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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

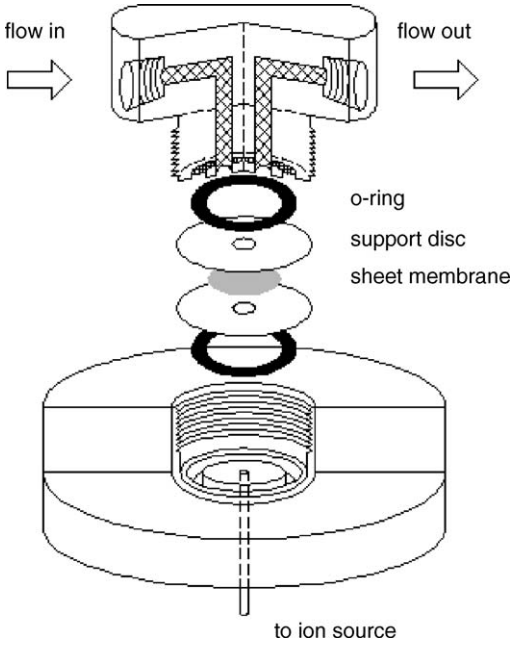

Fig. 1. Schematic of the membrane inlet assembly designed for sample introduction to a TOFMS.

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

of the membrane assembly. The typical sample flow rate was 300 mL/min.

A custom-built standard gas generation device supplied a gaseous standard in ppm volume concentrations for mass calibration and membrane characterization. The dilution system is constructed of electropolished 316 L stainless steel and uses all-metal mass flow controllers and valves. Room air, passed through a moisture trap, was used to dilute the sample. Spectrophotometric grade of benzene, toluene, *o*-xylene, 1,3,5-trimethylbenzene, iodomethane, 1-iodopropane, 1-iodobutane, iodobenzene, fluorobenzene, 1,2-difluorobenzene, and 1,2,3-trifluorobenzene from Sigma–Aldrich were used without further purification.

3. Results and discussion

A typical 70-eV electron impact TOF mass spectrum obtained for the membrane inlet sampling of benzene in air is displayed in Fig. 2. This spectrum was averaged over 500 pulses, with a data point taken every 4 ns. The prominent peaks at the low-mass region, corresponding to H_2O^+ (*m*/*z* 18), N_2^+ (*m*/*z* 28), and O_2^+ (*m*/*z* 32) at 3.75, 4.60, and 4.89 μs, respectively, result from air and water vapor that permeated through the membrane. In spite of a relatively low concentration of 1600 ppm benzene in air, the sample produces several significant peaks, including $C_3H_3^+$ (*m*/*z* 39), $C_4H_2^+$ (*m*/*z* 50), $C_4H_3^+$ (*m*/*z* 51), $C_4H_4^+$ (*m*/*z* 52), and parent $C_6H_6^+$ (*m*/*z* 78 at 7.45 μs) ions; thus, the most significant peak was from the $C_6H_6^+$ ion. This result demonstrates that the higher solubility of benzene molecules than inorganic air components in the hydrophobic silicone membrane leads to enrichment of the benzene after selective permeation through the membrane.

In MIMS experiments, the analytes must pass through a membrane before they enter the vacuum chamber. The permeation of a substance through the membrane is defined by a process that includes: (1) adsorption of analyte by the membrane surface,

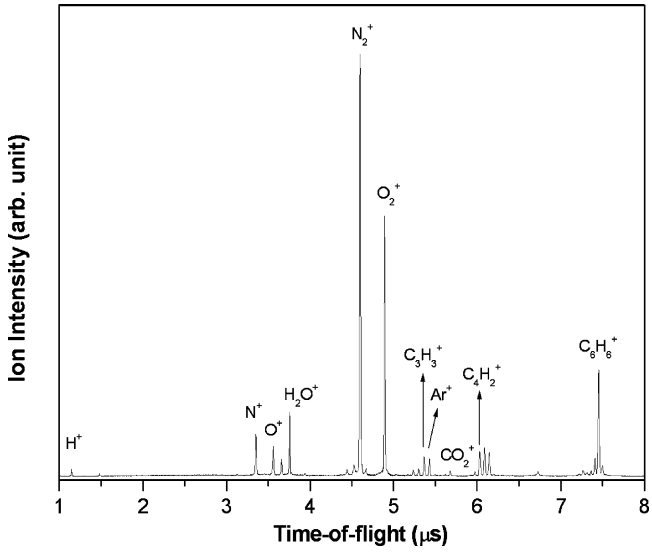

Fig. 2. A typical 70-eV electron impact time-of-flight mass spectrum of a benzene (1600 ppm) sample using the membrane inlet method. The spectrum is averaged for 500 shots at 4 ns per channel.

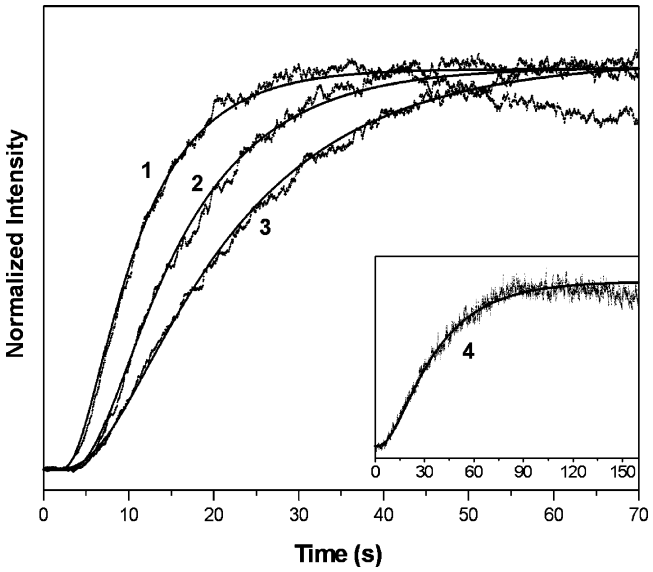

Fig. 3. Response time measurements for four analytes obtained using a 127-μm sheet membrane at room temperature: 1, benzene; 2, toluene; 3, *o*-xylene; and 4, 1,3,5-trimethylbenzene. The dotted lines correspond to the experimental values of permeating flux recorded with a step of 0.025 s. The solid lines correspond to the simulation results of non-steady-state permeation (Eq. (1)) using the first five terms ($n = 1$–5). The signal intensities were normalized to facilitate the comparison.

(2) diffusion through its body, and (3) release from the inner surface into the vacuum of the mass spectrometer [32]. Diffusion through the membrane is known to be the rate-determining process, whereas partitioning at the high-pressure surface and desorption from the low-pressure surface are considered to be instantaneous [33]. Thus, the permeation process across the membrane delays the response of the mass spectrometer to the analyte (flux). This is a measure of the time taken to achieve a maximum signal response to a sample of fixed concentration (i.e., to achieve a steady-state composition). For real-time sampling and analysis, it is therefore necessary to take the membrane response into account.

Fig. 3 shows an example of how benzene (1600 ppm), toluene (1000 ppm), *o*-xylene (1100 ppm), and 1,3,5-trimethylbenzene (170 ppm) samples are transmitted through the membrane after sample introduction and how long these samples take to reach a steady state at 25 °C. The time dependence of the ion intensity for each analyte was obtained from the integration of the largest peaks for benzene (*m*/*z* 78), toluene (*m*/*z* 91), *o*-xylene (*m*/*z* 91), and 1,3,5-trimethylbenzene (*m*/*z* 105) in the TOF spectrum for each sample as the gas flow through the membrane inlet was modulated between pure air and the sample gas. As expected, in each case, the signal increased with time and then saturated. The observed response times varied considerably for different substances, showing an increasing trend with the size of the analyte molecules. Ketola et al. obtained similar response times when analyzing VOCs in air with a 100-μm silicone sheet membrane [34]. These results are consistent with the fact that, if permeant molecules interact only weakly with the polymer or filler, the diffusion rate of the molecule will mainly depend on its size and less on its chemical properties.

Non-steady-state permeation can be described by Fick's diffusion equation. For a step change in concentration, the mathematical solution for the time-dependent flow $J(t)$ through a sheet membrane of thickness ℓ is [35,36]

$$J(t) = J_{ss}\left\{1 + 2\cdot\sum_{1}^{\infty}\left[(-1)^n\cdot\exp\left(-\left(\frac{n\pi}{\ell}\right)^2 Dt\right)\right]\right\} \quad (1)$$

where J_{ss} is the steady-state flow of an analyte in the extract stream, and D is the diffusion coefficient of the analyte in the membrane polymer. The permeation process exhibits an asymptotic approach to the steady state. The result of the best curve fit is presented in Fig. 3, which shows permeation through a sheet membrane when each analyte concentration is instantaneously changed from 0 to a steady-state level. Each experimental curve is well fitted by Eq. (1) using the first five terms (n = 1–5). The diffusion coefficients of benzene, toluene, *o*-xylene, and 1,3,5-trimethylbenzene were determined to be 2.2×10^{-6}, 1.8×10^{-6}, 1.2×10^{-6}, and 5.7×10^{-7} cm^2/s, respectively. The deviation of the experimental curve from the ideal is probably the result of a significant permeation of analyte into areas of the membrane that are not directly exposed to the sample contact area or the high vacuum. Another possible source of the deviation is the adsorption/desorption process at vacuum surfaces of the mass spectrometer.

To understand how the diffusion rate changes with the length of the alkyl chain, we investigated the general trends in the time-dependent ion intensities of monosubstituted iodoalkanes at room temperature. We chose these halogenated compounds for this experiment because, although they are volatile, their polarity decreases their ability to permeate through the silicone membrane [25]. Fig. 4 displays the normalized diffusion–response curves for iodomethane, 1-iodopropane, 1-iodobutane, and iodobenzene. The diffusion rate shows a steady decrease as the length of the aliphatic chain increases, whereas an unexpectedly slow diffusion is observed for iodobenzene. The measured diffusion coefficient of iodobenzene (3.5×10^{-7} cm^2/s) is an order of magnitude smaller than those for the aliphatic iodoalkanes, including iodomethane (4.2×10^{-6} cm^2/s), 1-iodopropane (2.8×10^{-6} cm^2/s), and 1-iodobutane (1.6×10^{-6} cm^2/s). The van der Waals interactions between the nonpolar alkyl group of iodoalkane molecule and the membrane polymer become stronger with increasing carbon chain length; thus, the diffusion through the membrane becomes slower. The low diffusion coefficient of iodobenzene compared to benzene and aliphatic iodoalkanes is presumably due to the fact that iodobenzene molecules stick to the surface of the membrane and do not evaporate as readily into the vacuum.

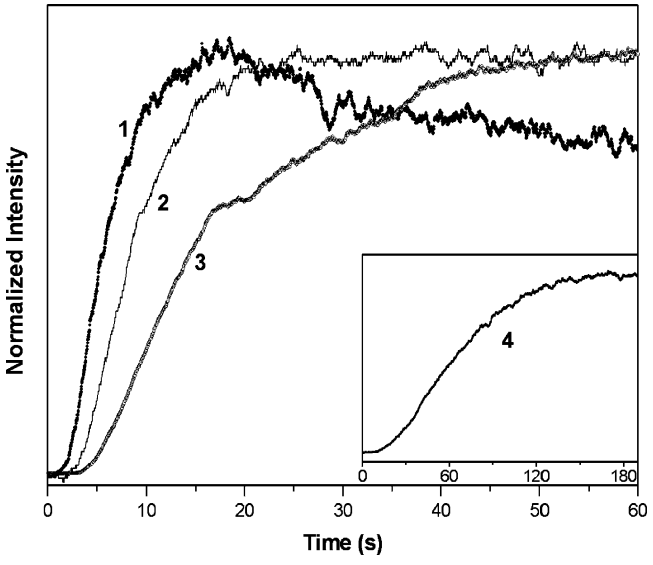

Fig. 4. Normalized diffusion–response curves for monosubstituted alkanes at room temperature: 1, iodomethane; 2, 1-iodopropane; 3, 1-iodobutane; and 4, iodobenzene.

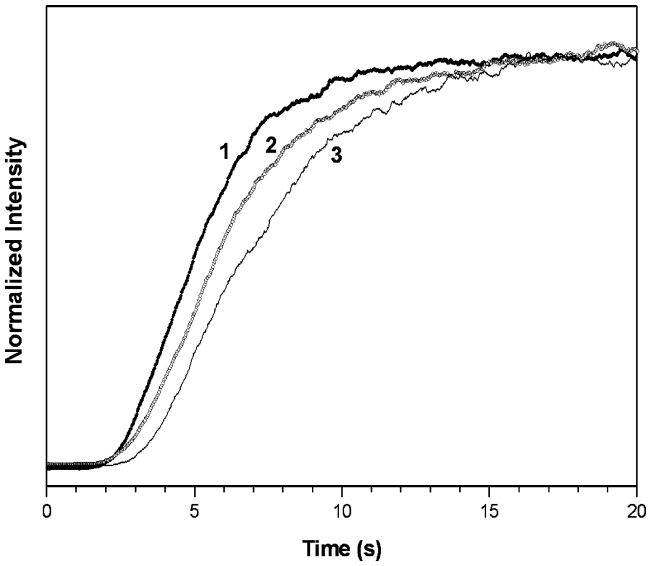

Fig. 5. Normalized diffusion–response curves for fluorobenzene (1), 1,2-difluorobenzene (2), and 1,2,3-trifluorobenzene (3) at room temperature.

Fig. 5 shows the normalized response curves for fluorobenzene, 1,2-difluorobenzene, and 1,2,3-trifluorobenzene. The diffusion rate of fluorine-substituted benzene slightly decreased with the number of fluorine atoms on the aromatic ring. Notably, the observed response curve is not related to the dipole moments of fluorobenzene (1.60 D), 1,2-difluorobenzene (2.46 D), and 1,2,3-trifluorobenzene (1.40 D) [37]. These results demonstrate that it is the total number of substituents rather than the polar property of the analyte that influences the diffusion rate. From the curve fit, the diffusion coefficients of fluorobenzene, 1,2-difluorobenzene, and 1,2,3-trifluorobenzene were determined to be 5.9×10^{-6}, 4.6×10^{-6}, and 4.0×10^{-6} cm^2/s, respectively.

Values for the diffusion coefficient (D) and response time for the signal intensity to rise from 10 to 90% of its maximum value ($t_{10\text{–}90\%}$) are summarized in Table 1 for all of the samples investigated. The most likely errors in our measurements are expected to arise from the adsorption of the organic compounds on the vacuum chamber walls as they issue from the membrane along with the time needed for a sample to come from the sampling cylinder to the membrane surface ($\leq$1 s). Both of these errors would result in smaller diffusion coefficients at higher numbers of carbons. The aromatic compounds benzene (16.9 s),

Table 1
Diffusion coefficient (cm^2/s) and response time $t_{10–90\%}$ (s) for selected VOCs at 25 °C

Compounds	Chemical formula	D	$t_{10–90\%}$[a]
Benzene	C_6H_6	2.2×10^{-6}	16.9
Toluene	C_7H_8	1.8×10^{-6}	21.2
1,2-Dimethylbenzene	C_8H_{10}	1.2×10^{-6}	31.8
1,3,5-Trimethylbenzene	C_9H_{12}	5.7×10^{-7}	67.0
Iodomethane	CH_3I	4.2×10^{-6}	9.1
1-Iodopropane	C_3H_7I	2.8×10^{-6}	13.6
1-Iodobutane	C_4H_9I	1.6×10^{-6}	23.8
Iodobenzene	C_6H_5I	3.5×10^{-7}	109.2
Fluorobenzene	C_6H_5F	5.9×10^{-6}	6.4
1,2-Difluorobenzene	$C_6H_4F_2$	4.6×10^{-6}	8.3
1,2,3-Trifluorobenzene	$C_6H_3F_3$	4.0×10^{-6}	9.5

[a] The response times were not concentration-dependent.

toluene (21.2 s), *o*-xylene (31.8 s), and 1,3,5-trimethylbenzene (67.0 s) gave slower responses than iodomethane (9.1 s), primarily due to their molecular size. Finally, the D and $t_{10–90\%}$ values obtained here are in good agreement with previously reported results [34,38,39].

The diffusion coefficients for the iodoalkanes show a steady fall as the length of the carbon chain increases. Regardless of their polarity, the most rapid diffusion was observed for those compounds having the weakest interaction with the membrane. The membrane used in the current studies was made of polydimethylsiloxane, which is a hydrophobic polymer that interacts most strongly with compounds bearing methyl or alkyl groups due to van der Waals interactions with the alkyl groups of the analyte. These interactions are proportional to the number of methyl groups or to the length of the alkyl chain of the analyte, thus increasing its diffusion through the membrane. Furthermore, the response times of flourinated compounds slightly increased from fluorobenzene to 1,2-difluorobenzene and from 1,2-difluorobenzene to 1,2,3-trifluorobenzene. This shows the analyte–polymer interaction is more strongly affected by the total number of substituents (fluorine atoms) than their structures or positions.

For real-time monitoring of gaseous samples that have rapidly changing analyte concentrations and compositions (e.g., car exhaust or process streams), quadrupoles and ion traps have been the typical instruments of choice in connection with GC/MS systems. TOFMS in the current MIMS setup can also acquire a full mass spectrum every 20 s with a good resolution (400 at m/z 78) [29]. This feature allows profiling of transient events in a sample stream that might be missed if ion intensities of the specific mass window were swept at time intervals of several minutes or more. Over time, ion current chromatograms for each mass are obtained from the repetitive measurement of distinct ion intensity. Because each analyte has a unique mass spectrum, accurate identification, and quantification of the individual components within a mixture is readily extracted from the time-dependent ion chromatogram.

In addition to the diffusion rate, the sensitivity of the membrane inlet system is also an important factor in the trace analysis. To measure the detection limits and linearity ranges of the membrane inlet system, we examined samples of air containing various concentrations of toluene, *o*-xylene, or iodomethane. This allowed us to estimate the sensitivity that can be obtained when using a membrane inlet. Fig. 6 shows the relationship between the sample concentration and the most intense peaks of toluene (m/z 91), *o*-xylene (m/z 91), and iodomethane (m/z 142) for each mass spectrum. The data fall approximately on a straight line, indicating reasonable linearity and instrumental stability. For quantitative purposes it is important that the steady-state abundances show a linear relationship with the concentration. The linear dynamic ranges for toluene (1–500 ppm), *o*-xylene (2–3000 ppm), and iodomethane (50–30000 ppm) are typically about three orders of magnitude. These wide dynamic ranges of the membrane inlet method are in good agreement with the dynamic ranges previously reported for other VOCs [34,40].

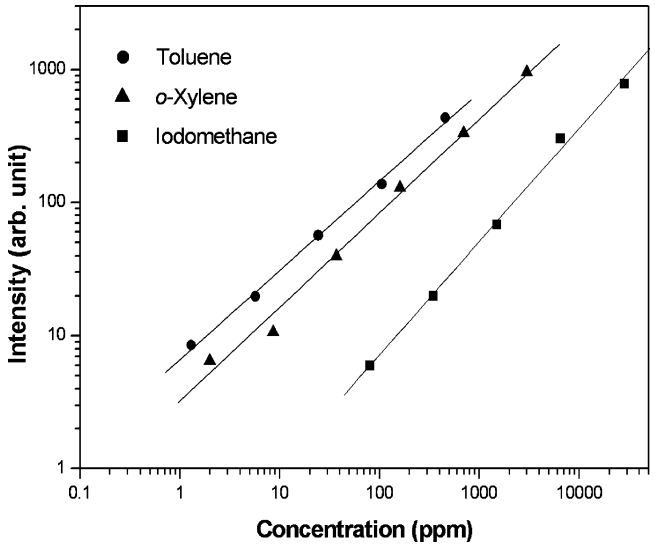

Fig. 6. Results of a typical calibration measurement of toluene (●), *o*-xylene (▲), and iodomethane (■) in air using the MIMS.

The permeability of an analyte depends on the product of the solubility and diffusion coefficients, whereas the diffusion rate depends only on the diffusion coefficient. In a recent characterization of a silicone membrane using a proton transfer reaction mass spectrometer, Märk and co-workers found that, for a homologous series of nonpolar compounds, the solubility increases and the diffusion rate decreases as the length of the carbon chain increases [38]. The lower limits for detecting toluene, *o*-xylene, and iodomethane in the present experiment were 0.06, 0.2, and 10 ppm, respectively. The lower detection limits for toluene and *o*-xylene suggest that nonpolar compounds may have a higher permeability through the membrane. Given that iodomethane has a larger diffusion coefficient, and toluene and *o*-xylene a higher permeability (the product of the solubility and the diffusion coefficient), toluene and *o*-xylene must be significantly more soluble in the silicone membrane. Similarly, analytes with longer alkyl chains have been shown to result in a lower detection limits because the solubility increases more than the diffusion coefficient decreases [38]. This implies that permeability is largely determined by the solubility of the analytes in the membrane.

4. Conclusions

In the present study, we constructed an easy-to-use membrane inlet assembly for real-time TOFMS analysis of VOCs in air. As part of evaluating the performance of this inlet assembly, we comprehensively examined the transient diffusion characteristics affecting mass transport of the analyte through a 127-μm silicone sheet membrane. The time-dependent diffusion characteristics, which were fit well by a non-steady-state flow equation, revealed that the diffusion rate increases with the size and carbon chain length of the analyte molecule. Representative aromatic hydrocarbons had detection limits at the sub-ppm level, whereas polar CH_3I compound had higher detection limit due to the hydrophobic nature of the silicone membrane. These studies show that integration of the simplicity and preconcentration capability of the membrane inlet technique with the prompt response and wide dynamic range of TOFMS will provide a powerful technique for field applications.

Acknowledgement

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