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Membrane Introduction Proton-Transfer-Reaction Mass Spectrometry

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Proton-transfer-reaction mass spectrometry (PTR-MS) is a rapidly expanding field that spans disciplines such as ion physics, atmospheric chemistry, food chemistry, and biology. The proliferation of PTR-MS research has been accelerated by the availability of a compact PTR-MS instrument resulting from the work of the late Werner Lindinger and associates at the University of Innsbruck¹. The PTR-MS does not require calibration because concentrations can be calculated from a ratio of ion signals and well-known rate constants. The inherent accuracy, high sensitivity and rapid time response of the PTR-MS have resulted in multiple applications including the monitoring of volatile organic compound (VOC) emissions from fruit, coffee and meat as well as VOC compounds in the ambient air.

Another area of research in mass spectrometry that has experienced a resurgence of activity in recent years is membrane introduction mass spectrometry² (MIMS). In MIMS, the analyte is introduced into the ionization region of a mass spectrometer through a selective, semi-permeable, polymer membrane. The most commonly used membrane materials are silicone polymers, such as poly-dimethylsiloxane (PDMS), used either in a sheet or tube configuration. We present the results of initial studies that combine PTR-MS and MIMS research. First, the unique abilities of the PTR-MS are exploited to measure certain fundamental physical properties of a PDMS membrane, including solubilities and diffusion coefficients. Second, we demonstrate how the chemical selectivity of a PDMS membrane can be used to extend the capabilities of the PTR-MS instrument for two separate applications.

MIMS introduces the analyte into the mass spectrometer through a semi-permeable membrane using a process known as pervaporation. Three steps are involved in this process, adsorption of the analyte onto the membrane, diffusion through the membrane, and desorption from the inner surface of the membrane into the low-pressure ionization region. The permeation process is described by Fick's diffusion equations, given below in (Eqs. 1- 4) with the solutions for a hollow fiber membrane³:

$$1) \quad F(x,t) = -AD \cdot \left[\frac{\partial C(x,t)}{\partial x} \right] \quad \longrightarrow \quad F_{st} = \frac{2\pi LD \cdot (C_{S1} - C_{S2})}{\ln\left(\frac{r_0}{r_1}\right)} \quad 3)$$

$$2) \quad \frac{\partial C(x,t)}{\partial t} = D \cdot \left[\frac{\partial^2 C(x,t)}{\partial x^2} \right] \quad \longrightarrow \quad t_{10-90\%} = 0,237 \left(\frac{l^2}{D} \right) \quad 4)$$

$F(x,t)$ is the flow rate of analyte molecules through the membrane, $C(x,t)$ is the concentration inside the membrane, D is the diffusion coefficient, A is the surface area of the membrane, x is the depth in the membrane, t is time, $t_{10-90\%}$ the rise time from 10% to 90% of the final signal level, L is the length of a tubular membrane, l is the membrane thickness, r_0 and r_1 are the inner and outer membrane diameters, F_{st} is the steady-state flow and C_{S1} and C_{S2} are the

concentrations of analyte in the membrane at the entrance surface and exit surface, respectively. These quantities are illustrated schematically in Fig. 1 below.

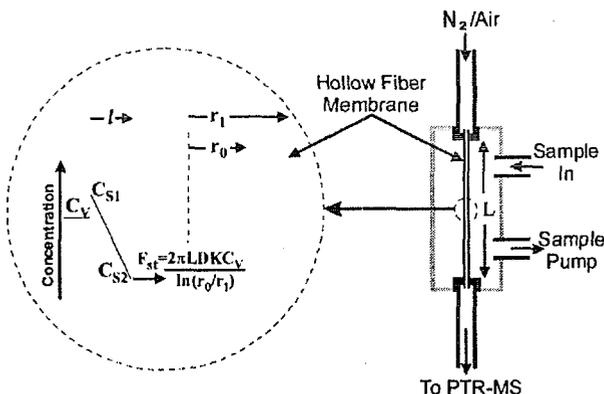


Fig. 1 Schematic diagram of the interface of the hollow fiber membrane to the PTR-MS with an illustration of the relevant experimental parameters

The right-hand side of Fig. 1 shows how the hollow fiber membrane physically interfaces with the sample stream and the PTR-MS. The membrane is mounted inside a stainless steel tube and sealed at each end as shown in Fig. 1. The interior of the membrane feeds directly into the PTR-MS drift region, held at a pressure of approximately 2 mbarr. A mass flow controller limits the flow of air or nitrogen through the membrane to 10 – 50 sccm, keeping the pressure near 2 mbarr. Sample air is drawn into the membrane assembly at atmospheric pressure and flows around the outside of the membrane at 100 – 200 sccm.

The left hand side of Fig. 1 shows a magnified section of the membrane labeled with the quantities described in Eqns. 1- 4. The steady static flow rate has been rewritten by setting $C_{S2} = 0$, because the inner surface of the membrane is swept by a carrier gas at very low pressure. The validity of this approximation will be demonstrated with experimental data. We then use the relationship $K = C_{S1}/C_V$, where K is the partition coefficient⁴ to rewrite F_{st} in Eqn. 5:

$$5) \quad F_{st} = \frac{2\pi LDKC_V}{\ln\left(\frac{r_0}{r_1}\right)}$$

We demonstrate how the PTR-MS can be used to determine F_{st} and $t_{10\% \rightarrow 90\%}$. These results can be related to the diffusion coefficient D and the partition coefficient K . The data will be presented as a function of membrane thickness and flow rate for VOC's with various functional groups that display a range of molecular properties such as polarity, polarizability and mass. Data will also be presented on the effect of temperature on both F_{st} and $t_{10\% \rightarrow 90\%}$. These will be explained using an Arrhenius-type relationship. An example of these results is shown in figure 2.

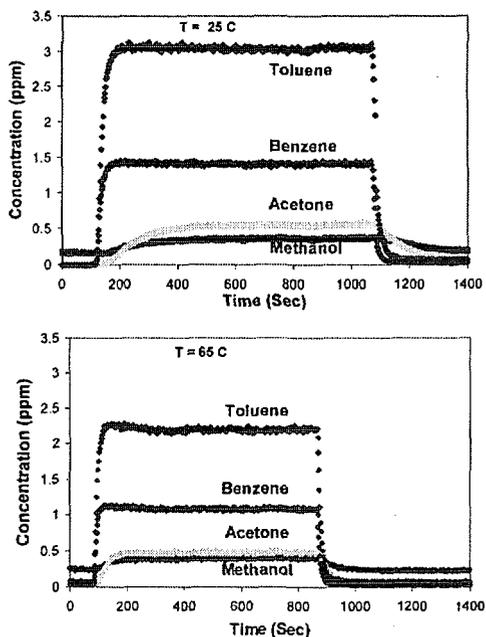


Fig. 2 Time dependent concentrations of VOC's inside the membrane for temperatures of 25 and 65 C

These data were obtained by using a three-way valve to modulate the composition of the sample stream between zero air and a mixture of several VOC's. The concentration of the VOC's in the mixture were determined by direct introduction into the PTR-MS and found to be 5 ppm for acetone, 3.5 ppm for benzene and toluene, and 2.8 ppm for methanol. Fig. 2 illustrates both the rise time and the steady state flow dependence of the different VOC's at two different temperatures. This serves as an illustration of how the ability of the PTR-MS to measure absolute concentrations of multiple chemical species can be used to quickly characterize critical physical properties of a semi-permeable membrane. Although this initial work used a relatively well-characterized membrane material, these results clearly demonstrate the potential of the PTR-MS to rapidly characterize new membrane materials for use in a variety of applications.

The second area that will be presented is the use of the properties of the semi-permeable membrane to enhance the capabilities of the PTR-MS. We demonstrate how the difference in transmission rates through the membrane can be used to eliminate certain isobaric interferences in the PTR-MS such as acetone and propanal at $m/Z = 59$. Fig. 3 shows the difference in both rise time and steady state concentration when 200 ppb samples of acetone and propanal are introduced to the membrane. The potential for time modulated MIMS in resolving this type of isobaric interference in the PTR-MS is discussed.

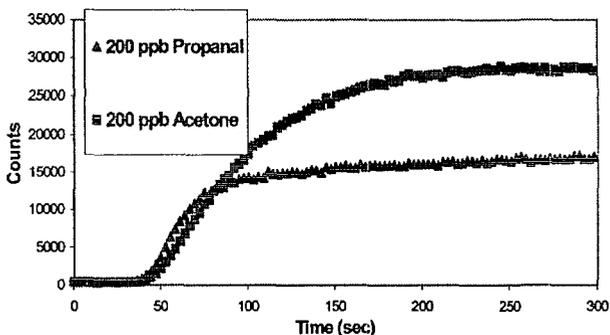


Fig. 3 Variations in rise time and steady state values for $m/Z = 59$ obtained for 200 ppb propanal and 200 ppb acetone in separate experiments

Finally, data will also be presented that show how the ability of the membrane to exclude water while transmitting volatile organic compounds can allow the use of the PTR-MS for making measurements in extremely humid environments. This further extension of the PTR-MS capabilities using membrane introduction is demonstrated in measurements of VOC's over the headspace of hot soup. The significance of these results and future research directions will be discussed.

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References

- [1] W. Lindinger, A. Hansel and A. Jordan, *Chem. Soc. Rev.* **27** (1998) 347
- [2] N. Srinivasan, R.C. Johnson, N. Kasthurikrishnan, P. Wong and R.G. Cooks, *Anal. Chim. Acta* **350** (1997) 257
- [3] F.L. Overney and C.G. Enke, *J. Am. Soc. Mass Spectrom* **7** (1996) 93
- [4] J.W. Grate and M.H. Abraham, *Sensors and Actuators B* **3** (1991) 85