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Characterization of a sheet membrane interface for sample introduction into a time-of-flight mass spectrometer

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Abstract

In the present study, we constructed a membrane inlet assembly for selective permeation of volatile organic compounds in air into a time-of-flight mass spectrometer. Temporal evolution of analyte through a 127-μm thick polydimethylsiloxane membrane was measured by monitoring the ion signal after a step change in the sample concentration. The results were well fitted by a non-steady-state permeation equation. The diffusion coefficient, response time, and sensitivity were determined experimentally for a range of polar (halogenated) and nonpolar (aromatic) compounds. We found that the response times for various volatile organic compounds were greatly influenced by the alkyl chain length as well as the number of substituted halogen atoms. The detection limits for toluene and *o*-xylene were 0.06 and 0.2 ppm by volume, with linear dynamic ranges greater than three orders of magnitude. These results indicate that the membrane inlet/time-of-flight mass spectrometer will be useful for a wide range of field applications, especially for real-time environmental monitoring.

Keywords: Membrane inlet; Time-of-flight mass spectrometer; Polydimethylsiloxane (PDMS); Diffusion coefficient

1. Introduction

The need for environmental monitoring of air samples has grown due to increasingly rigorous regulations and the importance of understanding the damage done to the environment by years of careless waste disposal activities. Membrane inlet mass spectrometry (MIMS) has come into widespread use for the direct sampling and mass analysis of volatile organic compounds (VOCs) at trace levels in water and air [1–7]. MIMS allows the direct introduction of specific components of a liquid or gas sample into a mass spectrometer. Its many advantages include simplicity, speed, high sensitivity, precision, and an ability to be used for in situ monitoring [8].

MIMS benefits from selective transport of analytes through a semipermeable membrane, which is usually a hydrophobic silicone polymer. Silicone is useful because it allows selective permeation of volatile organic analytes, while the primary components of air are mostly blocked. This difference in permeability is important because it facilitates direct monitoring (without any sample preparation) of volatile analytes over a wide range of concentrations in complex gaseous mixtures. The analytes are thus transferred without any extraction or pretreatment steps from the sample directly into the ion source of a mass spectrometer, in which they are ionized and detected normally at trace levels [9–12]. The membrane also serves as a physical barrier between atmospheric pressure and the high vacuum inside the mass spectrometer, which greatly reduces the pumping requirements of the instrument, extending the lifetime of the ion source and detector.

As the analyte stream permeates through a sheet or tube of membrane material, different compounds are adsorbed by the membrane to different degrees and diffuse at different rates. Thus, in real sampling and analysis situations, the diffusion rate determines the response time of the analysis, which in turn affects the precision of sample concentration during the real-time measurements. The situation becomes worse in scanning mass spectrometers such as quadrupole [13–17], ion trap [18–20], and magnetic sector [21] analyzers, where rapid changes in analyte concentration and composition are monitored. For such purposes, in situ analysis of volatile organic samples using a membrane inlet/time-of-flight (TOF) mass spectrometer, in which the membrane is exposed to analyte streams

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of changing conditions, has significant advantages over other mass detection methods [22,23].

TOF mass spectrometry (TOFMS) differs fundamentally from mass spectrometry using scanning instruments in that the formation of discrete ions and mass dispersion is accomplished in the time domain rather along a spatial axis. Because a complete spectrum is generated in each cycle, the relative intensities of ions in the source are accurately represented, even if source conditions change during the experiment. This dynamic range and rapid delivery of full mass spectra in TOFMS represents a large advantage over scanning instruments. TOFMS also has an intrinsic duty-cycle advantage that increases with the observed dynamic range in mass [24]. Additionally, TOFMS is characterized by outstanding transmission, and due to its simple setup, it is robust and insensitive to vibrations, which is particularly important for field applications.

There have been several reports of measurements of VOCs using MIMS, but only a few of these [25–27] have established a connection between molecular properties, membrane properties, detection limits, and response times. In addition, there have been few systematic comparisons of the molecular parameters affecting the performance of a silicone membrane interface. In the present study, we analyzed several aromatic and halogenated hydrocarbons to determine the factors affecting membrane performance.

2. Experimental methods

A schematic of the membrane inlet assembly, which was constructed on a standard 70-mm Conflat flange, is shown in Fig. 1. It consists of two sections (upper and lower) of the interface body, a sheet membrane, and a transfer capillary tube. Two 3-mm diameter holes allow the gas sample to be flushed through the

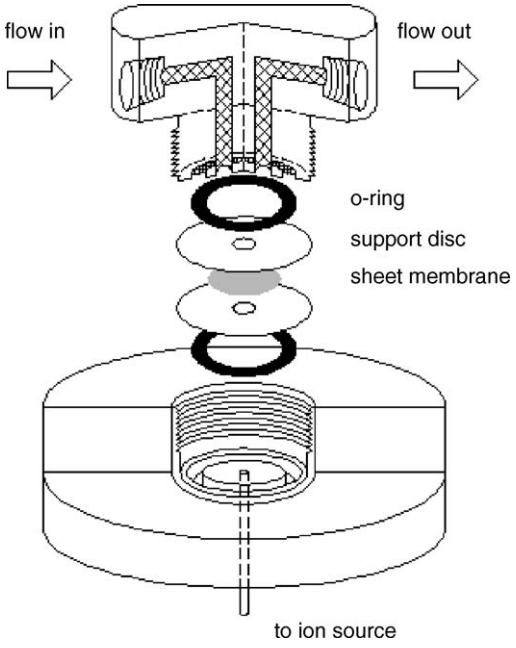

Fig. 1. Schematic of the membrane inlet assembly designed for sample introduction to a TOFMS.

flow chamber, in which the analytes directly contact the membrane surface. It is obvious that the larger the flow chamber, the worse the probe efficiency with respect to response sensitivity and sampling frequency [28]. Therefore, minimization of the chamber volume is essential for increasing the probe efficiency. To maximize the contact of analyte with the membrane, the dimensions were adjusted to minimize the ratio of the sample volume in contact with the membrane to the membrane surface area. The membrane material used was a 127-μm thick Silastic® (polydimethylsiloxane) medical grade silicone rubber sheet membrane (Dow Corning Corp.).

The membrane was placed flat between two support discs and was sealed with Viton o-rings mounted at both ends of an interface body made of aluminum material. The effective membrane area was 12.6 mm^2, which provides an acceptable compromise between sensitivity and the amount of air admitted into the high vacuum of the MS chamber (4×10^{-7} Torr). The membrane inlet assembly was located outside the custom-made TOF mass spectrometer [29], 7 cm away from the center of ion source. Efficient transport of permeated analytes from the membrane assembly to the electron ionization source of the TOF mass spectrometer was made possible by using a 0.5-mm i.d. deactivated silica capillary tube, which requires all of the material entering the mass spectrometer from the interface to pass through the ion source. Although it may be desirable to minimize the distance between the membrane inlet and the mass spectrometer, this distance is not generally transport rate-limiting.

The mass spectrometer used was a Wiley–McLaren two-stage design, operated with an electron-impact (70 eV) ion source and a pulsed acceleration field [30,31]. The ionization region is maintained field-free during the electron impact by applying a 1000 V dc to the repelling and extracting electrodes. Triggered by the start signal, the resulting ions are extracted toward the detector by applying a 150-V negative-going pulse to the extracting electrode, which was chosen to optimize the space-focusing condition. In the acceleration stage, a much stronger electric field accelerates the ions into the 25-cm flight tube. The ion signal from a chevron microchannel plate detector is fed directly into a transient digitizer (National Instruments; PCI-5112), which is programmed for automated data acquisition and signal averaging. Each mass spectrum, recorded with a repetition rate of 50 Hz and averaged over 500 pulses, was obtained within 20 s.

To measure response times for organic compounds, we used two flow channels, one connected to fresh air, and one containing a sample of the organic compound at a low concentration. The flow channels were connected to a three-way magnet valve placed in front of the membrane inlet. By switching the valve, it was possible to make a very rapid change from pure air to sample gas. The response time was determined by measuring the intensity of the ion signal as a function of the time after the valve was opened to allow the analyte through the membrane. The ion signal was averaged by a gated integrator/boxcar averager (Stanford Research Systems), where the boxcar gate was positioned at the arrival time of an interesting ion in the TOF spectrum. All of the measurements were made at room temperature. Sample flow over the membrane was regulated by means of a gear pump (Cole Parmer Instrument Co.) placed at the outlet