMS membrane (with the exception of H₂O).

Hydrostatic pressure curves

Hydrostatic pressure at the membrane module was increased in discrete steps. At each step the permeability \( P_G \) for each gas was quantified using the following relationship (Johnson et al., 2000):

\[
P_G = \frac{F_G L}{A P_p(G)} \tag{3.3}
\]

where \( F_G \) is the gas flow, \( A \) is the membrane surface area and \( P_p(G) \) is an upstream partial pressure of gas \( G \). Permeability characteristics obtained for each increasing hydrostatic pressure were calculated as \( P_G/P_G(1 \text{ bar}) \) and plotted (Figure 3.6) vs. hydrostatic pressure. Figure 3.6 clearly shows, for each gas, that the permeability of PNC membranes was much less affected by hydrostatic pressure than PDMS membrane. The PDMS membrane module obtained from MIMS Technology Inc. was only capable of tolerating hydrostatic pressures as high as 14 bars because higher water pressures caused water seepage through the seal that encased the PDMS membrane. The PNC membranes and custom-made supporting module were designed to tolerate hydrostatic pressures of 41 bars or more.
Figure 3.6. The $P_G/P_G(1 \text{ bar})$ ratios for each gas are plotted against hydrostatic pressure where (---) corresponds to PNC membranes and (—) refers to the PDMS membrane.

The difference in the permeability characteristics of the two types of membranes is attributable in part to their mechanical properties. The compression properties of materials can be expressed in terms of Young’s modulus (Ouseph, 1986). The stress-strain relationship for a material, expressed in terms of Young’s modulus ($E$), is given as:

$$E = \frac{F/A}{\Delta L/L} \quad (3.4)$$

where $F/A$ is the force per unit area applied to the material and $\Delta L/L$ is a fractional change in the linear dimension of the polymer material. Elastic polymer films experience a compression that is perpendicular to the support axis (e.g. a frit or oxide substrate). The
compressional change in thickness ($\Delta L$) of a polymer film is directly proportional to the applied hydrostatic pressure ($P_h$), and polymer membrane thickness ($L$), and inversely proportional to $E$: $\Delta L = P_h \cdot L / E$, where $P_h = F / A$. The enhanced molecular bonding properties of thin films result in mechanically stronger films and higher $E$ values (Jiang et al., 2007; Liu et al., 2009; O’Connell and McKenna, 2009; Li et al., 2011). The PDMS membrane is relatively elastic and therefore has a lower $E$ value than the thin polymer film (Thangawng et al., 2007). Compression of the PDMS membrane reduces free volume within the membrane, and therefore the rate of gas permeation through the polymer. Because of the inherent strength of the PNC matrix, the free volume within the thin polymer film was nearly constant. Consequently, as evidenced by the substantially constant $P_G / P_{G(1 \text{ bar})}$ ratios, gas permeabilities of the PNC membrane were nearly constant over a broad range of hydrostatic pressure.

PDMS membranes exhibit hysteresis when hydrostatic pressure is increased and decreased. Loops in $P_G / P_{G(1 \text{ bar})}$ vs. pressure plots caused by hysteresis results in variable $P_G$ at identical hydrostatic pressure. The PDMS membrane used in these experiments exhibited substantial hysteresis during hydrostatic pressure cycling (Figure 3.7). In contrast, hysteresis effects (Figure 3.7) for the PNC membranes were quite small. This attribute of the PNC membrane produced in this study should prove to be quite valuable in measurements of gas concentration profiles over the full range of ocean depth.
Figure 3.7. $P_G/P_{G(1 \text{ bar})}$ ratios for PDMS and PNC membranes are shown for CO$_2$ measurement, where (—) and (---) designates increasing and decreasing hydrostatic pressure. The substantial variations in $P_G/P_{G(1 \text{ bar})}$ shown for CO$_2$ measurements with the PDMS membrane were observed for all gases. For the PNC membrane, in contrast, all gases showed very little hysteresis.

Conclusions

Permeation of gases through PNC membranes was much less affected by hydrostatic pressure than permeation through a PDMS membrane. For a variety of gases, permeation through the PDMS membrane decreased by approximately 15% as pressure was increased to 14 bars. In contrast, gas permeation through the PNC membranes produced in this work changed by only few percent for hydrostatic pressures up to 41 bars. The relative insensitivity of PNC membranes to hydrostatic pressure greatly reduced the significance of hysteresis for PNC membranes relative to the PDMS.

The response times of gases permeating PNC membranes were substantially reduced relative to the PDMS membrane. The time required to attain 50% of steady state permeation through PNC membranes was approximately an order of magnitude smaller than that required using a PDMS membrane. The PDMS membrane produced high analyte-water permeation ratios relative to PNC membranes.

Nano-composite membranes are viable inlet devices for the detection and quantification of volatile analytes in solution. Thin polymer films can be used to
minimize compression effects and provide improved linearity of MIMS responses to analyte concentrations over a range of hydrostatic pressures. This feature could be very important for use of MIMS over the wide range of depths and pressures in seawater.

† I would like to take an opportunity to address some discrepancies published in Miranda et al. (2011). The term flux was misused throughout the text and it should instead be substituted by the term flow. Such correction was made in this dissertation.
Chapter 4

Calibration of membrane inlet mass spectrometric measurements of dissolved gases:
Differences in the responses of polymer and nano-composite membranes to variations in ionic strength

Abstract

This work examines the transmission behavior of aqueous dissolved methane, nitrogen, argon and carbon dioxide through two types of membranes: a polysiloxane nano-composite (PNC) membrane and a conventional polydimethylsiloxane (PDMS) membrane. Transmission properties at 30°C were examined by membrane introduction mass spectrometry (MIMS) at nearly constant gas partial pressures in NaCl solutions over a range of ionic strength (0 to 1 molal). Gas flow rates were examined as a function of dissolved gas concentrations using the Setschenow equation. Although MIMS measurements with PDMS and PNC membranes produced signal responses that were directly proportional to aqueous dissolved gas concentrations, the proportionalities varied with ionic strength and were distinctly different for the two types of membranes. With the exception of carbon dioxide, the PNC membrane had membrane salting coefficients quite similar to Setschenow coefficients reported for gases in aqueous solution. In contrast, the PDMS membrane had membrane salting coefficients that were generally smaller than the corresponding Setschenow gas coefficient for each gas. Differences between Setschenow coefficients and membrane salting coefficients lead to MIMS calibrations (gas-flow vs. gas-concentration proportionalities) that vary with ionic strength. Accordingly, gas-flow
vs. gas-concentration relationships for MIMS measurements with PDMS membranes are significantly dependent on ionic strength. In contrast, for PNC membranes, flow vs. concentration relationships are independent (argon, methane, nitrogen) or weakly dependent (carbon dioxide) on ionic strength. Comparisons of gas Setschenow and membrane salting coefficients can be used to quantitatively describe the dependence of membrane gas-flow on gas-concentrations and ionic strength for both PDMS and PNC membranes.

**Introduction**

Measurement of gas concentrations in aqueous solution is of great importance in a wide variety of scientific, regulatory and commercial applications (Bohátka et al., 1993; Kana et al., 1994; Hamme and Emerson, 2004; Osborn et al., 2011; Flynn et al., 2012). Detection and quantification of dissolved gases often involves the use of membranes in conjunction with colorimetric pH indicator techniques, polarography or mass spectrometry (Wang and Li, 1989; Kana et al., 1994; DeGrandpre et al., 1995; Hamme and Emerson, 2004). Colorimetric and polarographic techniques generally allow measurement of a single gas in solution (Wang and Li, 1989; DeGrandpre et al., 1995), while mass spectrometry facilitates measurements of multiple gaseous components simultaneously (Kana et al., 1994; Hamme and Emerson, 2004). As a second important distinction between mass spectrometric measurements of gas concentrations and other membrane-based techniques, membrane introduction mass spectrometry (MIMS) involves measurement of flow rates (Hoch and Kok, 1963), while other procedures are based on chemical equilibrations. As a result, MIMS can not only provide comprehensive
measurements of a variety of gases in solution but can also make measurements on much shorter time scales than are required by equilibrium techniques.

The responses of MIMS systems are strongly regulated by membrane permeability properties. The permeability of polydimethylsiloxane (PDMS), a frequently preferred membrane material, is strongly influenced by gas partitioning between the solution phase and the vapor phase through a process known as pervaporation. This process can be used to describe transmission properties of dissolved gases in solution through the membrane interface into the ion detector. Ordinarily MIMS measurements are performed at atmospheric pressure, but the substantial utility of this technique has also led to its *in situ* employment at hydrostatic pressures greater than one atmosphere (Short et al., 1999; Short et al., 2001; Camilli et al., 2009; Camilli and Duryea, 2009; Camilli et al., 2010). At higher hydrostatic pressures, conventional PDMS membranes have been reported to demonstrate variable permeability properties (Futó and Degn, 1994; Bell et al., 2007).

Miranda et al. (2011) recently described the gas transmission characteristics of polysiloxane nano-composite (PNC) membranes that were coupled to the inlet system of a mass spectrometer. The gas transmission properties of PNC membranes were compared to those of a conventional PDMS membrane over a range of hydrostatic pressures. The PDMS membrane exhibited compression of its siloxane matrix when hydrostatic pressure was increased, and exhibited hysteresis when hydrostatic pressure was subsequently decreased. Thus the permeability properties of the PDMS membrane are influenced by hydrostatic pressure in a manner that presents substantial challenges to quantitative calibration. In contrast, the transmission properties of the PNC membranes constructed
by Miranda et al. (2011) demonstrated little if any response to changes in hydrostatic pressure.

Having previously shown that PNC membranes are much less susceptible to hydrostatic pressure-induced variation in permeation properties than PDMS membranes, this work examines the comparative gas-transmission properties of PNC membranes and PDMS membranes over an environmentally-relevant range of ionic strengths. Using gas mixtures with constant compositions, gas concentrations in equilibrated solutions were varied (i.e. decreased) with increasing NaCl concentration (ionic strength) while gas partial pressures were essentially constant. This investigation shows that variations in ionic strength exert much smaller influences on the permeation of gases through PNC membranes than conventional PDMS membranes. Additionally, it is shown that the influence on ionic strength on MIMS calibrations (gas-flow vs. gas-concentration) can be well-described in terms of differences between membrane salting coefficients and Setschenow coefficients for both PDMS and PNC membranes.

Theory

Gas solubility theory

The concentration of gas \( C_{(aq)} \) in an aqueous solution when a gas phase and solution phase are in equilibrium can be described using Henry’s Law (Pilson, 1998):

\[
C_{(aq)} = \beta \cdot P_p \quad (4.1)
\]

where \( \beta \) is the solubility constant for a gas in an aqueous solution and \( P_p \) is the partial pressure of a gas in equilibrium with the solution. Gas concentrations in solution can be expressed in terms of gas activity coefficients \( \gamma_C \) via the following relationship: \( C_{(aq)} = \)
\( a_G/\gamma_G \), where \( a_G \) is the activity of a gas in solution. The concentrations (or solubility) of gases in aqueous solution are decreased by addition of salts (i.e. the salting-out effect) as \( \gamma_G \) increases with salt content. The relevant measure of comparative concentrations of a particular gas in solutions of variable salt content is the ionic strength, \( I \) (Stumm and Morgan, 1996). At constant temperature and partial pressure, the comparative solubility of a gas over a range of ionic strength can be well described using the Setschenow equation (Millero and Schreiber, 1982; Millero, 2000):

\[
\ln(\beta^\circ/\beta_s) = \ln(\gamma_{G,s}) = k_s I \quad (4.2)
\]

where \( \beta^\circ \) and \( \beta_s \) are solubility coefficients for a gas in pure water \( (I = 0) \) and a solution with ionic strength \( (I) \), \( \gamma_{G,s} \) is the activity coefficient of a gas in a solution with ionic strength and \( k_s \) is the salting-out coefficient for a given gas.

**Membrane introduction mass spectrometry (MIMS) theory**

Membranes (e.g. PDMS and PNC) act as interfaces between sample solutions and the vacuum of a mass spectrometer. Transport through the membrane (as a pervaporation process) is induced by maintaining the vapor pressure on the permeant side at a lower vapor pressure than in the feed liquid. The pervaporation process involves a sequence of three steps: (i) selective sorption of analyte(s) into the membrane on the feed side, (ii) diffusion of the analyte(s) through the membrane, and (iii) desorption of the analyte(s) into a vapor phase on the permeate side of the membrane (Mulder, 1996). The solution-diffusion model assumes that, at the solution/membrane interface the activity of an analyte in the feed liquid is equal to the activity of the analyte in the membrane (Wijmans and Baker, 1995). The activity \( (a_m) \) of an analyte in the membrane on the feed (solution)
side in the membrane is given as: \( a_m = \gamma_m \cdot C_m \), where \( \gamma_m \) and \( C_m \) are the activity coefficient and the concentration of an analyte in the membrane at the solution/membrane interface. Under steady-state conditions, the ion current (\( \Phi \)) measured by the mass spectrometer is directly proportional to the flow (\( F \)) of an analyte across a membrane and can be described by the following equations (Boddeker and Bengtson, 1990; LaPack et al., 1990; Freger et al., 1997; Srinivasan et al., 1997; Cocchini et al., 1999; Johnson et al., 2000; Lipnizki et al., 2004; Kujawski et al., 2007; Garcia et al., 2009a,b; Marszalek and Kaminski, 2012):

\[
F = \Phi \cdot \omega \quad (4.3a)
\]

\[
F = A \cdot D \left( \frac{a_m}{L} \right) \quad (4.3b)
\]

where \( \omega \) is a proportionality constant, \( A \) is the membrane surface area, \( D \) is the analyte diffusion coefficient, and \( L \) is the membrane thickness.

**Experimental procedures**

The PDMS membrane used in this work was of conventional design, with surface area and membrane thickness comparable to those of PDMS membranes reported by other research groups (Ørsnes et al., 1997; Srinivasan et al., 1997; Johnson et al., 2000; Tortell, 2005). In contrast, the PNC membranes used in this work were fabricated using novel techniques.

Synthesis and characterization of polysiloxane nano-composite (PNC) membranes are described in Miranda et al. (2011). An overview of the process is given as follows: An anodic aluminum oxide (AAO) membrane was mounted on a stainless steel frit and secured on a membrane module with vacuum epoxy. A thin polysiloxane film was
mechanically coated on the surface of the AAO using a room-temperature-vulcanizing silicon rubber. Two membranes were created in this manner and mounted in series on a custom-made manifold membrane module. The AAO membranes were 60µm thick and had pores with an average diameter of 200nm. Polysiloxane films were uniformly deposited across the upper surface of the AAO membranes and, on average, were 11µm thick. The cumulative area of the PNC membranes was ~ 6.2mm².

The PDMS membrane (Specialty Manufacturing Inc.) used in this work was 127µm thick and had a total area of 2.8cm². The PDMS membrane was mounted on a custom-made membrane module (Figure 4.1).

**Figure 4.1.** The above image shows the diagram of the PDMS membrane module. For comparison, the diagram of the PNC membrane module can be seen in Miranda et al. (2011).

Mass spectrometry measurements were conducted using an experimental configuration similar to that described in Miranda et al. (2011). The PNC and PDMS membrane modules were connected individually to a quadrupole mass spectrometer (Inficon, Transpector 2.0 Gas Analyzer System) via a Swagelok fitting. Solutions were
pumped through the membrane modules using a peristaltic pump. The peristaltic pump was placed downstream of the membrane module. MIMS measurements were made using a Faraday cup detector.

Four solutions, each in a 500 ml volumetric flask, were placed in a constant temperature water bath (30°C). One set of solutions, deionized (DI) water and a sodium chloride solution, were simultaneously equilibrated at atmospheric pressure with a gas mixture (Airgas certified) while the other set (of similar solution composition) were simultaneously equilibrated at atmospheric pressure with a baseline gas. Measurements were obtained using gas mixtures containing methane (CH$_4$), argon (Ar), carbon dioxide (CO$_2$), and nitrogen (N$_2$). Gas mixtures had variable CH$_4$, Ar and CO$_2$ concentrations in the parts-per-million, parts-per-thousand and parts-per-hundred levels with N$_2$ as the balance gas. Baseline values for CH$_4$, Ar and CO$_2$ measurements where obtained using an ultrapure N$_2$ gas (Airgas certified) bubbled through each experimental solution. The baseline gas had CH$_4$, Ar and CO$_2$ at lower parts-per-billion levels, well below the detection limits of our mass spectrometer. In the case of N$_2$, baselines were measured prior to each experimental run by degassing the solution at sample flow rate equal to zero (Miranda et al., 2011). Sufficient time was allowed for the sample to be thoroughly degased at the membrane interface. This baseline procedure for N$_2$ gas was performed solely using degassed solutions rather than solutions that had been equilibrated with gases. Gas streams were hydrated by bubbling through a flask that contained DI water before entering the volumetric flasks that contained the DI and NaCl solutions. DI and NaCl solutions were acidified to a pH ≈ 2 with concentrated HCl to prevent the formation of HCO$_3^-$ and CO$_3^{2-}$ that would otherwise occur in the presence of dissolved CO$_2$. 
The ion currents ($\Phi$) produced by diffusion of CH$_4$, N$_2$, Ar, and CO$_2$ through the PDMS and PNC membranes were analyzed at $m/z$ ratios of 15, 28, 40, and 44, respectively. Experimental runs were performed at steady rates of flow ($F$). Gas flow measurements were obtained when mass spectrometer signals ($\Phi'$) attained steady-state. Measurements were averaged for 100 scans and then baseline-subtracted to produce an ion current: $\Phi = \Phi' - \Phi'_{(\text{baseline})}$, where $\Phi'$ is the ion current obtained using a solution equilibrated with the gas mixture at a specific ionic strength and $\Phi'_{(\text{baseline})}$ is the ion current of the same gas observed using a solution equilibrated with the baseline gas at the same ionic strength (i.e. for CH$_4$, Ar, and CO$_2$) or the degassed solution (i.e. for N$_2$). For each measured $\Phi_3$ value obtained at ionic strength $I$, (0.1, 0.5 and 1.0 molal) a baseline-corrected ion current ($\Phi^\circ$) at $I = 0$ was also obtained using DI water. This procedure was repeated using NaCl solutions and DI equilibrated with various gas mixtures.

**Results and discussion**

To directly examine the dependence of gas flow on ionic strength, the flow ($F^\circ$) of each gas dissolved in pure water ($I = 0$) was ratioed to the flow of a gas ($F_3$) observed at each ionic strength ($I$). Plots of $\ln(F^\circ/F_3)$ vs. $I$ (where $F^\circ/F_3 = \Phi^\circ/\Phi_3$) for the PDMS and PNC membranes are shown in Figure 4.2.
Figure 4.2. Gas flow rates through PDMS and PNC membranes are plotted as $\ln\left(\frac{F^0}{F_s}\right)$ vs. $I$. Percent mole fractions (i.e. mole fraction × 100) for each gas in the gas mixtures are shown at the upper right of each figure. A best fit line for the data obtained at each percent gas concentration for the different ionic strengths is shown as (---).
The plots of $\ln(F^o/F_s)$ vs. $I$, shown in Figure 4.2, are highly linear and are consistent with expected gas solubility behavior based on the Setschenow equation (i.e. Equation (4.2)). Figure 4.2 demonstrates that the influence of ionic strength on gas flow for both types of membranes is well described by the following equation:

$$\ln\left(\frac{F^o}{F_s}\right) = k_m I \quad (4.4)$$

where $k_m$ can be termed a membrane salting coefficient (Bell et al., 2011). Figure 4.2 shows that the membrane salting coefficients of the PDMS membrane are different than those of the PNC membranes. The PDMS and PNC membrane salting coefficients ($k_m$) obtained using Equation (4.4) are directly compared in Table 4.1. Setschenow salting-out coefficients ($k_s$) for sea water are also presented in Table 4.1. The selected gas salting-out coefficients in Table 4.1 were chosen based on the high degree of precision in the selected works (Weiss, 1970; Weiss, 1974; Yamamoto et al., 1976; Wiesenbug and Guinasso, 1979). For the PNC membranes, Table 4.1 shows that, for CH$_4$, N$_2$ and Ar, $k_m$ and $k_s$ are essentially identical. In contrast, the $k_m$ value obtained for CO$_2$ with the PNC membranes is somewhat smaller than the $k_s$ value for sea water. For the PDMS membrane, $k_m$ values are consistently smaller than gas salting-out coefficients ($k_s$).
Table 4.1. Membrane salting coefficients for gases permeating through PDMS and PNC membranes at 30°C and salting-out coefficients for gases in sea water.

<table>
<thead>
<tr>
<th>Gas</th>
<th>PNC membranes</th>
<th>PDMS membrane</th>
<th>Salting-out Coefficients</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$k_m$</td>
<td>$k_m$</td>
<td>$k_s$</td>
</tr>
<tr>
<td>CH$_4$</td>
<td>0.331 ± 0.011</td>
<td>0.319 ± 0.019</td>
<td>0.331 ± 0.001$^a$</td>
</tr>
<tr>
<td>N$_2$</td>
<td>0.335 ± 0.005</td>
<td>0.289 ± 0.007</td>
<td>0.334 ± 0.001$^b$</td>
</tr>
<tr>
<td>Ar</td>
<td>0.313 ± 0.009</td>
<td>0.284 ± 0.008</td>
<td>0.310 ± 0.001$^b$</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>0.218 ± 0.006</td>
<td>0.173 ± 0.008</td>
<td>0.247 ± 0.001$^c$</td>
</tr>
</tbody>
</table>

Values of $k_m$ were calculated using Equation (4.4). Salting-out coefficients ($k_s$, kg-H$_2$O mol$^{-1}$) were calculated using Equation (4.2) and solubility coefficients reported previously at 30°C within a 0 to 15 range of salinity from the following data sources: a) The CH$_4$ coefficient was derived using solubility coefficients presented by Wiesenburg and Guinasso (1979). b) N$_2$ and Ar coefficients were derived from solubility coefficients presented by Weiss (1970). c) The CO$_2$ coefficient was derived using the solubility coefficients presented by Weiss (1974). Na$^+$ and Cl$^-$ ions are the two major ion components of sea water and, although salting-out coefficients are somewhat influenced by medium composition, the salting-out coefficients of sea water shown above can be used as reasonable representation of salting-out coefficients for NaCl solutions.

Additional constants used to correct solubility coefficients to mole per kg-H$_2$O units were found in the CRC press (Physical Constants of Inorganic Compounds Section). The ionic strength of sea water can be simulated with NaCl solutions and related to salinity using the following equation (Dickson and Goyet, 1994): $I = m\text{NaCl} = 19.924 \times S\%o / (1000 – 1.005 S\%o)$, where $m\text{NaCl}$ is the molality of the NaCl solution and $S\%o$ is the salinity in parts per thousand.

Gas flow can be related to gas concentrations and ionic strength by combining Equations (4.1), (4.2) and (4.4). At constant temperature and partial pressure, Equations (4.1) and (4.2) can be combined and written as follows:

$$\ln(C_{\text{aq}}^\circ/C_{\text{aq},s}) = k_s I \quad (4.5)$$

where $C_{\text{aq}}^\circ$ and $C_{\text{aq},s}$ are the concentrations of a gas dissolved in pure water and a solution with ionic strength. Equations (4.4) and (4.5) can then be combined and written as

$$\ln(F^\circ/F_s) - \ln(C_{\text{aq}}^\circ/C_{\text{aq},s}) = (k_m - k_s) I \quad (4.6)$$
Rearrangement of Equation (4.6) produces the following two equations:

\[ F_s = C_{(aq),s} \left( \frac{F^o}{C^o_{(aq)}} \right) e^{\left( k_s - k_m \right) I} \]  
\[ (4.7a) \]

\[ C_{(aq),s} = F_s \left( \frac{C^o_{(aq)}}{F^o} \right) e^{\left( k_m - k_s \right) I} \]  
\[ (4.7b) \]

The exponential terms in Equation (4.7), \( e^{\left( k_s - k_m \right) I} \) and \( e^{\left( k_m - k_s \right) I} \), demonstrate that relationships between gas-flow and gas-concentration are explicitly influenced by ionic strength unless Setschenow coefficients and membrane salting coefficients are identical. Examination of Table 4.1 shows that \( k_s \geq k_m \). As a result Equation (4.7a) shows that, for measurements made using PDMS membranes, \( F_s/C_{(aq),s} \) ratios (i.e. slopes of ion currents vs. gas-concentration) will consistently increase with ionic strength. In contrast, for measurements made using PNC membranes, \( F_s/C_{(aq),s} \) ratios are independent of ionic strength for methane, nitrogen and argon, but not carbon dioxide. Table 4.2 shows flow vs. concentration results at zero ionic strength normalized to the surface area of each membrane. For the PNC membrane, the zero ionic strength results shown in the table will not vary with ionic strength except in the case of CO\(_2\). The results in Table 4.2 also show that \( F_s \) vs. \( C_{(aq),s} \) for the PDMS membrane are uniformly higher than the corresponding slopes for the PNC membrane. Since \( F_s \) vs. \( C_{(aq),s} \) slopes for the PDMS membranes increase with ionic strength, the transmission properties of the two membranes will increasingly diverge with increasing ionic strength.
Table 4.2. Observed $F^\circ/C^\circ_{(aq)}$ slopes for CH$_4$, N$_2$, Ar and CO$_2$ normalized to the membrane surface area of the PDMS and PNC membranes where $(F^\circ/C^\circ_{(aq)})/A$. The total surface area of the PNC membranes is 6.2 mm$^2$ and 280 mm$^2$ for the PDMS membrane. (units: $C_{(aq)} = \mu$mol kg-H$_2$O$^{-1}$, $A = \text{mm}^2$, gas-flow rates were observed as a function of ion current, where $\Phi = \text{amps}$)

<table>
<thead>
<tr>
<th>Gas</th>
<th>PNC membrane $x10^{-15}$</th>
<th>PDMS membrane $x10^{-15}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_4$</td>
<td>1.542</td>
<td>1.732</td>
</tr>
<tr>
<td>N$_2$</td>
<td>1.777</td>
<td>1.837</td>
</tr>
<tr>
<td>Ar</td>
<td>1.225</td>
<td>2.024</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>0.302</td>
<td>0.438</td>
</tr>
</tbody>
</table>

Table 4.3 shows values of $e^{(k_s - k_m)I}$ for both membranes at each of the ionic strengths in this investigation. The results for CO$_2$ in the table show that $F_s$ vs. $C_{(aq),s}$ calibration slopes for PDMS membranes will be 7.6% higher at ionic strength 1 than at ionic strength zero. A smaller effect (~2.9%) for CO$_2$ is observed for the PNC membrane. The results shown in Table 4.3 indicate that gas-flow vs. gas-concentration relationships should be interpreted using Equation (4.7) when measurements are made over a range of ionic strengths. This observation will become particularly important when MIMS systems are used in estuaries over a range of salinities and ionic strengths.

Table 4.3. The exponential term in Equation (4.7a) (i.e. $e^{(k_s - k_m)I}$) is shown explicitly at several ionic strengths.

<table>
<thead>
<tr>
<th>$I$</th>
<th>PNC membrane</th>
<th>PDMS membrane</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CH$_4$</td>
<td>N$_2$</td>
</tr>
<tr>
<td>0.1m NaCl</td>
<td>1.000</td>
<td>0.999</td>
</tr>
<tr>
<td>0.5m NaCl</td>
<td>1.000</td>
<td>0.999</td>
</tr>
<tr>
<td>1.0m NaCl</td>
<td>1.000</td>
<td>0.999</td>
</tr>
</tbody>
</table>

In addition to our investigation of comparative gas permeation for the two types of membranes, our work demonstrated that PDMS and PNC membranes exhibited
different water permeation characteristics. Figure 4.3 shows, for each membrane, water flow plotted as $F/F^\circ$ vs ionic strength where $F^\circ$ represents water flow at zero ionic strength. The influence of ionic strength on water flow is different for the two types of membranes. Furthermore, it was observed that the overall water flow for the two membranes, normalized to membrane surface area, is quite different. For the PNC membrane the area-normalized water flow at $I = 0$ was $1.285 \times 10^{-11}$ amps mm$^{-2}$ whereas, for the PDMS membrane the area-normalized water flow at $I = 0$ was $0.803 \times 10^{-11}$ amps mm$^{-2}$ (water-flow rates were expressed in terms of ion current, where $\Phi = \text{amps}$).

![Figure 4.3](image)

**Figure 4.3.** Water flow through the PDMS and PNC membranes over a 0 to 1 molal range of ionic strength. The flow of water was plotted as $F/F^\circ$ vs. $I$. The transmission of water through the PDMS and PNC membranes was measured by the mass spectrometer at $m/z$ 17.

**Conclusions**

The close correspondence between gas-flow rates and gas-concentrations that was obtained with the PNC membrane over a range of ionic strength indicates that calibration and use of MIMS with PNC membranes is inherently simpler than is the case for measurements using PDMS membranes. This makes PNC membranes inherently
desirable for applications of MIMS in environments with large salinity gradients and variable hydrostatic pressures.

Our investigation develops a simple quantitative procedure for calibrating MIMS devices for use in salinity or ionic strength gradients. Our observations demonstrate that, toward the objective of MIMS measurements of gas concentrations in estuaries, MIMS calibrations should be performed at a minimum of two ionic strengths. In the simplest case, observations of ion current and gas concentration ratios at ionic strengths equal to 0 and 1 molal will allow direct calculation of the \( k_s - k_m \) term in Equation (4.6). This difference between \( k_s \) and \( k_m \) provides (via Equation (4.7)) a quantitative account of the influence of ionic strength on the responses of MIMS systems in salinity gradients.

Our results are consistent with the conclusion that MIMS gas-flow vs. gas-concentration relationships are dependent on ionic strength because the activity of water in membranes is dependent on the ionic strength of the solution being sampled. Variations of water activity in PDMS membranes significantly influence pervaporation characteristics of gases through the membrane. For the PNC membrane this influence was significant only for \( \text{CO}_2 \).

As the activity of water decreases with increasing ionic strength (Figure 4.3) the rates of water-flow through the PDMS and PNC membranes substantially decrease. As such, the simple relationships obtained between water flow and ionic strength (Figure 4.3) for the two types of membranes suggest that measurements of water flow rates can be used as a means of estimating the ionic strengths that are required in the Equation (4.6) and Equation (4.7) concentration vs. flow calibrations.
During our work it was observed that baseline values for CH$_4$, Ar and CO$_2$ were higher in DI water and progressively lower with increasing ionic strength (results not shown). This observation indicates that baseline values for MIMS calibrations are dependent on salinity and ionic strength. For MIMS measurements in salinity gradients appropriate calibration procedures should therefore include appropriate measurements of baseline values (i.e. using ultrapure N$_2$ gas) over a range of ionic strength.

A supplementary information (SI) section associated with this paper provides an interpretation of Equation (4.6) in terms of the physical-chemical characteristics of membranes. The SI section examines how the results presented in Table 4.3 are directly related to membrane sorption properties.

**Supplementary information (SI)**

MIMS responses are strongly regulated by the permeability properties of membranes. This section will describe how the behavior summarized by Equation (4.6) is consistent with previous descriptions of membrane phenomena. In particular, it will be shown that the results presented in Table 4.3 are directly related to sorption coefficient ratios. The membrane sorption coefficient or selectivity factor ($\alpha$) has been previously defined (Hung, 1991; Wijmans and Baker, 1995) as follows:

$$\alpha = \frac{\gamma_G}{\gamma_m} = \frac{C_m}{C_{(aq)}} \quad (4.8)$$

where $\gamma_m$ and $\gamma_G$ are the activity coefficients of an analyte in the membrane and the aqueous solution, and $C_{(aq)}$ and $C_m$ are the concentrations of the analyte in solution and in the membrane at the solution/membrane interface.

The Setschenow equation was used in this work to describe variations in the aqueous concentrations of gases with varying ionic strength (Equation (4.2)), and also the
influence of ionic strength on gas flow through the PDMS and PNC membranes (Equation (4.4)). In order to reconcile Equation (4.2) and Equation (4.4) with conventional membrane phenomena, these two equations can be described in terms of gas concentrations and their associated activity coefficients. As evident by Equation (4.2) and Equation (4.5), the Setschenow equation can be written in the following form:

$$\ln\left(\frac{C^{\circ}(aq)}{C_{(aq),s}}\right) = \ln(\gamma_{G,s}) \quad (4.9)$$

The solution-diffusion model assumes that the activity of an analyte inside the membrane at the solution/membrane interface is equal to the activity of the same analyte in solution (Wijmans and Baker, 1995). At constant temperature and gas partial pressure, the activity of a gas in pure water and in salt solution are identical (Randall and Failey, 1927a,b; Long and McDevit, 1952). Therefore, at constant temperature and partial pressure the gas activity inside the membrane at the solution/membrane interface does not vary with ionic strength,

$$a^\circ_m = a_{m,s} \quad (4.10)$$

where $a^\circ_m$ and $a_{m,s}$ are the respective activities of an analyte (e.g. gas) inside the membrane at the solution/membrane interface when exposed to pure water and a solution with non-zero ionic strength. Substituting the relationship $a_m = \gamma_m \cdot C_m$ in Equation (4.10) results in the following equation:

$$\ln\left(\frac{C^{\circ}_m}{C_{m,s}}\right) = \ln(\gamma_{m,s}) \quad (4.11)$$

where $C^{\circ}_m$ and $C_{m,s}$ are the respective concentrations of a gas in the membrane at the solution/membrane interface when the membrane is exposed to pure water and a solution with non-zero ionic strength. The coefficient $\gamma_{m,s}$ is the activity coefficient of the analyte.
in a membrane when exposed to the solution with ionic strength, \( I \). Equation (4.4) and Equation (4.11) can then be combined to produce the following equation:

\[
\ln\left(\frac{F^0}{F_s}\right) = \ln\left(\frac{C_m^0}{C_{m,s}}\right) \quad (4.12)
\]

Accordingly, the following relationship can also be established:

\[
k_m I = \ln(\gamma_{m,s}) \quad (4.13)
\]

The sorption coefficient \( (\alpha_s) \) for a gas in a solution with ionic strength, \( I \), can be ratioed to the sorption coefficient for a gas in pure water \( (\alpha^0) \) to produce the following relationship:

\[
\ln\left(\frac{\alpha_s}{\alpha^0}\right) = \ln\left(\frac{\gamma_{G,s}}{\gamma_{m,s}}\right) \quad (4.14)
\]

As a result, the sorption coefficient ratio, \( \alpha_s/\alpha^0 \), can be expressed in the following form:

\[
\frac{\alpha_s}{\alpha^0} = \left(\frac{C_{m,s}}{C_m^0}\right) / \left(\frac{C_{(aq),s}}{C_{(aq)}^0}\right) = e^{(k_s - k_m)I} \quad (4.15)
\]

Equation (4.15) shows that the ratio between membrane sorption coefficients of membranes in salt solution and pure water, \( \alpha_s/\alpha^0 \), is directly related to the Table 4.3 values for gases permeating through the PDMS and PNC membranes.
Chapter 5

Use of novel nano-composite membranes as introduction systems for in situ underwater mass spectrometry measurements of dissolved gases at sea

The nano-composite membranes presented in this dissertation were made in part to address hydrostatic pressure effects observed by conventional PDMS membranes coupled to the inlet system of a mass spectrometer. The nano-composite membranes have so far only been tested on controlled hydrostatic pressure systems in the laboratory and not in the environment (e.g. lakes, rivers, or the sea). Hydrostatic pressure increases by approximately 1 atmosphere for every 10 meters of water depth. One objective of my studies was to assess the in situ performance of nano-composite membranes and ensure their viability as membrane introduction systems for underwater mass spectrometry. This chapter presents in situ mass spectrometry measurements of dissolved gases at sea using nano-composite membranes as the introduction systems for underwater mass spectrometry. Nano-composite membranes created by coating an AAO membrane with a thin polymer film were coupled to the inlet system of an underwater mass spectrometer. Figure 5.1 show a picture of the underwater mass spectrometer used in this work.

The underwater mass spectrometer was deployed in the northern Gulf of Mexico on a R/V Weatherbird II (Figure 5.2) cruise dedicated to an assessment of the impact of Deepwater Horizon oil on Florida shelf ecosystems. The cruise originated at University of South Florida / College of Marine Science in St. Petersburg, FL and ended at
Pensacola, FL. The science party was responsible for collecting samples along several transect lines (Figure 5.3). Transect PCB extended across the shelf from Panama City and across DeSoto Canyon. The second transect, DSH, was located to the south of Mobile Bay. Twelve stations were surveyed (Figure 5.3).

Figure 5.1. Picture of the underwater quadrupole mass spectrometer.
During the cruise some of the underwater mass spectrometer modular utilities were malfunctioning. Communications between the computer and the CTD, altimeter and oxygen sensor did not function for the duration of the cruise. In addition, the pressure
vessel exhibited a small water leak, limiting deployment opportunities. In addition, the heating block that regulates the temperature of the membrane module was not stable for most of the casts, with the exception of one cast (DWH) where the temperature varied roughly ±1.5 degrees Celsius. The underwater mass spectrometer was deployed at four stations: PCB03, PCB04, DSH09 and Deepwater Horizon (DWH). Figure 5.4 shows the underwater mass spectrometer being deployed at DWH. The nano-composite membranes performed satisfactorily during underwater mass spectrometry deployment operations. The underwater mass spectrometer was in general able to record depth profiles of discrete dissolved gases in the water column. At the DWH station the underwater mass spectrometer was able to collect data representative of dissolved gas concentrations for nitrogen, oxygen and carbon dioxide.

Figure 5.4. The underwater mass spectrometer being deployed at the Deepwater Horizon site.
Figure 5.5 shows underwater mass spectrometry measurements for nitrogen, oxygen and carbon dioxide collected at the DWH station. The CTD and oxygen sensor connected to the underwater mass spectrometer were meant to coordinate depth, temperature, salinity, and oxygen concentrations with mass spectrometer measurements. Despite the lack of direct depth measurements, depth was estimated from the length of cable used to lower the instrument in the water column. At the DWH station the winch operator lowered the underwater mass spectrometer to a depth of 400 meters at a rate of 40 meters per minute. The underwater mass spectrometer subsequently collected data during the ascent, at an ascent rate of 5 meters per minute.

It was intended that the mass spectrometer would measure argon and nitrogen at \( m/z \) 40 and 28, respectively. However, constant power interruptions on the R/V *Weatherbird* II caused the instrument to shut down abruptly whereupon calibrations were lost for some mass measurements. Measurements of oxygen, carbon dioxide and nitrogen at \( m/z \) 32, 44 and 14, respectively, were not severely affected by the power disruptions.
To demonstrate that measurements of oxygen, carbon dioxide and nitrogen were representative of gas concentrations in the water column, mass spectrometer measurements were compared with dissolved oxygen concentrations obtained by the Rosette’s oxygen sensor, CTD and independently measured CO₂ system measurements.

The ship’s Rosette was deployed at the same location as the underwater mass spectrometer. Therefore, it was expected that all devices should demonstrate similar trends for the gases of interest (nitrogen, oxygen and carbon dioxide). At the DWH station the Rosette’s CTD sensor provided temperature and salinity measurements shown in Figure 5.6.

![Figure 5.6. Temperature and salinity at the DHW site.](image)

The temperature and salinity measurements were used to estimate the concentration of nitrogen in the water column with the Weiss (1970) characterization of nitrogen solubility as a function of temperature and salinity. Calculated nitrogen concentrations are plotted vs. depth in Figure 5.7 along with the ion current signal of nitrogen measured by the underwater mass spectrometer.
Figure 5.7. The figure on the left shows the concentration of nitrogen calculated using the Weiss (1970) parameterizations of nitrogen solubility as a function of temperature and salinity. The figure on the right shows the ion current signal of nitrogen (m/z 14) recorded by the underwater mass spectrometer.

The oxygen sensor on the Rosette was used for comparison with measurements obtained by the underwater mass spectrometer. Figure 5.8 shows the two types of oxygen profiles obtained at DWH.

Using spectrophotometric techniques, water samples collected at discrete depths from the Rosette’s Niskin bottles were analyzed for pH and total carbonate concentrations. The pH and carbonate data measured from these measurements were input into software developed by the Carbon Dioxide Information Analysis Center (CDIAC) to calculate dissolved carbon dioxide concentrations at each depth. Figure 5.9 shows pH vs. depth and pH vs. carbon dioxide concentrations obtained at each depth. Figure 5.10 shows a comparison of calculated carbon dioxide concentrations vs. depth and carbon dioxide ion current obtained with the underwater mass spectrometer.
Figure 5.8. The figure on the left shows oxygen concentrations measured by the oxygen sensor on the Rosette system. The figure on the right shows ion current signal for oxygen measured using the underwater mass spectrometer.

Figure 5.9. The figure in the left shows the pH measured at each depth and the figure in the right shows the carbon dioxide concentrations measured with changes in pH. Carbon dioxide concentrations were calculated using the software developed by CDIAC using pH and total carbonate data inputs.
Mass spectrometry measurements for nitrogen, oxygen and carbon dioxide exhibited similar profile trends as the concentrations of gases that were obtained by calculations and direct sensor measurements (Figures 5.7, 5.8 and 5.10). Mass spectrometry data are typically directly converted from ion current signals to concentration. However, power failures and subsequent instrumental problems precluded underwater mass spectrometer calibrations during the cruise. Despite such challenges, the nano-composite membranes demonstrated their potential as introduction systems for the underwater mass spectrometer. Underwater mass spectrometry measurements obtained using conventional polydimethylsiloxane (PDMS) membranes demonstrate permeability properties that are influenced by hydrostatic pressure (Bell et al., 2007). In contrast, underwater mass spectrometry measurements using the nano-composite membranes, as shown in this chapter, demonstrated no effects to changes in hydrostatic pressure.
Finally, the underwater mass spectrometer was also used to measure the presence of pollutants such as toluene and benzene spilled by the Deepwater Horizon oil. No toluene (m/z 91) or benzene (m/z 78) were detected by the underwater mass spectrometer during its deployment on the northern Gulf of Mexico. It is also possible, however, that power disruptions on the R/V Weatherbird II could have also affected calibrations for m/z 91 and m/z 78 rendering such measurements of questionable value. Therefore, questions regarding the utility of PNC membranes as effective membrane inlet systems for measurements of volatile organic compounds (VOCs) at trace levels were performed in the laboratory. A calibration of m/z peaks between m/z 80 and m/z 100 was performed using toluene dissolved in DI water. A mass spectrum of toluene is shown in Figure 5.11. The PNC membranes were then exposed to toluene concentrations at 1 part-per-million (ppm), 500 parts-per-billion (ppb), 250 ppb, 100 ppb and 50 ppb (Figure 5.12). As seen in Figure 5.12, the PNC membranes are clearly capable of measuring VOCs, such as toluene, at ppb levels.

Figure 5.11. Mass spectrum of toluene.
Figure 5.12. Mass spectrometry measurements of toluene using PNC membranes as the introduction system for the mass spectrometer.

Summary

Nano-composite membranes presented in this dissertation were demonstrated to be viable membrane introduction systems for mass spectrometers. These nano-composite membranes incorporated anodic aluminum oxide (AAO) membranes as membrane inlet substrates. It was shown that AAO membranes can be functionalized, thus ultimately influencing the physical/chemical properties of the nano-composite membranes. In some cases, the transmission properties of these nano-composite membranes were shown to be superior to conventional PDMS membranes as introduction systems, thereby making the nano-composite membranes highly desirable in a variety of membrane inlet mass spectrometry (MIMS) applications. Finally, nano-composite membranes were demonstrated to be effective as introduction systems for underwater mass spectrometry measurements.
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