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Valved Sampling Cell for Membrane Introduction Mass Spectrometry

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Membrane extractors comprising a membrane house inside of a valve have been developed to separate compounds of interest from a sample matrix and introduce these compounds into a mass spectrometer. Experimental control over parameters that affect permeability or that may damage the membrane, such as the membrane temperature, is provided with the valve. The valve was tested for response and response times with the valve separated from the mass spectrometer by various interface tube lengths. Data for steady state response measurements showed no significant change with the valve at different distances from the ion source. Polar compounds show a strong response time dependency on the interface tube length. This adsorption phenomenon is minimized by simply heating the interface tube. Other factors affecting the performance of the device are discussed.

A variety of membrane introduction (MI) devices have been developed to separate compounds of interest from a sample matrix and introduce these compounds into a mass spectrometer (MS).[1−14] The selectivity of the MIMS techniques allows for real-time analysis of low-level components in complex matrices including wastewater[2−6] and biological fermentation broths.[5,7−9] On-line analysis with MIMS can provide chemical reaction data[10−13] that can not be obtained with off-line techniques.

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A membrane extractor comprising a hollow fiber or sheet membrane housed inside a valve is described below. In the MI valve, the sample comes into contact with one surface of the membrane, and the compounds of interest selectively permeate through the membrane and into the valve cavity, which is exposed to the mass spectrometer vacuum. The ability to use either hollow fiber or sheet membranes is advantageous. Hollow fiber membranes provide greater extraction efficiencies than do sheet membranes because of the greater membrane surface-to-sample volume ratio and the higher sample linear velocities obtainable.[4] However, sheet membranes are available in a wider variety of materials and dimensions. Experimental control over parameters that affect permeability or that may damage the membrane, such as the membrane temperature, is provided with the MI valve.

A solenoid MI valve can be activated through the MS vacuum gauge controller so that, in the event of a ruptured membrane, the pressure surge would immediately result in the valve closing, minimizing the amount of the sample flowing into the mass spectrometer. This is of particular concern in process applications where the membrane may degrade by physical, chemical, or thermal means. Leaks may also occur due to failure of seals used to attach the membrane to the MI device. The surface area and void volume of the sample−MI interface and the MIMS interface should be minimized. Interface tubing, fittings, valves, and the MI device that contribute to the surface area and void volume are minimized with the MI valve. In processes where highly reactive analytes[11] or reaction kinetics[13] are to be measured, the shortest distance possible between the sample and the analyzer is desired to minimize loss of the analyte or skewing of the reaction profile. In applications where it is desirable to monitor multiple streams of gas and liquid process streams,[5] MI valves may be multiplexed. A description and evaluation of the MI valve are described below.

EXPERIMENTAL SECTION

Chemicals. Gas samples were prepared with reagent-grade solvents from Fisher Scientific in a 5-L Saran bag filled with air.

Apparatus. Samples were pumped through the MI valve at 100 cm^3/min by attaching one of the valve sample ports to the sample bag and attaching the other sample port to a vacuum pump. The solenoid for the MI valve was energized with a Heathkit regulated low-voltage power supply, Model IP-27. The data reported in this study were obtained using three different

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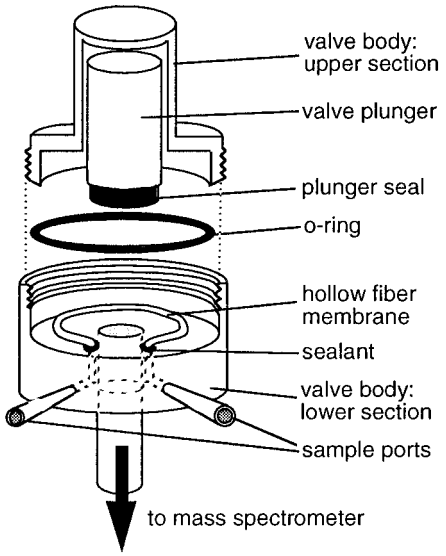

Figure 1. Exploded view of the hollow fiber membrane introduction valve.

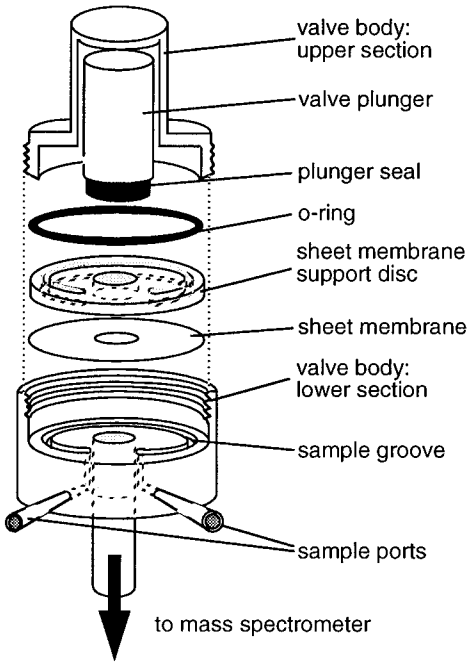

Figure 2. Exploded view of the sheet membrane introduction valve.

mass spectrometers. The MI valve was interfaced via $^1/_8$-in.-o.d. stainless steel tubing to the ion source of a Balzers QMG 511 mass spectrometer and a Hewlett-Packard 5971-A MSD modified for process analysis applications.[15] The MIMS interface was also made with a Finnigan TSQ-70B via the direct insertion probe described below.

DESCRIPTION OF DEVICE

An exploded view of the hollow fiber MI valve is shown in Figure 1. This MI device consists of two sections—upper and lower—of the valve body, a valve plunger, a hollow fiber membrane, and some sealant for attaching the membrane to the valve body. The lower section of the valve body was fabricated to fit the upper section and plunger from commercially available solenoid valves (1X259 24VDC normally closed solenoid valve from Kip Inc.). The lower section of the valve body is provided with two ports through which samples are pumped into the valve body, through the hollow fiber membrane, and out of the valve body. The membrane is a 2.5-cm length of 0.0305-cm-i.d., 0.0635-cm-o.d. Silastic medical grade tubing from Dow Corning Corp. The hollow fiber membrane is sealed into the two sample port openings in the valve with Dow Corning RTV 734 Silastic sealant. The compounds of interest selectively permeate through the membrane and into the valve cavity. The permeate stream flows into the mass spectrometer for analysis.

The sheet MI valve design in Figure 2 shows that the two sample ports are connected internally by a groove. The membrane lays across this groove, separating the sample from the valve cavity. The preferred method for sealing the sheet membrane in the valve is to "sandwich" the membrane between the valve body and a donut-like disk as shown in Figure 2. A groove through the disk corresponds to the sample channel in the valve body and provides a passage for permeating materials to enter the valve cavity.

The MI valves were mounted to a $^1/_2$-in. (1.27-cm)-o.d. direct insertion probe (DIP) with an internal $^1/_8$-in. (0.32-cm)-o.d., 0.22-cm-i.d. stainless steel tube conducting the gases from the valve to the ion source. The MIMS interface was made via the DIP inlet of the mass spectrometer. Both the hollow fiber and the sheet MI valves were successfully evaluated. The results given below were obtained with the hollow fiber MI valve.

RESULTS AND DISCUSSION

Measurement of Response. Both analytical responses and response times were obtained using the MI valve. The response time for each component was defined as the time required to reach 50% of the steady state signal, t_{50}, following a step change in sample concentration at t_0.[4] These response times were compared with the experimental rise time from t_{10} to t_{90} to describe the response time of the membrane introduction technique. If Fickian behavior is observed, then the correlation of t_{50} to this rise time time can be approximated from the mathematical solution for the permeation rate curve[4] to be

$$[t_{90} - t_{10}] = 0.6[t_{50} - t_0]$$

The analytical response was obtained from the measurement of the steady state permeation rate. The response and the response times were obtained with the MI valve separated from the MS by interface tube lengths of 40, 70, and 100 cm. At least two phenomena associated with the MIMS interface tube may result in extended response times and decreased sensitivity: adsorption of the permeating materials on the interface tube and poor conductance into the ionization region of the MS. The effects of both of these phenomena are addressed below.

Effects of Length of MIMS Interface on Response. The membrane not only serves to separate the components of interest from the sample matrix but also provides the necessary pressure drop from the ambient pressure sample to the high vacuum in the mass spectrometer. This large pressure drop is due to the small flow rates of components through the membrane. For example, the permeabilities[16] and flow rates through the mem-

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Table 1. Permeabilities and Flow Rates for Gases Through a Silicone Membrane[a]

compound	concentration by volume	permeability, $cm \cdot cm^2/(cm \cdot s \cdot c_i)$	flow rate (STP), cm^3/s
nitrogen	100%	2.1×10^{-6}	4.6×10^{-5}
dichloromethane	100 ppm	7.4×10^{-4}	1.6×10^{-7}
toluene	100 ppm	2.0×10^{-3}	4.4×10^{-7}
acetone	100 ppm	5.4×10^{-4}	1.2×10^{-7}
1-butanol	100 ppm	1.1×10^{-3}	2.4×10^{-7}

[a] The membrane is a 2.5-cm-long, 0.0305-cm-i.d., 0.0635-cm-o.d. silicone hollow fiber.

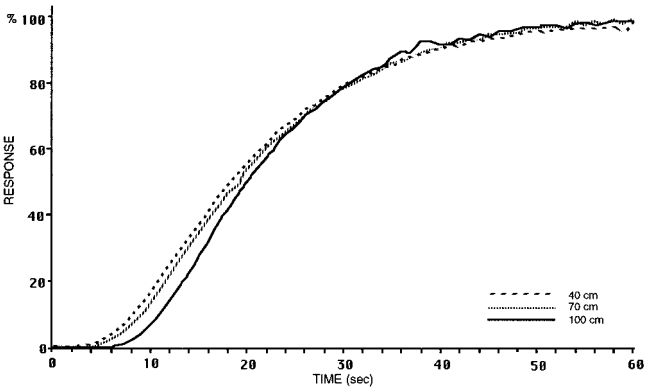

Figure 3. Effect of interface tube length on the response curves for *m*/*z* 92 following a step change in the concentration of toluene in air.

brane are given in Table 1 for nitrogen, dichloromethane, toluene, acetone, and 1-butanol. The organic compounds are assumed to be 100 ppm by volume in a nitrogen matrix. These values were determined from the solution for a hollow fiber to Fick's first law of diffusion:

$$F_i = 2\pi LP_i c_i / \ln(\text{o.d.}/\text{i.d.})$$

where F_i is the flow rate of component i, L is the length of the hollow fiber membrane, P_i is the permeability of component i, c_i is the concentration of component i in the sample, and o.d. and i.d. are the outer and inner diameters of the hollow fiber membrane, respectively.

Since the permeate side of the membrane is under high vacuum, molecular flow conditions prevail in the interface tube. In the two-step process of diffusion through an amorphous polymer followed by molecular flow through a tube, the diffusion step will be rate limiting. Since the analytical response for a component is dependent upon the conductance of the component into the ion source, then any effect that the interface tubing might have on conductance would be observed in both the response and the response time. Data for steady state response measurements for dichloromethane, toluene, acetone, and 1-propanol showed no significant change with the hollow fiber MI valve at distances of 40, 70, and 100 cm from the ion source.

Effects of Analyte Adsorption. No significant effect of interface tube length on response time for toluene was observed, as illustrated by the response curves in Figure 3. Plots of response time versus interface tube length for dichloromethane, toluene, acetone, and 1-butanol are shown in Figure 4. Only 1-butanol show a dependency on the tube length, as illustrated in Figure 5.

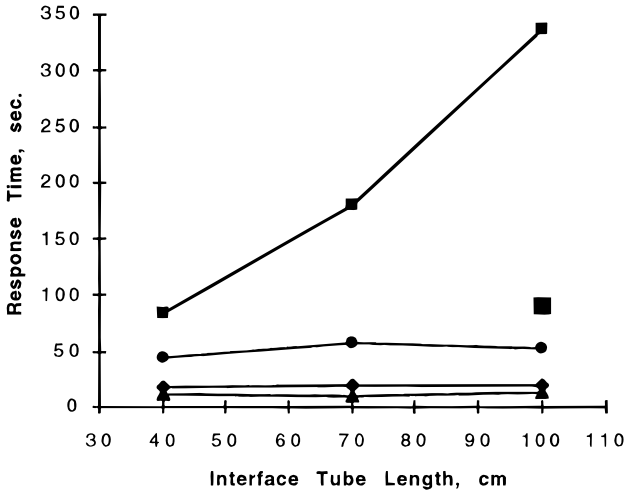

Figure 4. Response time versus MIMS interface tube length for (■) 1-butanol, (○) acetone, (◆) toluene, and (▲) dichloromethane. The large square indicates the response time measurement for 1-butanol with the interface tube heated to 150 °C.

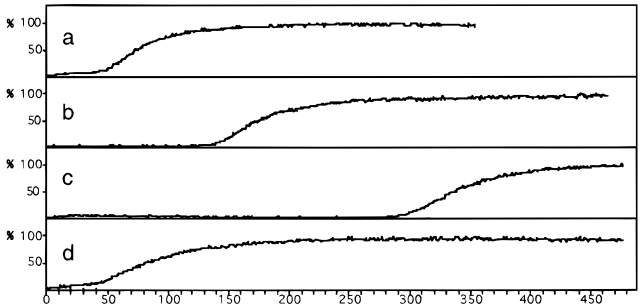

Figure 5. Response curves for 1-butanol (*m*/*z* 56) with different lengths of MIMS interface tube lengths: (a) $l = 40$ cm, (b) $l = 70$ cm, (c) $l = 100$ cm, (d) $l = 100$ cm; 150 °C. The measurements for a–c were obtained with the interface tube at 23 °C.

Table 2. Comparisons between Response Time ($t_{50} - t_0$) and Rise Time ($t_{90} - t_{10}$) for 1-Butanol

interface tube length, cm	$t_{50} - t_0$, s	$t_{90} - t_{10}$, s
40	75	95
70	180	100
100	340	100
100 (150 °C)	80	110

This pronounced dependency on the interface tube length or, more precisely, on the interface tube surface area for alcohols has also been reported by Lauritsen.[17] In the present study, this adsorption phenomenon is shown to be minimized by simply heating the interface tube, as demonstrated by plot d in Figure 5.

Fickian behavior is not observed when adsorption/desorption of the analyte on the membrane or analyzer is the rate-limiting step to attain steady state. Values for the rise time and t_{50} are given in Table 2 for 1-butanol. These data illustrate that the rise time is relatively constant and independent of t_{50} for this compound. The most useful characterization of analytical response time should provide a reference to the sample, e.g., $t_{50} - t_0$ or $t_{90} - t_0$, in addition to the rise time.[8]

Another major factor that has not been addressed in the above discussion is the effect that the mass spectrometer may have on the response time. The geometry of the ion source and the

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Table 3. Effects of Analyzer Conductance on Response Time

analyzer	response time, s	
	dichloromethane	toluene
Finnigan TSQ-70	11	14
HP 5971-A MSD	10	11
Balzers QMG-511	20	35

vacuum chamber may have a significant effect on the response time that is independent of the membrane extractor and interface tube. The response times for dichloromethane and toluene are given for three different mass spectrometers in Table 3. Whereas the response time data collected with the MSD and the TSQ are comparable, the response times measured with the Balzers instrument are significantly longer. This phenomenon is presumably due to poor sample gas conductance through the 0.08-cm orifice in the Balzers gas-tight ion source to which the $^1/_8$-in. MIMS interface tube is connected. The interfaces to the MSD and the TSQ-70 ion sources are more open.

The MI valve possesses a unique combination of attributes for an extraction/sampling device. The MI valve combination provides small void volume and surface area relative to a membrane extractor and valve in series. The void volume in the MI valves (1 cm^3) did not cause an excessive pressure surge in the MS when the valve was opened. The MI valve may be placed as close as possible to either the process or the analyzer, depending upon the requirements of the analysis. Although it may be desirable to minimize the distance between the MI and the MS, this distance is not generally a transport-rate-limiting parameter. The interface tube is typically heated independently of the MI valve to prevent adsorption.

The temperature of the membrane and flow rate of the sample may be well controlled, and the solenoid in the MI valve may be activated through the vacuum-protection circuit of the mass spectrometer so that, in the event of a ruptured membrane or failed seal, the mass spectrometer can be instantly isolated from the sample. The MI valve may be useful in multiple stream sampling where each sample stream requires a separate MI device. If the membranes are housed inside three-way valves, then when one MI valve is not activated, the valve cavity may be evacuated through the divert port to an auxiliary vacuum pump to prevent accumulation of permeate.

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