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Membrane introduction proton-transfer reaction mass spectrometry

Michael Alexander[a,*], Elena Boscaini[b], Werner Lindinger[b,✣], Tilmann D. Märk[b]

[a] *Pacific NW National Laboratory, P.O. Box 999, Richland, WA K8-93, USA*
[b] *Institut für Ionenphysik der Leopold-Franzens-Universität, Innsbruck, Austria*

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Abstract

The combination of membrane introduction mass spectrometry (MIMS) and proton-transfer reaction mass spectrometry (PTR-MS) is explored. The PTR-MS is used to measure properties of a well-characterized membrane material, poly-dimethyl-siloxane (PDMS). It is found that the ability of the PTR-MS to measure absolute concentrations in real-time makes it an ideal tool for the characterization of membrane properties and the interaction of the membrane with multiple organic species. Values for the diffusion coefficients of several molecules are measured and found to be in agreement with literature values. Time modulation of the analyte across the membrane is explored as a method of resolving isobaric interferences for different chemical species. This is demonstrated for acetone and propanal. Finally, the benefit of combining MIMS with PTR-MS is demonstrated by the direct analysis of organic species in the headspace of a hot water solution where the high humidity would not allow analysis using the PTR-MS alone. (Int J Mass Spectrom 223–224 (2003) 763–770)

Keywords: Membrane; Diffusion coefficient; Proton-transfer reaction mass spectrometer; Headspace analysis

1. Introduction

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 Innsbruck [1]. 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 [2].

Another area of research in mass spectrometry that has experienced a resurgence of activity in recent years is membrane introduction mass spectrometry [3–5] (MIMS). Research has focused on the application of MIMS to measurements in real-world systems [6–9], theoretical calculations of membrane properties

* Corresponding author. E-mail: michael.alexander@pnl.gov
✣ Deceased.

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and the processes involved in MIMS [10–12] and characterization of membrane materials [12–14]. 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 to measure absolute concentrations with rapid time response are exploited to determine certain fundamental physical properties of a PDMS membrane, including solubilties and diffusion coefficients. 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 $m/z = 59$. The potential for time modulated MIMS in resolving this type of isobaric interference in the PTR-MS is discussed.

Finally, data will be presented that show how the ability of the PDMS membrane to exclude water while transmitting volatile organic compounds can allow the use of the PTR-MS for making measurements in extremely humid environments. If the water concentration in the sample and therefore the drift tube becomes too high, clustering reactions of H_3O^+ with H_2O to form $H_3O^+(H_2O)_n$ begin to dominate, causing significant reduction of the H_3O^+ primary ion. This prohibits using the PTR-MS for direct measurements in such environments as the headspace of boiling soup. Using the PDMS membrane in conjunction with the PTR-MS can eliminate this problem. This further extension of the PTR-MS capabilities using membrane introduction is demonstrated in measurements of VOC's over the headspace of hot water containing aromatic compounds typical of soup or other foods. The significance of these results and future research directions will be discussed.

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 membrane [11]:

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

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

$F(x, t)$ 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.

The left hand side of Fig. 1 shows a magnified section of the membrane labeled with the quantities described in Eqs. (1)–(4). The steady state 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 $K = a_s/a_m \cong C_{S1}/C_V$ [11], where K is the partition coefficient and a_s and

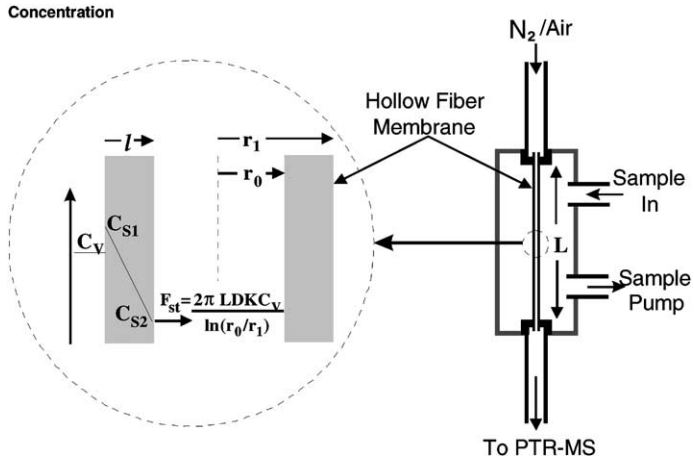

Fig. 1. Schematic diagram of the interface of the hollow fiber membrane to the PTR-MS with an illustration of the relevant experimental parameters.

a_m are the activities in the stationary and mobile phase, to rewrite F_{st} in Eq. (5):

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

We present preliminary data demonstrating how the PTR-MS can be used to determine F_{st} and $t_{10–90\%}$. These results are then used to calculate 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. These results will be compared to experimental and theoretical values in the literature.

2. Experimental

The details of the PTR-MS have been well documented [1,2] so will not be described here. The most important characteristics of the PTR-MS are the ability to measure multiple chemical species simultaneously, absolute measurement without calibration, rapid time response, and high dynamic range. These properties of the PTR-MS allow rapid, accurate characterization of membrane properties under a range of conditions.

The right-hand side of Fig. 1 shows how the hollow fiber membrane physically interfaces with the sample stream and the PTR-MS. For the work presented here, the membrane used was Silastic™ (Dow Corning) tubing. The dimensions were: i.d. 0.64 mm, o.d. 1.19 mm, wall thickness 0.28 mm, and length 4 cm. 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 mbar. A mass flow controller limits the flow of air or nitrogen through the membrane to 10–50 sccm, keeping the pressure near 2 mbar, the pressure of the drift region of the PTR-MS. Sample air is drawn into the membrane assembly at atmospheric pressure and flows around the outside of the membrane at 100–200 sccm controlled by a second mass flow controller. The entire membrane assembly is enclosed in an insulated box containing heaters and a thermocouple connected to a temperature controller.

Data were obtained by using a three-way valve to modulate the composition of the sample stream between zero air and various VOC samples in air. For the studies on rise times, a mixture of several VOC's in compressed air was used. The concentrations 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. Demonstration of the potential for resolution of isobaric interferences using time modulation with the membrane was done with 200 ppb of acetone and 200 ppb of propane in air in separate containers. These standards were created by adding appropriate quantities of acetone and propanal to water as determined by using Henry's law and sampling the air from the headspace. Measurements of rise times were made by running for 5–10 min with zero air, switching the three-way valve to the sample, allowing steady-state to be reached, switching the valve back to zero air and again allowing steady state to be reached.

Measurement of aromatic compounds in humid environments is demonstrated by spiking an aqueous solution with a number of compounds, alcohols, aldehydes, esters and lactones that are typically found in foods. The water solution was contained in a temperature-controlled oven and the headspace was sampled through the membrane assembly in the same manner as described earlier. The assembly was maintained at the same temperature as the water solution to avoid condensation.

3. Results and discussion

One of the assumptions that was made in the calculation of F_{st} was that the concentration at the inner surface of the membrane, C_{S2}, is equal to zero because it is being swept by the air or nitrogen flowing through the membrane. The PTR-MS signal in counts per second (CPS) is proportional to the concentration of analyte in the carrier gas. If the assumption is valid then F_{st} (molecules/second) is independent of the carrier gas flow rate and the concentration (molecules/cm^3) is inversely proportional to the flow rate. Fig. 2 shows the PTR-MS signal in CPS plotted vs. carrier gas flow rate for toluene, benzene and acetone. The solid lines are a fit to a simple inverse dependence and match the observed signal, indicating that under the operating conditions used for these studies the assumption that $C_{S2} = 0$ is valid.

Given that the steady state conditions are valid, it is now possible to use the system to measure basic membrane parameters. Fig. 3 shows the time dependent signal from the PTR-MS as the sample gas flow around the membrane was modulated between zero air and the sample tank. It is immediately apparent that

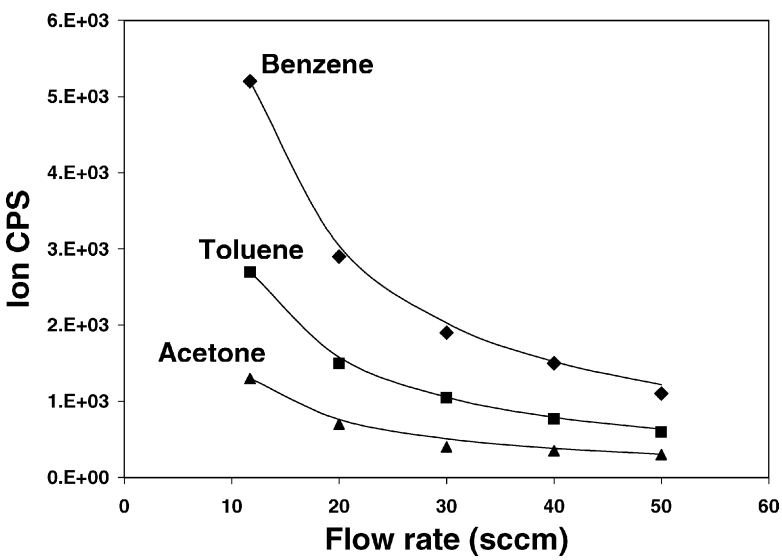

Fig. 2. This demonstrates that the measured concentration in counts per second (CPS) is inversely proportional to the flow rate through the membrane so that F_{st} is independent of carrier gas flow rate.

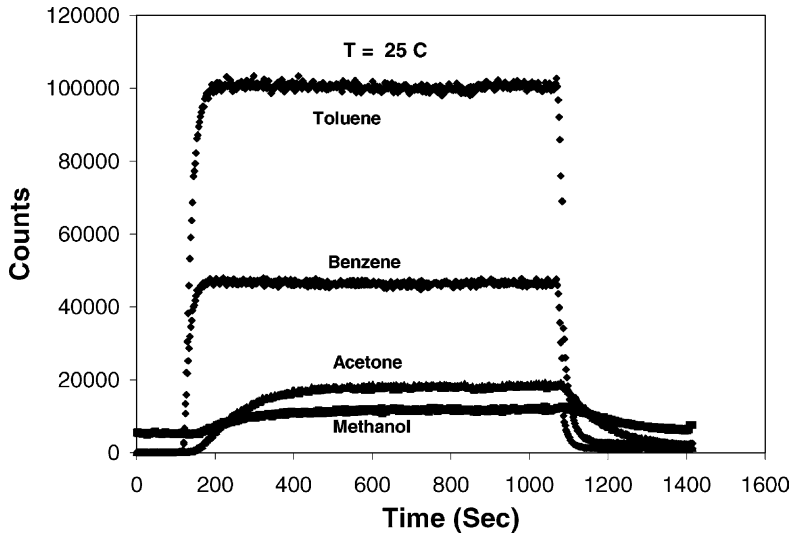

Fig. 3. Time dependent concentrations of VOC's inside the membrane at a temperature of 25 °C.

the less polar species, benzene and toluene, have both faster rise times and higher steady state values than acetone or methanol as is expected for a non-polar membrane material like PDMS. The concentration of acetone, determined without the membrane is 5 ppm, higher than that for benzene and toluene, 3.5 ppm. Referring to Eqs. (3)–(5) for steady state flow and rise time, we see that the rising part of the curves in Fig. 3 depend only on the diffusion coefficient D, while the asymptotic regions depend on both the diffusion coefficient and the partitioning or solubility of the different gases in the PDMS membrane. While the differences between the polar and non-polar compounds is not surprising, the difference between toluene and benzene is not as obvious. Empirical models of solubility [14,15] predict that the partition coefficient for toluene in PDMS should be slightly larger than that for benzene, but not of the magnitude observed here. Further investigations are underway to understand this effect in terms of basic molecular properties including polarizabilty and dipole moments. This simple experiment demonstrates how the ability of the PTR-MS to measure absolute concentrations in real time can quickly give information on membrane properties and lead to new insights into membrane–sample interactions.

It is also interesting to see how the results from these initial studies compare with previous work. Fig. 4 shows the diffusion coefficients calculated using Eq. (4) by measuring $t_{10–90\%}$ for the curves shown in Fig. 3 for benzene, toluene and methanol. Also shown are literature values [12] for the same gases in PDMS. The agreement is quite good, especially considering the wall thickness for the membrane is specified by the manufacturer to only 50%. This agreement is significant because the data is obtained quite easily and simultaneously for a number of species, indicating great potential of the PTR-MS for the characterization of new membrane materials.

The other aspect of this preliminary study of MIMS PTR-MS is to investigate possible ways the membrane can be used to enhance or extend the capabilities of the PTR-MS. One weakness of mass spectrometry in general is the possibility of more than one chemical species with a given mass-to-charge ratio or isobaric interference. There are certain isobaric interferences in the PTR-MS as in any mass spectrometric method. One example is propanal and acetone, both with a protonated mass-to-charge ratio of 59 (Fig. 5). In the data shown in Fig. 3, it was observed that even similar species such as benzene and toluene have

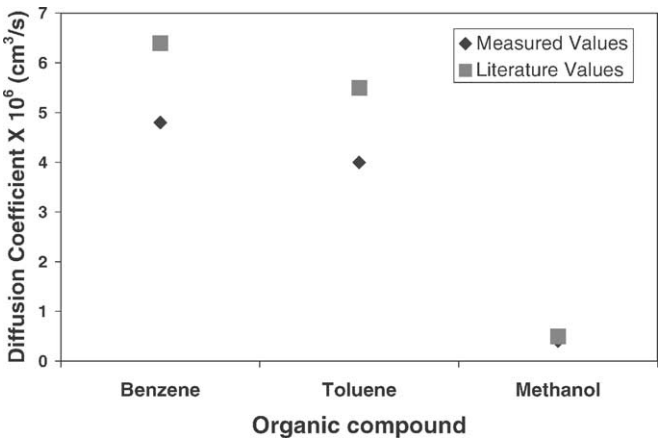

Fig. 4. Diffusion coefficients calculated from the rise times for benzene, toluene and methanol compared to literature values.

different diffusion coefficients. It is interesting to see if the time-resolved signal resulting from modulation of sample gas across the membrane shows a difference for acetone and propanal. Fig. 3 shows the result of this experiment. Propanal clearly has a faster rise time (higher diffusion coefficient), but is less soluble in the membrane. The membrane thickness, 0.28 mm, is relatively large compared to other commercially available membranes. The use of a thinner membrane, combined with the fast response, less than 1 s, of the PTR-MS could make this a useful method for real-time measurements, in a manner similar to that demonstrated for membrane introduction ion trap mass spectrometry [9]. Future work will include the analysis of mixtures of species such as acetone and propanal.

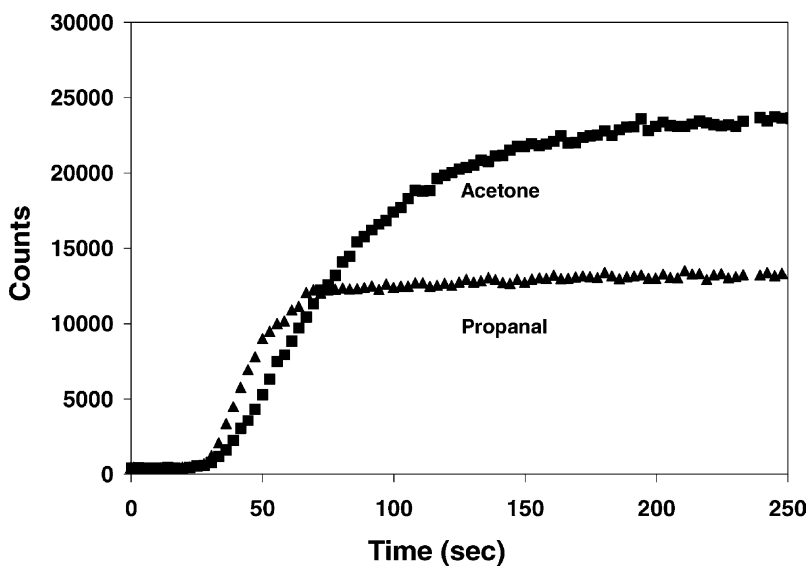

Fig. 5. Differences between rise time and steady state values for $m/z = 59$ obtained for 200 ppb propanal and 200 ppb acetone in separate experiments.

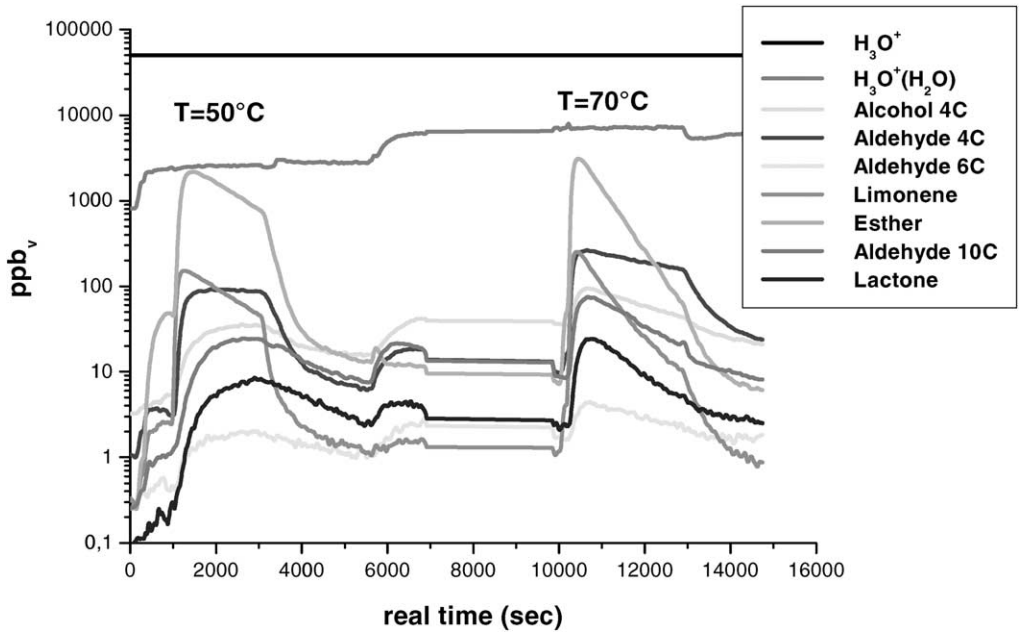

Fig. 6. PTR-MS signal for H_3O^+, $H_3O^+(H_2O)$, and various organic species characteristic of soup in headspace of hot water at 50 and 70 °C.

Another way of extending the capabilities of the PTR-MS is to use the hydrophobic nature of the PDMS membrane to exclude high concentrations of water that would completely deplete the H_3O^+ ion, making the PTR-MS unresponsive to other species. Fig. 6 shows data taken by sampling the headspace of a water solution at 50 and 70 °C. The solution contains a number of organic species typical of hot soup. The top trace is the primary H_3O^+ ion signal, indicating that it is not depleted even though the first water cluster $H_3O^+(H_2O)$ increases by about an order of magnitude over the course of the experiment. The water cluster shows an initial increase when the hot headspace is sampled compared to zero air, but does not decrease when the zero air is turned on again. It is not clear if this memory effect is due to the membrane itself or residual moisture in the assembly. Nevertheless, it is clear that the organic species can penetrate the membrane and be detected while the water concentration is sufficiently reduced to allow measurement by the PTR-MS. Further work is needed to demonstrate quantitative detection and to understand the memory effects of both the water and the organic analytes, but the use of the PDMS membrane clearly allows measurements to be made in a high humidity environment by the PTR-MS.

4. Conclusions

This initial study of MIMS PTR-MS has clearly demonstrated the potential of the PTR-MS for characterization of membrane materials and for understanding the details of membrane–analyte interactions. Data acquired for the PDMS membrane was in good agreement with existing literature values for diffusion coefficients, but also indicated some interesting discrepancies in solubility models [16]. More detailed measurements using the PTR-MS have the potential to lead to more fundamental understanding about the relationship between molecular properties and membrane characteristics. One interesting future direction would be to understand the effect of high concentrations of multiple species on the diffusion coefficients and solubilities in the membrane. The effects of temperature also will be explored. It was also seen

that MIMS has the potential to extend the capabilities of PTR-MS by resolving isobaric interferences and allowing measurements in high humidity environments where it would not be possible otherwise. Other membrane materials could further extend the ability of the PTR-MS to make measurements in the headspace of wine or beer, where the high ethanol concentration precludes detection of other species in a similar manner to high humidity environments.

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