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Sheet Materials for Use as Membranes in Membrane Introduction Mass Spectrometry

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Several polymer sheets including silicone, latex, PVC, Teflon, polyurethane, polyimide, polyethylene, and nitrile were used as membranes for membrane introduction mass spectrometry (MI/MS). The relative performance of each material was explored for its potential utility in MI/MS analyses where samples are delivered via flow injection. Each of the membrane materials was tested by exposing it to separate aqueous solutions containing the analytes benzene and ethanol in order to represent the results that may be achieved for environmental analyses and fermentation monitoring, respectively. Flow injection delivery of these solutions was used to measure the relative analyte quantification limits, response times, and permeation of water as a function of temperature for each membrane material. It was observed that latex and polyurethane membranes yield MI/MS performance characteristics (in aqueous matrix) similar to those of the commonly used silicone membranes for both benzene and ethanol solutions. Polyethylene was observed to work well with benzene as an analyte and simultaneously provided improved selectivity over water. While the other materials allowed aqueous matrix MI/MS to be performed, poor quantification limits and/or slow response times made these materials undesirable for this purpose. Two membrane materials which showed especially low organic permeability and higher water permeability, polyimide and Teflon, were briefly tested with polar analytes and nonpolar solvent. For the polyimide material, the analytes acetone, acetic acid, chloroform, ethanol, ethyl acetate, and water were readily observed in hexane solvent.

In 1963, membrane introduction mass spectrometry (MI/MS) was presented as a tool for monitoring respiratory gases in situ during photosynthesis.[1] In the decade that followed, interest in the use of MI/MS was focused primarily on monitoring blood gases in vivo.[2−5] Since then, MI/MS has evolved into an important tool for the analysis of low-level volatile organics in two key analytical application areas, environmental analyses[6,7] and fermentation monitoring.[8−13] Both of these applications of MI/MS typically have utilized a silicone membrane as an interface between the sample and the mass spectrometer. The advantage of using silicone is that the volatile organic analytes selectively permeate the membrane at rates that are at least a few orders of magnitude greater than the permeation of the aqueous matrix. This difference in permeabilities facilitates direct monitoring (without any sample preparation) of volatile analytes over a wide range of concentrations in complex aqueous matrixes.

While silicone is a good membrane material, alternative permselective materials have not been systematically tested in the context of current MI/MS instrumentation or applications. The current use of silicone can be traced to the 1974 report by Westover et al.[7] which concluded, based on qualitative comparison with a limited range of materials, that silicone was the best choice of membrane material for MI/MS. The most thorough testing of different membrane materials has been carried out in conjunction with the earlier work involving analysis of gases, where silicone, latex, polyethylene, and Teflon were examined in several studies.[1−5] However, most of these studies involved the analysis of only O_2 and CO_2 in vivo in blood, and much of the emphasis was given to the size, durability, flexibility, and construction of the membrane probe.[2−5] In the decades that have passed, MI/MS interfaces,[14−16] mass spectrometers,[8,16,17] and the common MI/

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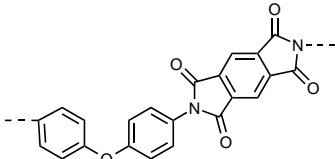(12) Degn, H. *J. Microbiol. Methods* **1992**, *15*, 185.
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Table 1. Materials Tested as Membranes for MI/MS

membrane material	chemical structure	thickness	supplier	product name
silicone	poly(dimethylsiloxane)	5 mil (125 μm)	Dow Corning	Silastic sheeting
latex (Flexam)	polyisoprene (*cis*-1,4-)	0.9 mil (23 μm)	Baxter	Flexam latex gloves
latex (Hygenic)	polyisoprene (*cis*-1,4-)	4 mil (100 μm)	Hygenic	natural latex sheeting
polyethylene	polyethylene	1.5 mil (38 μm)	Baxter	diSPo polyethylene gloves
polyurethane (polyether)	copolymer of 4,4-methylenediphenyl diisocyanate, 1,4-butanediol, and poly(tetramethylene ether diol)	1 mil (25 μm)	Deerfield Urethanes	Duraflex polyurethane PT 6100 S
polyurethane (polyester)	proprietary polyester-type polyol	1 mil (25 μm)	Deerfield Urethanes	Duraflex polyurethane PS 8010
nitrile	copolymer of acrylonitrile and butadiene	3 mil (75 μm)	Ansell Edmont	Nitratouch gloves
PVC	poly(vinyl chloride)	5 mil (125 μm)	Baxter	diSPo PVC gloves
polyimide		1 mil (25 μm)	DuPont	Kapton H film
Teflon	copolymer of tetrafluoroethylene and hexafluoropropylene	0.5 mil (13 μm)	DuPont	Teflon FEP film

MS applications[18] all have undergone extensive changes, while the permselective membrane material used in MI/MS (silicone) has remained essentially constant. Given the extensive changes, silicone may no longer be the most appropriate membrane material for MI/MS.

In this paper, we describe the quantitative comparison of the relative performances for 10 permselective membrane materials examined under some typical MI/MS analysis conditions using flow injection sample delivery. The 10 membrane materials compared are listed in Table 1. In order to represent the results that may be achieved for environmental analyses and fermentation monitoring, these membrane materials were tested with separate aqueous solutions of benzene and ethanol. With these solutions, the quantification limits, response times, and relative selectivity over water have been measured as a function of membrane temperature. The result of this work is that we have found several membrane materials (in addition to silicone) which are suitable for MI/MS analyses. Furthermore, we have discovered unique permselective properties in some of the membrane materials that should allow them to be especially useful in some specific MI/MS applications.

EXPERIMENTAL SECTION

Mass Spectrometer. The mass spectrometer used in this work was a Finnigan TSQ 45 triple-stage quadrupole mass spectrometer with the vacuum manifold held at 100 °C. The instrument was equipped with an electron impact (EI) ion source (held at 190 °C) and was used in the single-stage mass spectrometer mode. Data were acquired by the standard Data General Nova 4X data system with version 6.1 INCOS software. All experiments were carried out over a 6 week period without adjustment or maintenance of the instrument. The mass spectrometer was equipped with the standard calibration gas inlet. The calibration gas perfluorotributylamine (FC-43) was used as an external standard for all measurements.

Membrane Interface. A schematic of the membrane interface is shown in Figure 1. The membrane is positioned between

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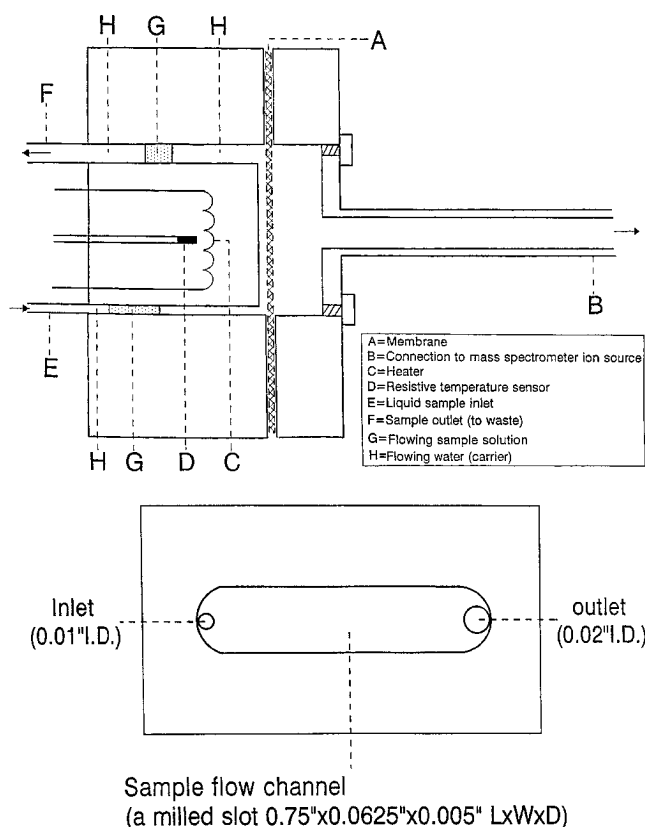
Figure 1. Schematic of the membrane interface used in the experiments to test different potential membrane materials. Bottom: A view from the plane of the membrane of the volume where sample is exposed to the membrane.

two machined stainless steel blocks. The entire interface is heated under the control of the Finnigan data system by a four-element heater (Finnigan P/N 40005-60270), and temperature was monitored by a Pt resistive temperature sensor (Finnigan P/N 40005-60230). The heaters are placed 7/16 in. away from the solution flow channel, and the temperature sensor is placed 1/32 in. away from the center of the flow channel. The locations of the heaters and sensor combined with the fact that the interface is a 1 kg block of stainless steel, ensure that heating of the interface is uniform.

The bottom of Figure 1 shows the volume exposed to the solution flow across the membrane. The dimensions of the milled

slot are intended to maximize the ratio of the membrane surface area (exposed to the sample solution) to sample volume (exposed to the membrane) in order to maximize the delivery (contact) of analyte to the membrane (i.e., the thin-layer approach[19]). As the solution progresses through the interface, the cross-sectional area of the flow path increases so that back pressure on the membrane (if any) is minimized. The outlet normally is located in the uppermost position so that any gas bubbles may easily pass through the interface.[20]

The membrane interface is located outside the mass spectrometer, 16 in. away from the ion source. The membrane interface is connected by a Swagelock union to a 0.5 in. o.d. × 0.25 in. i.d. transfer tube which is inserted into the probe inlet and connects the interface to the ion source of the Finnigan TSQ 45. The end of the transfer tube is shaped such that a tight connection is maintained with the ion volume. The transfer tube is heated indirectly by contact with the 190 °C ion source at one end, contact with the membrane interface at the other end, and enclosure by the 100 °C vacuum manifold through most of the middle portions. Complete characterization of the interface, described elsewhere, suggests there is no loss of mass transfer efficiency using the 16 in. transfer tube relative to interfaces that locate the membrane at the ion source.[20]

In this work, 10 different membrane materials were evaluated. The membranes, thicknesses, and sources are listed in Table 1. The membranes were washed with HPLC grade water and then with high-purity hexanes from Aldrich. The water was used to remove any salts or particulates and the hexane to remove any volatile organics that may be present in the membrane or adsorbed on the membrane surface.

Other Apparatus. Degassed HPLC grade water from Baxter was used as a carrier stream for flow injection experiments and was pumped across the membrane by a Spectra Physics SP8700XR gradient LC pump. The use of degassed water allows the LC pump to deliver highly accurate and stable flow rates. A Micromeritics 725 autosampler equipped with a pneumatic Rheodyne 7010 sampling valve and fitted with a 200 μL loop was used for automated flow injection sample delivery.

Experimental Procedures. Benzene and ethanol (from Aldrich) stock solutions were prepared using degassed HPLC grade water. Solutions of different concentrations were prepared by further dilution of the stock solutions. Benzene solutions were prepared from 0.01 ppb to 0.1% (limited by solubility of benzene in water), and ethanol solutions were prepared from 10 ppb to 10% (each of the concentrations stepping up in factors of approximately 3). All sample solutions were introduced via flow injection. The use and importance of flow injection sample delivery in MI/MS has been described elsewhere.[9,20] Quantification limits were determined by adjusting the analyte concentrations to obtain a signal-to-noise ratio of 15, where the signal is defined as the height of a 200 μL flow injection peak (aqueous carrier at 1.0 mL/min) and the noise as the root-mean-squared (RMS) range of the baseline.[20] In testing the quantification limits, lower concentrations were tested first, and the concentrations were stepped up to higher levels. Response times were measured as the full width at half-maximum (fwhm) time for a 200 μL flow injection peak (aqueous carrier at 1.0 mL/min).[20] The fwhm of

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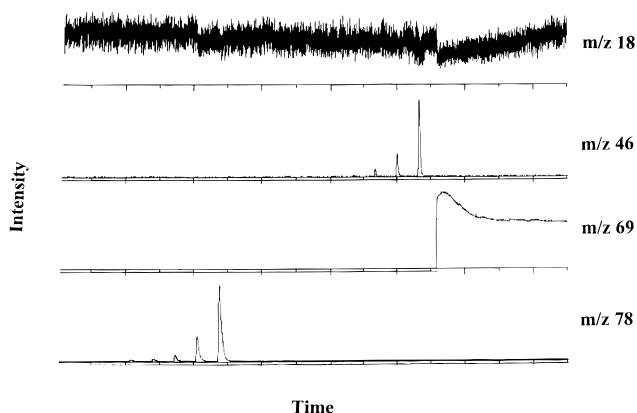(20) Dongre, A. R.; Hayward, M. J. *Anal. Chim. Acta*, in press.

Figure 2. Example of the data obtained during a single experiment to measure the performance characteristics of polyurethane at 60 °C. The ethanol (*m/z* 46) and benzene (*m/z* 78) peaks shown are for concentrations stepping up in factors of 3, where 200 μL injections are performed every 5 min. The calibration gas (*m/z* 69) was switched on after all of the benzene and ethanol solutions had been injected.

the flow injection profile for benzene was independently measured using an ABI 783 UV/visible absorbance detector operated at 254 nm and was found to be 14 s.

Each membrane material was tested in series of four experiments performed at each of the following four temperatures: 30, 40, 50, and 60 °C. Each experiment was carried out as follows: First, the entire series of benzene solutions (0.01 ppb to 0.1%) were injected one at a time in 5 min intervals via automated flow injection, starting with the lowest concentration and stepping up (in factors of approximately 3) to the highest. The entire series of ethanol solutions (10 ppb to 10%) were then injected one at a time in 5 min intervals via automated flow injection, starting with the lowest concentration and stepping up (in factors of approximately 3) to the highest. Finally, FC-43 was introduced via the standard calibration gas inlet until a sustained steady state signal for CF_3^+ was recorded. EI was used to monitor benzene, ethanol, FC-43, and water without interferences in the selected ion monitoring (SIM) mode with the following scan times: 0.001 s for *m/z* 18 (as the H_2O signal is far more intense), 0.1 s for *m/z* 69, 0.5 s for *m/z* 46, and 0.5 s for *m/z* 78. Figure 2 shows representative data from an individual experiment carried out as described above. The scaled SIM measurements are required in order to simultaneously measure the large signals from the H_2O and the small signals from benzene and ethanol. The *m/z* 31 for ethanol was not used because overlap from *m/z* 32 from O_2 background makes this measurement difficult. The calibration gas signal was used as an external standard to allow any drift in the mass spectrometer sensitivity to be accounted for in the comparisons between each experiment. The mass spectrometer sensitivity was found to slowly decrease by about 30% during the course of the experiments. By later repeating the experiments, it was found that using the FC-43 signal to correct for drift yielded results that agree within 5% or better of each other. All data reported are averaged, FC-43-corrected results normalized to the absolute values obtained for the silicone membrane.

RESULTS

Aqueous Matrix MI/MS. Quantification limits, response times, and water responses have been systematically measured for the 10 potential membrane materials described in Table 1. The flow injection mode of sample delivery[8] was used in these

Table 2. MI/MS Characteristics at 60 °C for 10 Membranes

membrane material	ethanol quantification limit[a] (ppm)	ethanol response time[b] (s)	selectivity ethanol[c]	benzene quantification limit[a] (ppb)	benzene response time[b] (s)	selectivity benzene[c]	water response[c]
silicone	36	19	1.0	2.8	20	1.0	1.0
latex (Flexam)	58	16	0.90	13	22	0.31	0.56
latex (Hygenic)	32	19	0.90	56	23	0.031	1.1
nitrile[d]	310	22	0.045	83	63	0.015	1.5
PVC	4200	82	0.011	1900	180	0.0019	2.0
polyimide	180	120	0.082	not observed	not observed	not observed	0.27
Teflon	2600	550	0.013	13000	56	0.00020	2.4
polyurethane (polyether)	19	16	0.69	49	18	0.017	1.9
polyurethane (polyester)	19	16	0.96	60	22	0.029	1.4
polyethylene	440	37	5.5	41	18	4.8	0.010

[a] Quantification limits are the concentration that yields S/N = 15 for a 200 μL injection into a 1 mL/min carrier stream of water. [b] Response times are measured as fwhm for a 200 μL injection into a 1 mL/min carrier stream of water. [c] Values are relative to those for the silicone membrane. [d] Values are given for the 40 °C experiment. Nitrile is not mechanically stable at 50 °C and above.
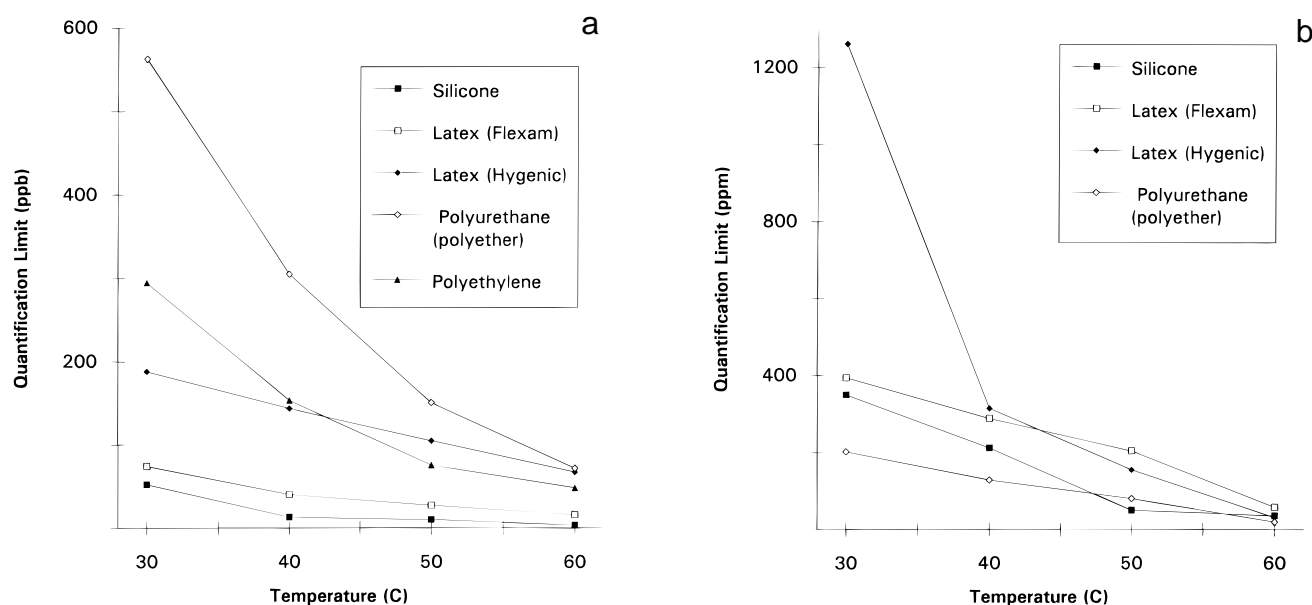

Figure 3. Quantification limits as a function of temperature for each of the most promising membranes tested using 200 μL sample injections of benzene (a) and ethanol (b) into a 1 mL/min aqueous carrier stream.

measurements because of its practical importance (speed, sample economy, ease of automation, and quantitative accuracy) in routine MI/MS analysis.[9,20] Furthermore, flow injection is among the most reproducible ways to consistently deliver analyte to the MI/MS interface so that comparative measurements can be performed with maximum precision.[8,9,20] Evaluation of these measurements, particularly the quantification limits, should be considered only as relative to the similar measurements presented here for the other membranes. Recent work has shown that sensitivity and detection limits can vary by several orders of magnitude depending on the mass spectrometer chosen.[21] The triple quadrupole instrument used in this work probably represents a worst case in sensitivity, where as an ion trap would probably yield the lowest detection limits.[20] In this work, we accepted the sensitivity of the mass spectrometer without applying any effort to improving it. Instead, we focused our attention on standardizing each measurement and achieving the highest reproducibility possible so that comparison of the membrane materials could be performed under constant (and well-defined) conditions. Note that the thickness of the membrane materials tested spans a full order of magnitude.

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While it would seem ideal to use the same thickness in all cases, no attempt has been made to correct results to a single thickness for the following three reasons: (i) in several cases, the only thicknesses available for the material were those which were tested, (ii) sufficient data (for these materials) do not yet exist to assume ideal behavior over a full order of magnitude difference in thickness, and (iii) the thinnest possible membrane (while retaining its structural integrity, i.e., resistance to breakage during use) is desired for MI/MS analysis.[20] Since unsupported silicone membranes seem to be limited by the structural integrity to about 5 mil (125 μm), suitable structural integrity at smaller thicknesses is viewed as a performance improvement.

Table 2 shows the relative performance characteristics at 60 °C for each of the membranes tested in aqueous matrix. These results can be used to initially determine which membranes are not appropriate for use with aqueous matrix MI/MS. The nitrile membrane was not suitable for use with MI/MS because it is not mechanically stable at elevated temperatures (~50 °C). In addition, the PVC, polyimide, and Teflon membranes were not suitable for MI/MS use because they exhibit poor quantification limits and long response times. Furthermore, the quantification limit and response time experiments for ethanol with polyethylene

suggest that this membrane may not be suitable when using MI/MS for fermentation monitoring. In contrast, the polyethylene membrane performs well (low quantification limit and response time) with benzene, suggesting that it may be useful for environmental analyses with MI/MS. The silicone, latex, and polyurethane membranes exhibit excellent MI/MS performance characteristics with both ethanol and benzene. Based on these results, we believe that silicone, latex, polyethylene, and polyurethane (polyether) are good candidates for further consideration as potentially useful membranes for MI/MS. In the paragraphs that follow, the performance characteristics of these potentially useful membranes are examined in greater detail.

Membrane temperature is known to be an important parameter in achieving optimal MI/MS performance.[15,17,20,22] Similarly, an important characteristic for the further consideration of the potentially useful membrane materials is the variation in the relative quantification limits as a function of membrane temperature. Figure 3 shows quantification limits for ethanol and benzene as a function of temperature for the most promising of the membranes tested. While the polyurethane (polyester) membrane performs well at 60 °C, its performance is poor at lower temperatures. Including data for polyurethane (polyester) in this and the remaining figures would not permit the temperature trends for the other membranes to be readily observed. Therefore, polyurethane (polyester) is not considered to be an appropriate alternative membrane material for the MI/MS performance comparisons described here.

The observed benzene quantification limits (Figure 3a) suggest that silicone yields better quantification limits throughout the 30−60 °C range. However, there is very little difference in benzene quantification limits between the silicone and latex (Flexam) membranes, with the two consistently tracking each other throughout the temperature range examined. While the polyethylene, polyurethane (polyether), and latex (Hygenic) yielded significantly poorer benzene quantification limits at lower temperatures (∼30 °C), these values were similar to those for the silicone and latex (Flexam) at higher temperatures (∼60 °C). The observed quantification limits for ethanol (Figure 3b) suggest that polyurethane (polyether) yields better quantification limits throughout most of the 30−60 °C range. However, throughout the 30−60 °C temperature range, the differences in ethanol quantification limits for the latex (Flexam), polyurethane (polyether), and silicone membranes are not large. The latex (Hygenic) membrane also yields similar performance for ethanol quantification limits at elevated temperatures (40−60 °C).

Another important characteristic for the further consideration of the potentially useful membrane materials is the variation in the relative response times as a function of temperature. Figure 4 shows response times for ethanol and benzene as a function of temperature for the most promising of the membranes tested. The observed benzene response times (Figure 4a) suggest that silicone yields better response times throughout the 30−60 °C range. However, there is very little difference in benzene response times between the latex (Hygenic) and silicone membranes, with the two consistently tracking each other throughout the temperature range examined. While the polyurethane (polyether), latex (Flexam), and polyethylene yielded somewhat longer benzene response times at lower temperatures (∼30 °C), these values were similar to those for the silicone and latex (Hygenic) at higher
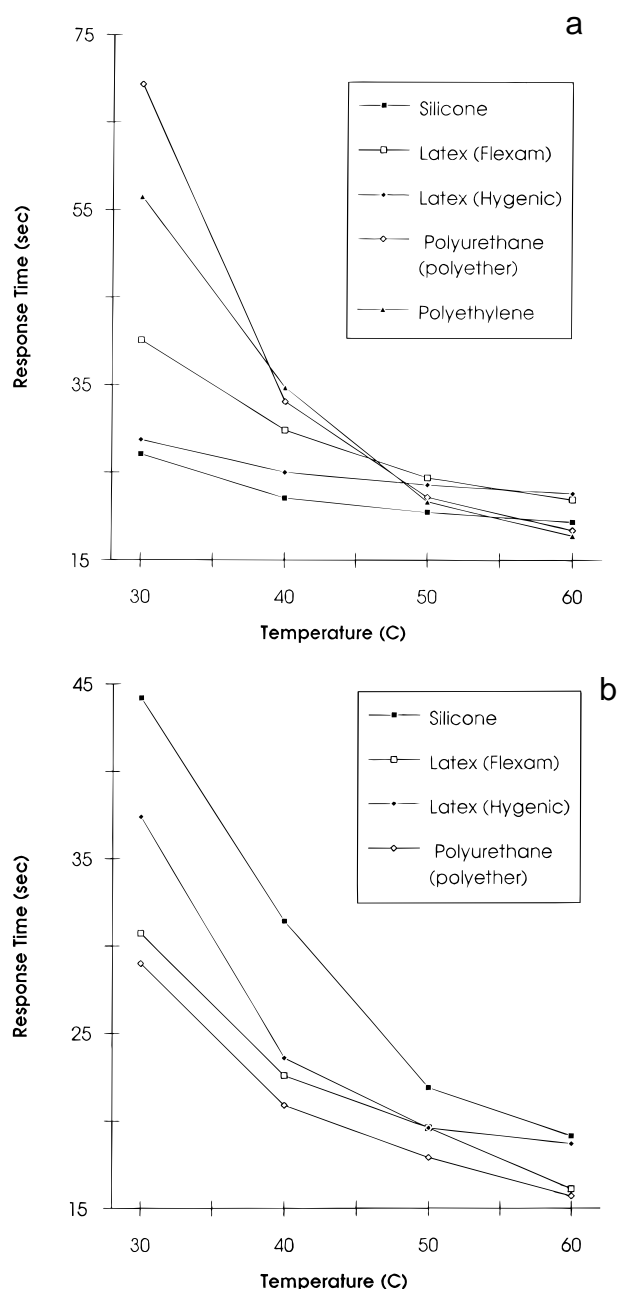
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Figure 4. Response times as a function of temperature for each of the most promising membranes tested using the analytes benzene (a) and ethanol (b). Response times were measured as the full width at half-maximum (fwhm) for the flow injection profile resulting from 200 μL injections into a 1 mL/min aqueous carrier stream.

temperatures (∼50−60 °C). The observed response times for ethanol (Figure 4b) suggest that polyurethane (polyether) yields better response times throughout most of the 30−60 °C range. However, the ethanol response times for the polyurethane (polyether) and latex (Flexam) membranes are very similar throughout the 30−60 °C temperature range. The latex (Hygenic) membrane also yields similar performance for ethanol response times at elevated temperatures (40−60 °C). It is interesting that the temperature trend for the alternatives to silicone seems to behave in a manner opposite to that of silicone.[20] The alternative membrane materials have larger changes in response times as a function of temperature (higher pervaporation activation energies) for benzene, whereas silicone has larger changes for ethanol. These results suggest a greater solubility of ethanol and lower benzene solubility in the alternatives relative to silicone.

Table 3. Membrane Materials Suitable for MI/MS Analysis of Aqueous Matrix Samples and Their Relative Performance Levels in a Variety of Categories[a]

	performance characteristic			
	fermentation monitoring[b]	environmental analyses[c]	selectivity over water (30 °C)	selectivity over water (60 °C)
membrane materials giving best performance[a]	1. polyurethane (polyether)	1. silicone	1. latex	1. polyethylene
	2. latex	2. latex	2. silicone	2. silicone
	3. silicone	3. polyethylene		
		4. polyurethane (polyether)		

[a] Listed in order of performance level with the best listed first. [b] Based on quantification limits and response times for ethanol. [c] Based on quantification limits and response times for benzene.

Based only on the quantification limits and response times, silicone membranes appear to provide the best performance for environmental applications, where compounds like benzene would be examined. For the application of fermentation monitoring, where compounds like ethanol would be examined, polyurethane (polyether) membranes appear to provide the best quantification limit and response time performance. For both applications, latex membranes provide comparable quantification limit and response time performance throughout the 30−60 °C temperature range tested. However, there is another performance consideration, permeation of the aqueous matrix, that may be important to the utility of MI/MS.[20] Limiting the admission of water is especially critical to the performance of MI/MS with dynamic range-limited mass spectrometers such as ion traps.[17,23] As a result, momentum separation devices recently have been employed in between some membrane interfaces and mass spectrometers in order to reduce the amount of water entering the mass spectrometer.[16] Given the potential importance of membrane selectivity, the response for water also was measured during all tests of each of the membranes. Figure 5 shows the relative water responses as a function of temperature for the most promising membrane materials tested. At lower temperatures, the latex (Hygenic) and polyurethane (polyether) membranes tend to have lower permeation of water. For the polyurethane (polyether) membrane at lower temperatures, the selectivities (relative to silicone) are low because the permeability of the analytes also is low. However, the latex membranes have the highest selectivity of benzene and ethanol at 30 °C, about 1.8 times that of silicone, because the analyte permeabilities remain relatively high. Perhaps even more interesting is the polyethylene membrane, where the permeation of water decreases with increasing temperature. This decrease is quite substantial in that, at 60 °C, silicone permits the admission of 100-fold more water to the mass spectrometer than does polyethylene. We attribute this trend to the hydrophobic effect,[24] where the free energy of solvation of water in polyethylene is dominated by entropic considerations. Polyethylene's rejection of water also is consistent with its lower (poor) performance with the polar analyte ethanol. The result of the hydrophobic effect for the polyethylene membrane is that the analyte selectivity over water is roughly 5 times that of the silicone membrane at 60 °C. These results suggest that latex (Flexam) and polyethylene have a clear selectivity (over water) advantage relative to the silicone membrane.

Organic Matrix MI/MS. An area of recent interest in MI/MS is the permselective introduction of polar compounds in
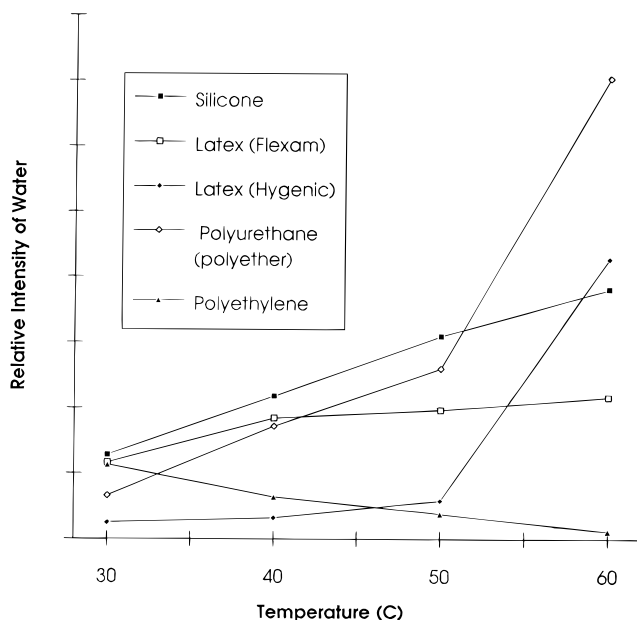

Figure 5. Relative response of water permeating the membrane over a 30−60 °C temperature range for the most promising membranes tested. The decreasing permeation of water with increasing temperature for the polyethylene membrane leads to improved benzene selectivity over water relative to the other membrane materials.

organic matrix.[25,26] After observing the very low benzene permeabilities for Teflon and polyimide, it seemed appropriate to briefly qualitatively test these two materials for permselective introduction of polar compounds in organic matrix. In order to test the Teflon and polyimide membranes for use with an organic matrix, acetone, acetic acid, chloroform, ethanol, ethyl acetate, and water were each dissolved (500 ppm) in hexane and injected into a 1 mL/min hexane carrier stream flowing past these two membranes. With either membrane, the hexane carrier permeated the membrane enough to produce a significant background signal in the mass spectra. As a result each of the spectra observed (in the EI mode) had some CI characteristics ([M + H]⁺ ions). Acetone, ethyl acetate, and water were readily observed with the Teflon membrane, but acetic acid, chloroform, and ethanol were not. For the polyimide membrane, all six analytes were observed. These preliminary results suggest that the polyimide membrane may be useful for permselective MI/MS of polar compounds in organic matrix.

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CONCLUSIONS

The results of comparing potential MI/MS membrane materials suggests that there are several alternatives to the traditional silicone membrane material. One possible alternative is polyimide for permselective MI/MS of polar compounds in organic matrixes. Table 3 lists the alternative membrane materials that performed best in a variety of categories for the more common aqueous matrix. While the silicone membrane material is an excellent all-around performer, its performance is closely mirrored in all categories by the far easier to obtain latex materials. In fact, at elevated temperatures (~60 °C), where the best performance is observed, the silicone, latex, polyurethane (polyether), and polyethylene all perform comparably. For the specific application of fermentation monitoring in the MI/MS configuration tested, polyurethane (polyether) membranes provide the best quantification limits and response times. For the specific application of environmental analyses in the MI/MS configuration tested, silicone membranes provide the best quantification limits and response times. However, selectivity over water also may be an important performance consideration for MI/MS,[20] especially in dynamic range-limited mass spectrometers.[17,23] At lower temper-atures (~30 °C), latex membranes provide the highest selectivity, while polyethylene, under the influence of the hydrophobic effect,[24] provides the highest selectivity at elevated temperatures (~60 °C). The advantage of these higher selectivities (especially those of polyethylene) may be as an alternative to the use of momentum separation between the membrane interface and the mass spectrometer[16] or that they could be readily utilized by changing the membrane dimensions (decreased thickness or increased surface area) to increase analyte flux. For example, the membrane surface area for a polyethylene membrane could be increased (or thickness decreased, also reducing response times, structural integrity permitting) 100-fold in order to increase the analyte flux 100-fold at 60 °C while admitting no more water than a silicone membrane 1/100 its size.