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# Continuous permeation of analytes through a thin poly(dimethylsiloxane) membrane followed by sorbent trapping for their gas chromatographic monitoring

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## Abstract

Parameters that affect the permeation of analytes across a thin (0.025 mm) flat membrane of polysiloxane in a membrane and trap interface coupled to a gas chromatograph are examined taking into account a mechanism of mass transport for porous and nonporous materials and the permeation of carrier gas in the direction opposite to that of the analytes. The best permeation rate was reached with hydrogen as carrier gas at a flow-rate between 3 and 5 ml/min, an agitation of analytes outside the membrane above 0.4 m/s and thin membrane. The parameters that affect the residual diffusion time of analytes in membrane were also examined. A practical application of the thin membrane in membrane and trap interface was demonstrated by gas chromatographic monitoring of six volatile organic compounds in air. The limit of detection is at the nmol/ml level depending on the time of trapping and the parameters that affect the permeation through the membrane. © 2002 Elsevier Science B.V. All rights reserved.

**Keywords:** Membranes; Air analysis; Extraction methods; Volatile organic compounds

## 1. Introduction

In recent years, there has been an increased interest in the determination of volatile pollutants from air. Many of these volatile organic compounds (VOCs), such as aromatic hydrocarbons and chlorinated solvents are known to be suspect cocarcinogenics, tumour promoting agents and irritant compounds. The need for fast monitoring of the traces of VOCs in the environment is necessary in order to protect the public against chronic exposure. Analytical techniques such as open path Fourier

transform infrared (FT-IR) [1,2], X-ray fluorescence spectrometry [3], direct mass spectrometry (MS) [4], and gas chromatography (GC) [5,6] have been adapted for on-line monitoring. Chromatographic techniques can separate the analytes prior to their detection allowing a flexible qualitative and quantitative analysis of complex mixtures that cause particular problems in direct MS and FT-IR. On-line GC monitoring was done using multi-port valves for sample injection. These valves have certain limitations such as mechanical wear, sample band broadening and no sampling of analytes during injection. Many disadvantages of the multi-port valve injection can be avoided by using a membrane and trap interface (MTI), which can perform a

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continuous isolation of the analytes from sample by their permeation through a membrane, followed by continuous concentration of analytes on a sorbent trap. The trapped analytes are introduced into the GC analytical column by fast heating of the trap from time to time.

Permeation of analytes from sample matrix through a membrane and their continuous transportation into an analytical instrument for analysis was applied for the first time for direct MS [7]. The first membranes used in GC for continuous isolation of VOCs were the supported flat membrane [8] and then the hollow fibre [9–16] from poly(dimethylsiloxane) (PDMS) with wall thicknesses between 100 and 400  $\mu\text{m}$ . Although, a hollow fibre is easier to use, it is not acceptable under the high-pressure required in a fast analysis when a supported membrane [17–19] was more suitable. The membranes are usually made from PDMS because of their unique ability to allow various gases to permeate rapidly through them. The solubility coefficients for gaseous compounds into a PDMS membrane are comparable to those of most polymers, but the diffusion rates are nearly 10 times greater than any other membrane polymers. This phenomenon is primarily due to the flexible siloxane linking and the absence of crystallinity. Another characteristic of the PDMS membranes is their selectivity, which is achieved by differences in solubility and diffusivity. Substitution in polysiloxane of methyl groups with other groups like phenyl gave a reduction of permeability, but sometimes increased the selectivity [20]. A similar effect was observed when the membrane is a copolymer between PDMS and other polymers [21].

The effects of the physical and chemical properties of the polymers and analytes on mass transport have been systematically investigated [22–25]. However, relatively little is known about the permeation of VOCs in a very thin flat membrane from PDMS.

This paper describes for the first time the dual behaviour, like porous and non-porous material, for very thin membrane consisting of PDMS in an MT interface for GC analysis. The main parameters were tested with several VOCs in order to determine the optimal experimental conditions for mass transport through PDMS membrane when the sensitivity of the system is highest.

## 2. Experimental

### 2.1. Reagents and materials

Benzene (98%), toluene (99.9%), trichloroethylene (98%), tetrachloroethylene (99.9%) ethylbenzene (98.9%) and *o*-xylene (98.5%) were purchased from Merck (Darmstadt, Germany). The sorbent in trap was Tenax-TA and Amberlite XAD-2 from Supelco (Bellefonte, PA, USA). Hydrogen, helium, nitrogen and compressed air were from Linde (Timisoara, Romania). Samples were prepared by direct injection of analytes into the extraction chamber or with a standard gas mixture generator. The flat membrane consisted of PDMS from Speciality Silicone Products (Ballston Spa, NY, USA) with a thickness of 0.025, 0.100 and 0.165 mm. The outlet surface of the membrane exposed to analytes was 200  $\text{mm}^2$ .

### 2.2. Apparatus and methods

A schematic diagram of the MTI–GC system used in this study is presented in Fig. 1. The main components of this system are membrane module, sorbent trap and gas chromatograph.

A schematic diagram of the membrane module is presented in Fig. 2. A flat membrane is not self-supported, and therefore requires a special holder to support it in the membrane module. One side of the

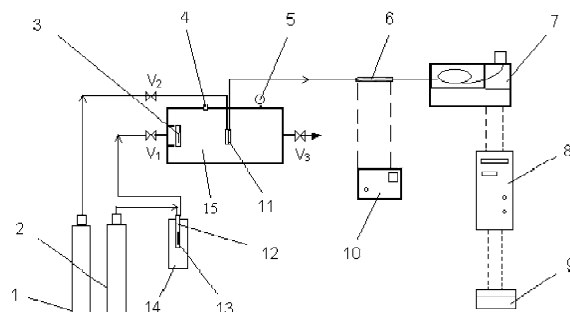


Fig. 1. Schematic diagram of the experimental system. (1) Hydrogen cylinder; (2) nitrogen cylinder; (3) fan; (4) injector port-hole; (5) pressure gauge; (6) trap; (7) gas chromatograph; (8) computer; (9) printer; (10) capacitive discharge power supply; (11) membrane module; (12) permeation cell; (13) permeation tube; (14) aluminium block; (15) extraction chamber; ( $V_1$ ), ( $V_2$ ), and ( $V_3$ ) flow-rate regulators.

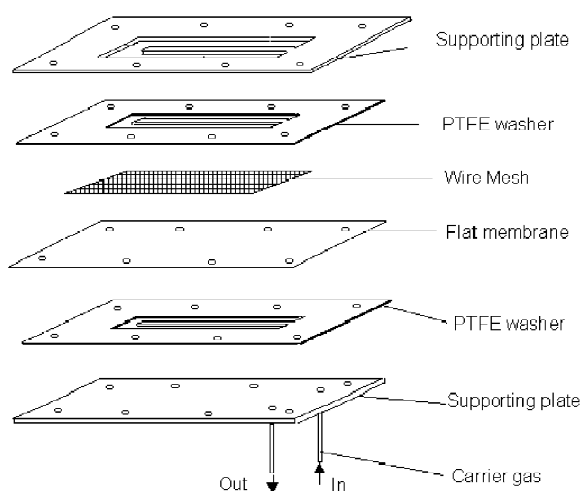


Fig. 2. Main components of the flat membrane module.

membrane is exposed to the sample and the other to the carrier gas. On both sides of the membrane are PTFE washers and stainless steel plates. A fine stainless steel mesh wire, mounted in a stainless steel plate, supported one side of the membrane. Both plates were screwed with 10 bolts. The carrier gas was supplied to the module through small-diameter PTFE tubing fitting tightly into the PTFE washer. The pressure of carrier gas lifted the membrane and allowed free access of the gas to the outlet tubing on the opposite side of the membrane surface. After leaving the membrane module, the carrier gas and analyte go to a sorbent trap.

The porosity of this polymer was evaluated by scanning electronic microscopy and was carried out for 0.025- and 0.165-mm membrane thickness with a Hitachi SEM model S 570 (Hitachi, Mito, Japan) at 8 and 15 kV acceleration voltages of the electron flux.

The trap was made by packing stainless steel tubing (0.5 mm I.D.×0.65 mm O.D.) with sorbent. This small trap was heated by passing current directly through the wall of the metal tubing for about 1 s by discharging from time to time a capacitor [26]. The temperature was modified by changing the electrical potential applied on the ends of the metal tubing. The cycle of trapping and heating was repeated automatically using a timer. The measurement of temperature was difficult to carry out but was at a value when decomposition of sorbent was minimized. A capacitive discharge

power supply controlled all the parameters of the trap.

The air with analytes was agitated outside the membrane with a fan. The measurement of the air velocity on the surface of the membrane was carried out by the hot wire principle with an air velocity meter model HHH51 from Omega (Stamford, CT, USA). A thermistor was maintained at 1200 °C, and the voltage across the thermistor was processed to give a direct digital reading of air velocity. The measurements were performed in a 500-ml extraction chamber at different fan speeds. The speed of the fan was adjusted by modifying the voltages with a potentiometer. The extraction chamber was wrapped with heating tape and was thermostated at 25 °C for all experiments by applying a constant electric potential to the heating tape.

GC measurements were performed on an HP 6890 gas chromatograph (Hewlett-Packard, Avondale, PA, USA) equipped with a flame ionization detection (FID) system.

### 2.3. Membrane permeation and trapping procedure

The membrane module was set in the middle of the extraction chamber. The sample was injected through a silicon rubber into the extraction chamber or was taken from the standard gas generator. The carrier gas passed through the membrane module. The volume between membrane and PTFE washer must be as small as possible to increase the velocity of carrier gas. The gas carrying analytes from the membrane module was passed into the trap with 2.0 mg sorbent. The analytes were adsorbed on the sorbent. The trapping time was from a few seconds to hours. The profile of the diffusion through the membrane was determined without the trap, when the analytes went directly to the detector.

### 2.4. Standard gas generator procedure

The standard analyte–nitrogen mixture gas was generated by the permeation method [27]. The generator was built from an aluminium block equipped with an electric heater and with six holes inside. Into these holes (120 cm long, 2.0 cm I.D.) was introduced six glass vials each having a screw cap and silicone septum for sealing. In each glass

vial was one PTFE permeation tube with one analyte inside. The permeation tubes were sealed at both ends. The aluminium block was thermostated at 60 °C by applying a constant electric potential to an electric heater. The temperature was monitored by a digital temperature indicator (Cole-Parmer, Chicago, USA). Nitrogen gas was introduced through stainless steel tubing into the glass vial at constant flow-rate, which was controlled by a compressed gas regulator and monitored by a calibrated flowmeter. The glass vial is the permeation cell because in it was generated the mixture between nitrogen and analyte. The gas mixture flowed from permeation cell through stainless steel tubing into the extraction chamber.

### 3. Results and discussion

The PDMS membrane used in this study is a cross-linked polymer obtained by reaction of linear PDMS with tetraethoxysilane. The PDMS polymer was swelled but not dissolved in aromatic and chlorinated compounds tested in this experiment.

PDMS is a rubbery polymer known as a non-porous material [28], but the presence of SiO<sub>2</sub> [29] and pores in the range of nanometres in very thin PDMS polymer membranes is impossible to avoid [30] and is dependent upon the thickness and preparation procedure. Scanning electronic microscopy of the surface of the PDMS membrane showed the presence of SiO<sub>2</sub> filler particles and cracks on the surface of the membrane material which are the opening side of the pores. These cracks are larger for very thin membrane material, but they disappear for a thicker membrane. The filler particles are desired in the membrane to improve its mechanical properties.

Due to the presence of these small pores, the mechanism of mass transport in a very thin membrane will be a mixture between the mechanism for non-porous and porous materials. In non-porous material, the rate of gas permeation through a membrane is determined by the permeability coefficient [31], and the amount of gaseous analyte transported across a unit cross-sectional area per unit time is given by the first Fick's law [32]. When the flow of carrier gas is high, we can assume that the concentration of analyte on the inside surface of the

membrane is zero and Fick's law can be expressed after some modifications as:

$$J = D K C_g / d \quad (1)$$

where  $J$  is the flux of mass transported per unit cross-sectional area and unit time, expressed in mol/s per m<sup>2</sup>,  $D$  is the diffusion coefficient,  $K$  is the distribution constant of the analyte between the membrane and gaseous phase,  $C_g$  is the concentration of analyte in gaseous phase and  $d$  is the thickness of the membrane.

The membrane will also be permeated by carrier gas in the opposite direction to the analytes. The solubility of the carrier gas molecules in silicone polymers [28] is lower, but their diffusivity is high. With a high coefficient of diffusivity and a high pressure, the carrier gas will hinder by collision and friction the transport of analyte in the membrane.

The amount of analyte permeated through the membrane as a function of the permeation time gives the permeation profile (Fig. 3). The dead time of the system can be measured between points I and II of the permeation profile and was minimised to a few seconds by increasing the agitation of the analytes on the surface of the membrane, and using short, deactivated and heated connection tubes [19]. The permeation profile curve can be useful to measure the time of permeation and to evaluate the diffusion coefficient from the half time of permeation. The maximum mass transport of analyte through the

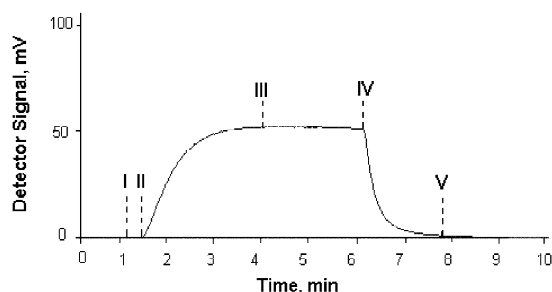


Fig. 3. Permeation profile through the membrane at the change in benzene concentration in headspace. Concentration of analyte in headspace was 1.5 nmol/ml benzene in air; the temperature of the extraction chamber was 25 °C; the carrier gas was hydrogen at 5 ml/min; the temperature in the GC oven was 60 °C. (I) Injection point; (II) beginning of permeation; (III) beginning of steady state; (IV) beginning of residual diffusion time of analyte; (V) finish of residual diffusion time of analyte.

membrane was determined at steady state. Fig. 3 shows that the permeation through the membrane was not suddenly decreased when the concentration of analyte was suddenly changed to zero on the outside surface of the membrane by removing very quickly the membrane module from the extraction chamber. This profile of permeation indicates that due to the small diffusion coefficient in the membrane, the diffusion of analyte continues in the membrane for a few seconds. This time could be called the residual diffusion time (RDT) of analytes. This phenomenon is also known as the memory effect of the membrane and is important for monitoring of analytes with the MTI–GC system. The RDT should be as small as possible in order to eliminate the interference with other analytes and to increase the sensitivity of detection.

### 3.1. Influence of the carrier gas

The carrier gas has two important influences upon the permeation process through the membrane because, first, it permeates through the membrane in an opposite direction to the analytes and second, it transports the analytes from the inner surface of the membrane to the trap. The presence of carrier gas diffused through the membrane can be detected with an electronic leak detection system or can be seen very easily as very small bubbles on the surface of the membrane when the membrane module is emerged in a water bath and the flow of carrier gas on the inner surface of the membrane was increased.

Table 1 shows the influence of the type of carrier gas on the mass transport in the membrane for benzene, toluene, trichloroethylene and tetrachloroethylene. Physical and chemical properties of the carrier gas can modify the mass transport. All

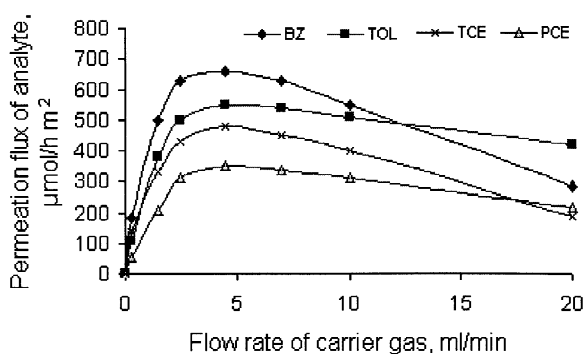


Fig. 4. Effect of the carrier gas flow-rate on the permeation flux of benzene (BZ), toluene (TOL), trichloroethylene (TCE) and tetrachloroethylene (PCE). The concentration of all analytes in extraction chamber was 1.5 nmol/ml; the trapping time was 15 s on 2.0 mg Tenax-TA; the temperature of the extraction chamber was 25 °C; the temperature in the GC oven was 60 °C.

experiments were carried out at the same flow-rate and implicit at the same velocity. The influence of the type of carrier gas on mass transport is difficult to attribute only to one property of the carrier gas. Table 1 shows the decreasing mass transport with increasing molecular mass and volume and decreasing viscosity of the carrier gas. A carrier gas with higher volume will hinder the diffusion of analytes due to a higher probability of collision and friction in pores with the analyte molecules, which have an opposite diffusion. The optimum mass transport through the membrane was obtained with hydrogen as carrier gas.

Fig. 4 shows the influence of the flow-rate of carrier gas on mass transport in the PDMS membrane. The flow-rate of carrier gas was measured before the detector but the same value was just after the membrane module. An increase can be seen until a maximum of the amount permeated through mem-

Table 1  
Influence of the type of carrier gas on mass transport in the membrane

Carrier gas	Permeation flux of analyte ( $\mu\text{mol/h per m}^2$ )			
	Benzene	Trichloroethylene	Toluene	Tetrachloroethylene
Hydrogen	660	485	550	351
Helium	543	435	383	288
Nitrogen	426	300	255	201
Air	390	257	213	158

Flow of carrier gas, 5 ml/min; time of trapping, 10 s; concentration of analyte in air, 1.5 nmol/ml.

brane for all analytes when the flow was increased and then a decrease in the amount of analyte permeated. The increase in permeation through the membrane can be explained by the reduction of the static boundary layer thickness on the surface of membrane at high velocity of carrier gas, but the decreasing slope of the curve cannot be attributed to the breakthrough of the sorbent because in the same experimental conditions with at a flow-rate of 20 ml/min the shortest breakthrough time was after 44 s for benzene and the trapping time in this analysis was 15 s. An explanation for this decrease in the flux of analytes through the membrane is the increase in the carrier gas pressure by increasing the flow-rate and implicit the flux of carrier gas permeated through the membrane. This flux of carrier gas was in the opposite direction to the flux of analytes decreased the permeation rate of analytes. For volatile compounds like benzene and trichloroethylene, the permeation flux decreased more quickly. Toluene and tetrachloroethylene with higher boiling points had a slow decrease in mass permeated. Since solubility in polymers increases with condensability [23] and molecular mass [25] of analyte, toluene and tetrachloroethylene have a stronger interaction with the polymer, and a high flux of carrier gas stripped them more difficult.

The optimum range of carrier gas flow-rate differs from analyte to analyte, but between 3 and 5 ml/min, the modifications of the permeation flux with flow-rate are 5–8% from the maximum value. However, the shape of the peaks is improved and the deviation from baseline at short time of trapping could be decreased at higher flow-rates.

The type of carrier gas also had an impact on the residual diffusion time of analyte in the membrane. The residual diffusion time of analyte was measured from the permeation profile through the membrane when the concentration of analyte was suddenly changed to zero until the intensity of the signal decreases to 99% of its value. Table 2 shows the influence of the type of carrier gas on the residual diffusion time of analyte. The analyte with lower volatility and bulk had a higher residual diffusion time with the same carrier gas because it had a stronger interaction with the polymer [24]. The residual diffusion time decreased when the molecular mass of carrier gas was higher. However, the re-

Table 2  
Influence of the type of carrier gas on residual diffusion time of analyte

Analyte	Residual diffusion time of analyte (min)			
	Hydrogen	Helium	Nitrogen	Air
Benzene	3.17	2.61	2.37	2.08
Toluene	4.76	4.35	3.66	3.05

Flow of carrier gas, 5 ml/min; speed of air in extraction chamber, 0.75 m/s; concentration of analyte in air, 1.5 nmol/ml.

sidual diffusion time with hydrogen was only about 1.5 times higher than with air as carrier gas. When the concentration of analyte is zero to the outer surface of the membrane, the analyte from the membrane will diffuse to both surfaces of the membrane. Increasing the flow of all above carrier gases, the residual diffusion time decreased, because a high flow-rate generated a higher flux of carrier gas through the membrane removing the analytes more quickly. The bulky carrier gases permeating out through the membrane stripped the analyte more easily from the membrane by more friction and collision.

### 3.2. Influence of the velocity of gaseous sample on membrane

The velocity of the air with analytes on the outlet surface of the membrane can modify the thickness of the boundary layer between air and the surface of the membrane. Increasing the air velocity, the static boundary layer became thinner and the diffusion improved. The permeation rate increased by increasing the velocity of air with sample on the outside of the membrane until a constant value was reached. All the analytes reached steady state above 0.4 m/s.

### 3.3. Influence of the membrane thickness and area

As is expressed by Eq. (1), the permeation flux is inversely proportional to the membrane thickness. For a given substance and polymer membrane, the permeation flux will decrease when membrane thickness is reduced. The permeation flux of benzene was about three times lower through 100- $\mu$ m than 25- $\mu$ m membrane thickness. Similar modifications were noticed for the all analytes in this study. The amount

of analyte extracted with a thin membrane was always better, but a membrane thinner than 25  $\mu\text{m}$  was limited to commercial availability.

The area of membrane does not affect the permeation flux per unit area, but using a membrane with a higher surface, the amount of analyte extracted through the membrane was higher and the sensitivity of the system was improved. The unique design of the holder had a U profile of the flat membrane with a high speed of carrier gas on the inner side of the membrane which minimised the boundary layer. The membrane is held firmly without wrinkling or tearing.

### 3.4. Influence of the membrane temperature

The modification of carrier gas temperature will alter the membrane temperature. The carrier gas was heated by applying voltages to the supply metal tubing. The temperature of the membrane was measured with a thermocouple outside the membrane module. The effect of the membrane temperature on permeation flux is a very complex process since in a large range of temperatures, the diffusivity and solubility coefficients are modified very differently. The dependence of the permeability coefficient can be described by a temperature Arrhenius-type equation [32]. Solubility decreases much more than the increase in diffusivity but in a very small range around room temperature the amount permeated in the PDMS membrane is not modified [25]. In the range 15–35  $^{\circ}\text{C}$ , the permeation flux of benzene, toluene, trichloroethylene and tetrachloroethylene was enhanced very slowly by increasing the temperature.

### 3.5. Influence of the analyte concentration

Fig. 5 shows the variation of the permeation flux as a function of the concentration of analyte outside the membrane. In accordance with Eq. (1), the permeation flux has a linear variation with analyte concentration when the analyte obeys Henry's law. Up to 3 nmol/ml analytes in air, the permeation flux had a linear variation ( $J=433.88C_{\text{BZ}}$ ,  $R^2=0.9947$ ;  $J=358.87C_{\text{TOL}}$ ,  $R^2=0.9952$ ;  $J=319.37C_{\text{TCE}}$ ,  $R^2=0.9960$ ;  $J=224.31C_{\text{PCE}}$ ,  $R^2=0.9934$ ) which can be

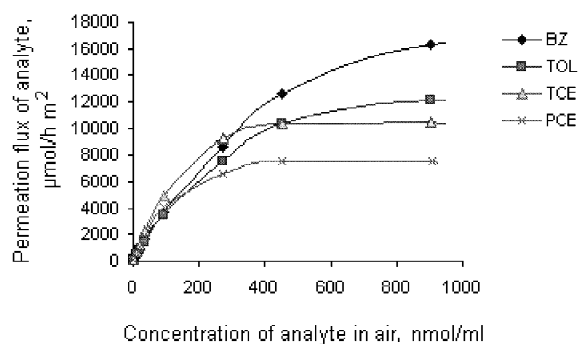


Fig. 5. Influence of the concentration of benzene (BZ), toluene (TOL), trichloroethylene (TCE) and tetrachloroethylene (PCE) outside the membrane on their permeation flux. The trapping time was 15 s on 2.0 mg Tenax-TA; the temperature of the extraction chamber was 25  $^{\circ}\text{C}$ ; the temperature in the GC oven was 60  $^{\circ}\text{C}$ .

used for quantitative measurements. At higher concentrations, a calibration curve must be used.

The RDT of analyte in membrane was also affected by the concentration of analytes in air as can be seen in Fig. 6. When the concentration of analyte was increased, the amount of analyte accumulated in membrane was higher and the time necessary for its diffusion was also longer. After a certain concentration, the value of the RDT reached a plateau. The analyte with high boiling points and solubility in membrane such as toluene had a longer RDT.

### 3.6. Influence of the pressure outside the membrane

The permeation process can be spontaneous only

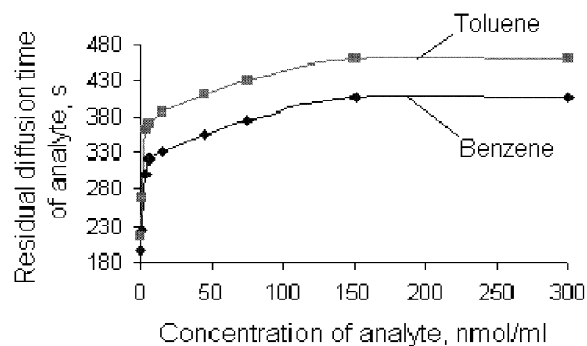


Fig. 6. Influence of the concentration of benzene and toluene outside the membrane on the residual diffusion time. Experimental conditions as in Fig. 3.

when the partial pressure of analyte outside the membrane is greater than the partial pressure inside the membrane. The permeation flux is proportional to the partial pressure of analytes outside the membrane module when the partial pressure of analytes inside the membrane module is supposed to be zero at high speed of carrier gas. A high partial pressure of analytes was generated by a high concentration of analytes in the headspace. The permeation flux response curves for a step change in sample pressure has the same variation as in the modification of concentration.

Increasing the air pressure outside the membrane module, the permeation flux decreased since a high pressure of air generates a low partial pressure of analytes in the extraction chamber. At the same time, the air penetrates more easily through the membrane because its partial pressure increased. When the pressure outside the membrane module is higher than the pressure of carrier gas, the permeation flux was zero because the membrane was stuck to the PTFE washer and the flux of the carrier gas was stopped. A high pressure of air outside the membrane can decrease the permeation flux, but can also increase the amount of air and water in the system. Small modifications ( $\pm 30$  mmHg; 1 mmHg = 133.322 Pa) of the air pressure do not modify the flux of the analyte through the membrane.

### 3.7. Applications

The MT interface with a very thin flat membrane can have many applications in the analysis and monitoring of various environmental matrices. This method provides an excellent approach for sampling in closed containers and for spot air monitoring. The most important contaminants from the environment are VOCs such as aromatic and chlorinated compounds. The MT interface with a thin PDMS membrane was tested for continuous monitoring by GC with a mixture of benzene, toluene, ethylbenzene, *O*-xylene, trichloroethylene and tetrachloroethylene. The parameters that affect the MT interface were selected at optimum values. The sensitivity of the GC is dependent on the amount of analyte injected, which is a function of the permeation flux, and time of trapping. The amount of VOCs accumulated in the trap and injected into the GC is greater when the

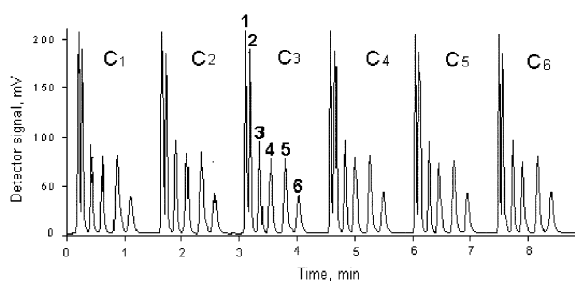


Fig. 7. Consecutive gas chromatogram of six contaminants in air. Peaks: (1) benzene; (2) trichloroethylene; (3) toluene; (4) tetrachloroethylene; (5) ethylbenzene; (6) *o*-xylene. SPB-1 fused-silica capillary column (3 m  $\times$  0.32 mm I.D.) with 3- $\mu$ m PDMS film thickness at 80 °C; 0.8 nmol/ml of each analyte; hydrogen was the carrier gas at 5 ml/min; trapping time was 90 s.

time of permeation and trapping is longer. Fig. 7 shows consecutive gas chromatograms ( $C_1$ – $C_6$ ) for monitoring of six analytes. For each heating of the trap a similar chromatogram was obtained. The shape of the peaks was very good and relative standard deviations for peak areas and retention times of six analytes were approximately 1% for six consecutive injections, which is better than direct syringe injection. Quantitative analysis will require a calibration step, which can be done by placing the membrane module inside the extraction chamber to control the flow on the surface of the membrane. The MT interface can also be used for analysis in the headspace of solid or liquid samples [19]. The limit of detection depends on the time of trapping and the parameters that affect the permeation through the membrane. In our experimental conditions, the limit of detection was at the nmol/ml level.

### 4. Conclusions

MTI can operate with a thin flat membrane from PDMS if it is firmly installed in a holder. The permeation flux was improved with a thinner membrane. This study demonstrated a dual behaviour of the membrane as a porous and non-porous material in the mass transport process. Even if the residual diffusion time of analytes in the PDMS membrane is the highest for hydrogen, it remains the best carrier gas because the mass transport of analytes through the membrane was the highest and efficiency of



separation was not affected very much at high flow-rates. The optimum flow-rate was between 3 and 5 ml/min. At a high flow-rate, the shape of the peak and sensitivity was improved, time of analysis and residual diffusion time significantly reduced. The permeation through the membrane was improved when the analytes were agitated on the surface of the membrane. Increasing the partial pressure and concentration of analyte outside the membrane, the mass transport through the membrane was enhanced. Variation of the membrane temperature around room temperature gave no significant modification of the permeation flux. The normal variation of the atmospheric pressure did not affect the permeation flux.

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