

Investigation of fundamental physical properties of a polydimethylsiloxane (PDMS) membrane using a proton transfer reaction mass spectrometer (PTRMS)

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Abstract

A membrane introduction proton transfer reaction mass spectrometer (MI-PTRMS) has been employed for the characterisation of a polydimethylsiloxane (PDMS) membrane. For this purpose the diffusion and partition coefficients (which serve as a measure for solubility) have been determined experimentally for different classes of chemical compounds both non-polar and polar species, i.e., aromatics, alcohols, and ketones. It turned out that not only polar compounds exhibit strong interaction with a hydrophobic membrane such as the PDMS, but also non-polar compounds as trimethylbenzene or propylbenzene show strong interaction with a PDMS membrane. Stronger analyte–membrane interaction leads to a slower diffusion coefficient and larger partition coefficient. The effect of the temperature on the diffusion coefficient and partition coefficient has also been investigated, i.e., at higher temperature diffusion becomes faster and solubility lower. Permeability can be calculated from diffusion and partition coefficients and the activation energy has been derived from corresponding Arrhenius plots. The MI-PTRMS system shows detection limits in the order of tens of ppt, and its response is linear for more than four orders of magnitude. © 2004 Elsevier B.V. All rights reserved.

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1. Introduction

Nonporous polymers membranes of different materials and structures provide selective permeation of fluids and gases. Due to this characteristic they can be used for many different applications ranging from gas purification, to gas separation from liquids, i.e., dehydration of liquid organic solvents, water desalination, or to food packaging [1,2]. They also find application in the analytical field when used as introduction system for mass spectrometers (MIMS; mem-

brane inlet mass spectrometry) [3–5]. In fact the selective permeation of organic compounds in comparison to water or air components through the membrane allows the direct insertion of the analyte from the sample matrix into the vacuum of the mass spectrometer without the necessity of solvent evaporation or analyte concentration. A consequence is that on-line measurements are possible either with air at atmospheric pressure or with liquid and that low detection limits can be reached. Different membrane materials are used depending on the applications. Glassy materials, i.e., polyimides, are mainly used for gas purification such as the recovery of expensive gases (H₂, CO₂, H₂S, N₂) from natural gases or industrial gas streams. Rubbery materials, i.e., polydimethylsiloxane (PDMS), are used in gas separation from liquids or as membrane inlet for mass

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spectrometers, or for food packaging (i.e., polyethylene) [2].

Up to now silicone polymers have been shown to be the materials with the best performance for analytical purpose, in fact they show fast and efficient permeation of a wide range of volatile organic compounds (VOCs) with respect to air and water, except for polar compounds such as alcohols [6]. New polymer materials have been thus synthesised either to improve the analysis of polar compounds or for other specific applications, although they have not reached the performances of standard commercial materials yet [6]. MIMS, besides been a powerful tool for the analysis of VOCs in air or water, may be used also to characterise the most commonly used and newly synthesised membrane materials. Recently MIMS has being combined with a proton transfer reaction mass spectrometer (PTRMS) [7], and the resulting MI-PTRMS system turned out to be a useful tool for the characterisation of membrane materials [7,8]. MI-PTRMS was also successfully employed for the direct analysis of VOCs in water [9].

PTRMS is a chemical ionisation mass spectrometry technique based on proton transfer reactions from H_3O^+ ions to VOCs. This method is suitable for on-line measurements of trace gases, and has so far been applied to various fields ranging from atmospheric chemistry, to food flavour, and medical diagnostics [10]. The details of the instruments have been described elsewhere [11–13]. The most important characteristics of the PTRMS are (i) the ability to measure multiple chemical species simultaneously and to determine approximate absolute concentrations without calibration, (ii) a rapid time response (with on-line capability), and (iii) a large dynamic range (ca. 10 ppt_v to 10 ppm_v). These properties of the PTRMS allow rapid, accurate characterisation of the membrane properties under a range of conditions.

The overall mass transport of analytes through a membrane constitutes the permeation process, which involves three steps: absorption into the membrane, diffusion through the membrane, and evaporation from the membrane surface to the vacuum. Each step depends on molecular properties of the analyte, membrane material and dimension, temperature, and inlet configuration. The permeation process is described by Fick's diffusion equations [7,14–16], whose solution for steady state conditions results in expressions for the flow rate of a substance through the membrane:

$$F_{\text{st}} = \frac{2\pi LDKC_v}{\ln(r_0/r_1)} \quad (1)$$

and for the rise time between the 10 and 90% of the steady state:

$$t_{10-90\%} = 0.237 \left(\frac{l^2}{D} \right) \quad (2)$$

where D is the diffusion coefficient, K is the partition coefficient, L is the length of the membrane, r_0 and r_1 the inner and the outer membrane diameters, l the membrane thickness, and C_v the concentration of the analytes in the matrix.

F_{st} and $t_{10-90\%}$ thus depend on dimension and geometry of the membrane, concentration of the analyte and temperature. The coefficients D and K are specific of the membrane material and depend only on temperature, hence they represent the basic parameters to describe the chemical–physical properties of membrane materials.

Experimentally it is possible to measure F_{st} and $t_{10-90\%}$ from which values of D and K are easily calculated using the following expressions derived from (1) and (2):

$$K = \frac{(F_{\text{st}}^* \ln(r_0/r_1))}{(2\pi LDC_v)} \quad (3)$$

$$D = 0.237 \left(\frac{l^2}{t_{10-90\%}} \right) \quad (4)$$

Diffusion is the rate-determining step in the permeation process, while solution, a measure of which is given by K , is essentially instantaneous [1]. The overall permeation process is described by permeability values (P), defined as the product between diffusion and partition coefficient. Permeation is a temperature dependent phenomenon obeying the Arrhenius relation [1,14]:

$$P = P_0 \exp \left[-E_p \left(\frac{1}{RT} - \frac{1}{RT_0} \right) \right] \quad (5)$$

where the initial permeability, P_0 , is given at some initial temperature, T_0 and E_p is the activation energy for permeation.

In this work we will show the capability of the PTRMS to characterise a silicone membrane commonly used in MIMS. For this purpose the diffusion and partition coefficients of several compounds in air matrix belonging to different chemical classes and including isomers and homologues are determined. Their dependence on temperature is investigated, and values for the permeability and activation are derived. Linearity of the system is demonstrated and detection limits are obtained for some of the compounds analysed.

2. Experimental

2.1. Caution

The analytes used in these experiments are known health hazards. Care should be exercised to minimise exposure during handling and use.

A combination of membrane inlet and PTRMS (MI-PTRMS) was used throughout the experiments. The PTRMS has been described elsewhere [7,9,11–13], and no further details will be given here. A SilasticTM (Dow Corning) tubing with dimensions of i.d. 0.30 mm, o.d. 0.64 mm, and a length of 8.172 cm was used as interface between the gas sample and the drift tube of the PTRMS (a similar set-up was used in previous studies [7–9]). A schematic diagram is shown in Fig. 1. The interior of the membrane feeds directly into the PTRMS drift region, held at a pressure of approximately 2 mbar. A mass flow controller limits the flow of air

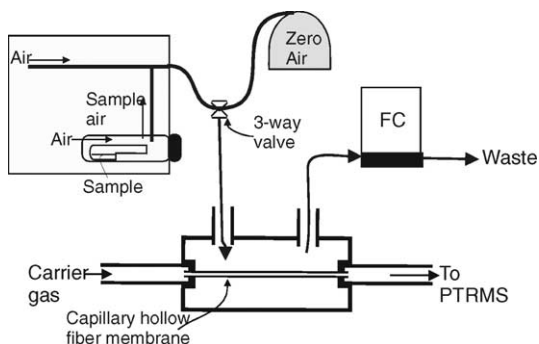


Fig. 1. Schematic view of the MI-PTRMS and sampling set-up.

through the membrane to 10 ml/min, keeping the pressure near 2 mbar. Sample air is drawn into the membrane assembly at atmospheric pressure, and flows around the outside of the membrane at 200 ml/min controlled by a second mass flow controller. The entire membrane assembly is enclosed in a temperature insulated box containing heaters and a thermocouple connected to a temperature controller.

Temperature effects on the permeation process was studied varying the temperature from 25 to 65 °C. Fifteen compounds were analysed in these studies the corresponding air samples were prepared with a gas dynamalibrator (Model 340, VICI Metronics Inc., Santa Clara, CA, USA). Pure compounds (Sigma-Aldrich) were placed in diffusion vials (VICI Metronics Inc.) and held at a constant temperature of 30 °C in the chamber of the gas calibrator. Air samples were drawn with a constant zero air stream out of the chamber and then diluted with zero air to achieve the desired concentration. Dynamalibrator outlet and membrane sample inlet were directly connected with a 1/4-inch Teflon line. The concentrations of the gas samples before dilution were measured directly with the PTRMS and found to be 2124 ppb_v (part per billion in volume) for benzene, 834 ppb_v for toluene, 224 ppb_v for *o*-xylene, 286 ppb_v for *m*-xylene, 377 ppb_v for *p*-xylene, 73 ppb_v for 1,2,4-trimethylbenzene (TMB), 81 ppb_v for 1,3,5-trimethylbenzene (mesitylene), 235 ppb_v for ethylbenzene, 62 ppb_v for propylbenzene, 1220 ppb_v for methanol, 218 ppb_v for ethanol, 2255 ppb_v for acetone, 3404 ppb_v for butanone, 1250 ppb_v for 2-pentanone, 1224 ppb_v for 3-pentanone.

Detection limits and linearity of the system were investigated employing a prearranged mixture of several VOCs in compressed air and by serial dilution with zero air of the latter. The concentration of the VOCs in the gas mixture was determined by direct introduction into the PTRMS and found to be in this case 108 ppb_v for benzene, 100 ppb_v for toluene, 77 ppb_v for *p*-xylene, 65 ppb_v for 1,2,4-trimethylbenzene (TMB), 312 ppb_v for methanol, 270 ppb_v for acetone, 206 ppb_v for butanone.

Concentrations (mixing ratios) in ppb_v of original samples and compounds transmitted through the membrane were calculated from the measured counts per seconds (cps) using the

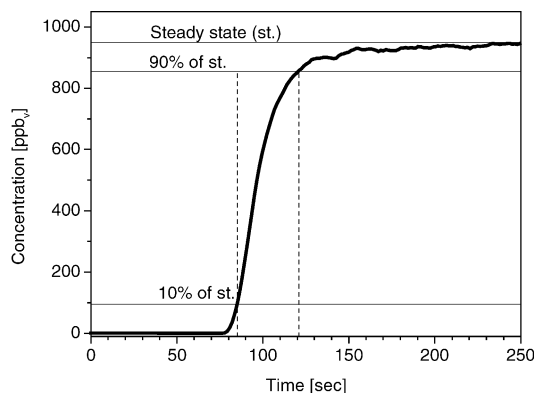


Fig. 2. Transmission of benzene through the membrane when switching from zero air to sample air. The rise time (from 10 to 90% of the steady state) and steady state concentration inside the membrane can be derived from these data.

following formula [11–13]:

$$[B] = \frac{1}{kt} \left(\left[\frac{BH^+}{H_3O^+} \right] \right) \quad (6)$$

where [B] is the concentration in ppbv of the neutral compounds of interest, [BH⁺] the cps of the protonated compound, [H₃O⁺] cps of primary ion, *k* is the reaction rate constant and *t* the resident time.

All the experiments were performed using selected-ion-mode (SIM) operation of the PTRMS.

3. Results and discussion

Fig. 2 shows as an example how benzene (at a concentration of 2124 ppb_v) is transmitted through the membrane when switching from zero air to sample air and how long benzene takes to reach a steady state at 25 °C. From such an experiment the rise time (from 10 to 90% of the steady state) and steady state concentration inside the membrane can be easily calculated. The steady state flow inside the membrane is then calculated by multiplying the steady state concentration and the flow of the carrier gas inside the membrane. Values for diffusion (*D*) and partition coefficients (*K*) are then derived employing expression (3) and (4), and summarised in Tables 1 and 2 for all the samples investigated here.

The fastest diffusion is observed for those compounds having the weakest interaction with the membrane. This is the case for aromatic compounds not bearing substituent groups or just one methyl group, i.e., benzene and toluene. In fact polydimethylsiloxane (PDMS) membranes are hydrophobic polymers which interact most strongly with polar compounds, either through hydrogen bonding between the siloxane group of the membrane and alcoholic or acid hydrogen of the analyte or through polar-polar interaction. Inorganic fillers might play a role in the interactions with polar groups as well. However, PDMS membranes can also show relative strong hydrophobic interaction with

Table 1
Diffusion coefficient [D ($\times 10^{-6}$) (cm^2/s)] for 15 VOCs from air matrix and their dependence on temperature

	Temperature ($^{\circ}\text{C}$)					Increase factor ^a
	25	35	45	55	65	
Benzene	1.34	1.80	2.04	2.17	2.46	1.8
Toluene	1.15	1.32	1.58	1.76	1.60	1.4
2C-benzenes						
<i>o</i> -Xylene	0.49	0.82	1.19	1.32	1.60	3.3
<i>m</i> -Xylene	0.51	0.90	1.16	1.37	1.48	2.9
<i>p</i> -Xylene	0.43	0.99	1.41	1.83	1.67	3.9
Ethylbenzene	0.47	0.64	1.03	1.52	1.68	3.5
3C-benzenes						
TMB	0.30	0.43	0.64	1.00	1.16	3.8
Mesitylene	0.31	0.56	0.72	0.92	1.23	4.0
Propylbenzene	0.35	0.52	0.63	0.75	0.79	2.3
Alcohols						
Methanol	0.30	0.47	0.63	0.80	0.96	3.2
Ethanol	0.15	0.24	0.30	0.42	0.57	3.7
Ketones						
Acetone	0.10	0.16	0.22	0.38	0.55	5.7
Butanone	0.17	0.25	0.34	0.49	0.57	3.3
2-Pentanone	0.14	0.23	0.28	0.38	0.54	3.9
3-Pentanone	0.22	0.29	0.43	0.53	0.74	3.4

^a The increase factor is calculated as ratio of D (65°C) divided by D (25°C).

compounds bearing methyl or alkyl groups due to Van der Waals forces between the methyl groups of the polymer and the alkyl groups of the analyte. These interactions turned out to be proportional to the number of methyl groups or to the length of the alkyl chain of the analyte, indeed increasing the number of the former or the length of the lat-

ter diffusion through the membrane becomes slower. Aromatic compounds give a good example of this effect. Diffusion coefficients are dramatically decreasing when going from benzene to toluene to C2-benzenes and to C3-benzenes. Furthermore single ring aromatic compounds whose substitute groups have the same total number of carbons as

Table 2
Partition coefficient (K) for 15 VOCs from air matrix and their dependence on temperature

	Temperature ($^{\circ}\text{C}$)					Decrease factor ^a
	25	35	45	55	65	
Benzene	690	449	339	279	212	3.25
Toluene	1,802	1,312	917	684	625	2.88
2C-benzene						
<i>o</i> -Xylene	8,376	4,207	2,444	1,859	1,300	6.44
<i>m</i> -Xylene	7,500	3,680	2,408	1,721	1,331	5.64
<i>p</i> -Xylene	9,899	3,777	2,190	1,431	1,216	8.14
Ethylbenzene	7,719	4,824	2,487	1,435	1,068	7.23
3C-benzene						
TMB	25,531	15,319	8,830	4,724	3,586	7.12
Mesitylene	18,836	9,119	6,130	4,071	2,616	7.20
Propylbenzene	16,363	9,604	6,808	4,757	3,864	4.23
Alcohols						
Methanol	781	449	303	223	174	4.50
Ethanol	1,902	1,056	768	503	335	5.68
Ketones						
Acetone	2,363	1,275	840	442	274	8.62
Butanone	3,338	1,973	1,267	779	586	5.69
2-Pentanone	7,976	4,155	2,801	1,763	1,063	7.50
3-Pentanone	6,161	3,862	2,142	1,545	936	6.58

^a The decrease factor is calculated as ratio of K (25°C) divided by K (65°C).

C2-benzenes (here we measured as an example *o,m,p*-xylene and ethyl-benzene) or C3-benzenes (here we measured as an example propyl-benzene, mesitylene, TMB) have very similar values for the diffusion coefficient. This shows that it is rather the total number of carbons on the substituent more than the structure or the position of the substituent, which mostly influences the interaction analyte–polymer as well as the diffusion. The length of the alkyl chain influences the diffusion of alcohol as well, in fact the diffusion coefficient of methanol is nearly two times that of ethanol. An opposite effect seems to occur for ketones. Indeed the diffusion coefficient for acetone is smaller than the one of butanone, which is smaller than the one of 3-pentanone. 2-Pentanone whose *D* value lies between the one of acetone and butanone represents an exception to this trend. Generally increasing the carbon chain length yields a decrease of the polarity of ketones, thus polar–polar analyte–polymer interactions become weaker and diffusion through the membrane faster. Previous data reported in literature for benzene, toluene and methanol show larger values for *D* than ours [17]. However, this discrepancy might be due to different data analysis and experimental set-ups used.

Solubility, a measure of which is given by the partition coefficient *K*, increases in a homologous series as the carbon chain length or the number of methyl groups increases. Aromatic compounds give a very good example of the influence of the substituent group on solubility. Indeed benzene, not bearing any substituent group, has a partition coefficient less than twice that of toluene, bearing one methyl group. The partition coefficients increase even more for 2C-benzenes and 3C-benzenes. The formers have values more

than 10 times and the latter between 24 and 37 times larger than benzene. Single ring aromatic compounds (with substitute groups) whose total number of carbons is equal to that of, e.g., C2-benzenes or C3-benzenes, have values for the partition coefficient in the same order of magnitude as those of C2 and C3 benzenes. However, differences up to 25% for 2C-benzenes and 35% for 3C-benzenes allow a distinction between the isomers on the basis of their partition coefficients. Carbon chain length also affects the solubility of polar compounds. Ethanol has a partition coefficient more than twice as large than that of methanol, and along the homologue series of ketones the solubility increases with the number of carbons. However, this effect is not so strong for ketones as it is for non-polar compounds, i.e., aromatics. The effect of number and length of alkyl groups on *D* and *K* has been previously described in the literature [14,16,18,19] and it is in agreement with our results.

The overall permeation process depends on both solubility and diffusion constants, and a measure of it is given by the permeability, a product of diffusion and partition coefficients (Table 3). Permeability is higher for hydrophobic compounds than polar ones, and it increases with the hydrophobicity. Thus aromatic compounds show higher permeability than alcohols or ketones and 3C-benzenes permeate at a greater extent than 2C-benzenes, which permeate at a greater extent than toluene and benzene. Similarly the permeability of alcohols and ketones increases with the number of carbons of the alkyl chain, however, at a smaller extent than aromatic compounds.

For compounds with a high permeability enrichment occurs inside the membrane with respect to the air matrix,

Table 3
Permeability [$P (\times 10^{-6})$] for 15 VOCs from air matrix and their dependence on temperature

	Temperature (°C)					β^a
	25	35	45	55	65	
Benzene	908	790	679	592	511	0.45
Toluene	2029	1694	1415	1177	978	1.00
2C-benzene						
<i>o</i> -Xylene	3986	3374	2854	2401	2039	1.96
<i>m</i> -Xylene	3773	3247	2725	2301	1922	1.85
<i>p</i> -Xylene	4128	3660	3021	2566	1982	2.03
Ethylbenzene	3578	3005	2497	2135	1753	1.76
3C-benzene						
TMB	7576	6518	5503	4619	4057	3.72
Mesitylene	5676	5004	4335	3678	3148	2.79
Propylbenzene	5608	4884	4177	3507	2995	2.75
Alcohols						
Methanol	232	206	187	176	163	0.11
Ethanol	285	252	224	207	185	0.14
Ketones						
Acetone	223	201	182	163	148	0.11
Butanone	560	487	417	371	326	0.27
2-Pentanone	1081	916	767	656	558	0.53
3-Pentanone	1304	1106	908	797	677	0.64

^a β is the enrichment factor: calculated as ratio of concentration inside the membrane and concentration in the air sample.

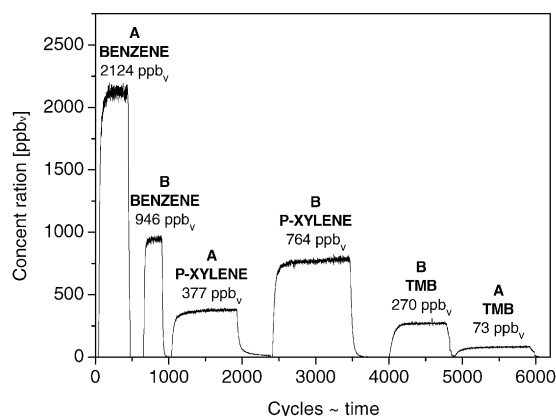


Fig. 3. Concentration of sample air (A) compared with the concentration inside the membrane (B) for benzene, *p*-xylene, and TMB. Benzene does not show enrichment through the membrane, while the enrichment factors for *p*-xylene and TMB are 2.0 and 3.7, respectively.

corresponding to a situation where more analyte than air is crossing the membrane. The enrichment factor (β) is given as the ratio between concentration in the sample air (C_v) and concentration of the analyte inside the membrane (C_i):

$$\beta = \frac{C_i}{C_v} \quad (7)$$

No enrichment effect is observed for the polar compounds, benzene and toluene, while the enrichment factors for 2C-benzene and 3C-benzene are 2 and 2.75–3.75, respectively (Table 3). In Fig. 3 the concentration of original air samples is compared with the concentration of the same compounds transmitted through the membrane (B) for benzene, *p*-xylene, and TMB to show the enrichment effect.

The temperature of the membrane inlet is one of the major parameters influencing the solubility and diffusion of gas through the polymer. We investigated the effect of the temperature on the permeation process over a range from 25 to 65 °C. These temperature limits were chosen to avoid changes in the membrane structure such as degradation at high temperature or transition to a glassy state at low temperature. Increasing the temperature the permeating gases achieve higher kinetic energy, the interaction of analyte–polymer becomes weaker, and compounds diffuse faster through the membrane (Table 1). However, diffusion of compounds, which weakly interact with the membrane, i.e., benzene and toluene, are less affected by the temperature changes.

Solubility, in contrast to diffusion, decreases with the temperature (Table 2). Indeed solution of gases and vapours in polymers is generally an exothermic process; hence solubility tends to decrease with increasing temperature [1]. As in the case of diffusion, the solubility of compounds with weak interaction with the membrane is less affected by a temperature increase.

Permeability, as well as solubility, decreases at higher temperature and this effect is observed for all the compounds analysed in this study (Table 3). The temperature dependence of the permeability is thus determined by the temperature de-

Table 4

Activation energy for the permeation process (E_p) for 15 VOCs from air matrix

E_p (kcal/mol)	
Benzene	-2.88 ± 0.07
Toluene	-3.65 ± 0.09
2C-benzene	
<i>o</i> -Xylene	-3.36 ± 0.07
<i>m</i> -Xylene	-3.38 ± 0.13
<i>p</i> -Xylene	-3.6 ± 0.3
Ethylbenzene	-3.54 ± 0.11
3C-benzenes	
TMB	-3.19 ± 0.09
Mesitylene	-2.97 ± 0.15
Propylbenzene	-3.17 ± 0.13
Alcohols	
Methanol	-1.72 ± 0.09
Ethanol	-2.11 ± 0.06
Ketones	
Acetone	-2.05 ± 0.05
Butanone	-2.71 ± 0.05
2-Pentanone	-3.31 ± 0.05
3-Pentanone	-3.28 ± 0.09

pendence of the solubility. The temperature dependence of permeability obeys the Arrhenius relation [1,14]. To verify if our experimental values obey this relation $\ln P$ was plotted versus $1/T$ and the data interpolated with a linear regression. As shown in Fig. 4a–e the linear fit to the permeability values is in good agreement with the experimental data, with regression coefficients above 0.99 for all compounds. This confirms that the present data obey indeed the Arrhenius relation (5) and thus corresponding values for the activation energy E_p can be derived from the slope of the fitted lines yielding in all cases negative values for E_p (see Table 4). E_p contains two contributions: the difference of heats of solution between the membrane and the sample matrix ($\Delta H_s < 0$, for most of the volatile compounds) and the activation energy for diffusion ($E_d > 0$). Negative values for E_p (see Table 4) indicate that the contribution of ΔH_s dominates over that of E_d . This result confirms our previous statement and agrees with LaPack's result, confirming that permeability for organic compounds in air samples decreases with increasing temperature [14].

A low permeability through the membrane, besides the background/noise of the PTRMS, is the major limiting factor for the sensitivity of the MI-PTRMS system for a specific compound. Indeed those compounds showing the highest permeability can be detected with the lowest concentrations. The worst detection limits were found for ketones: 17.2 ppb_v for acetone and 13.2 ppb_v for butanone. The detection limit for methanol was also of the same order of magnitude (10 ppb_v), while aromatic compounds have a detection limit of about 100 ppt_v or less. The detection limit for benzene was 120 ppt_v, for toluene 105 ppt_v, for *p*-xylene 90 ppt_v and for TMB 70 ppt_v. So the best detection limits are found

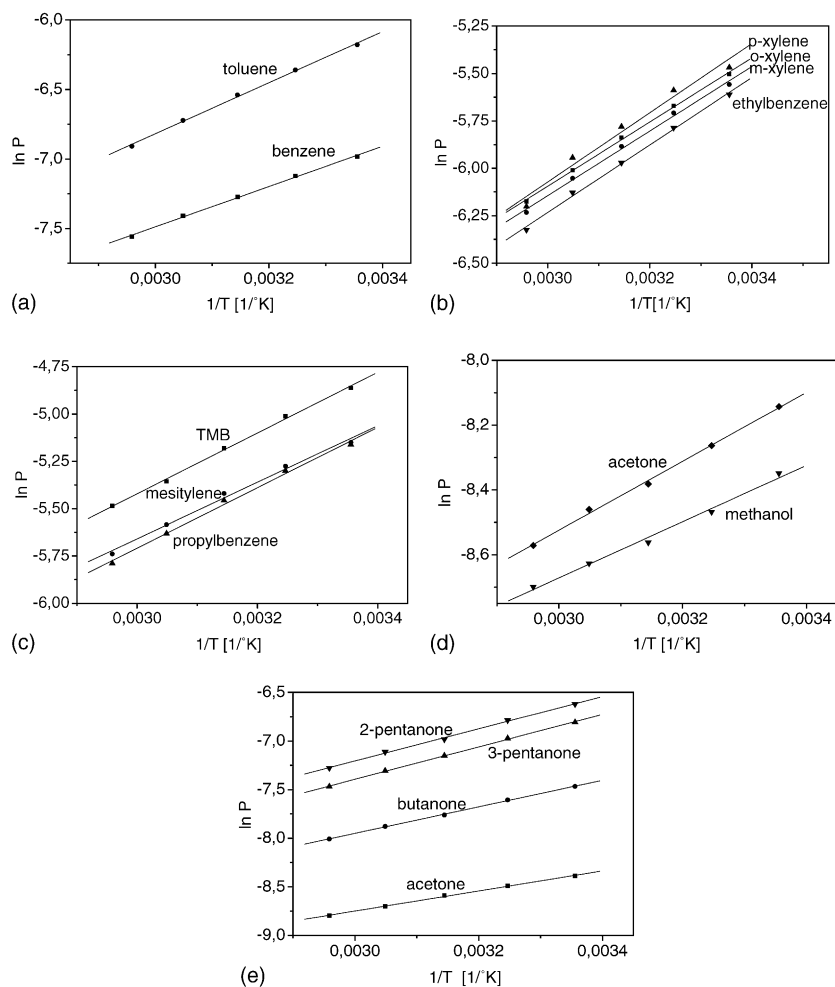


Fig. 4. Arrhenius plots for the permeability. The linear fit of $\ln P$ vs. $1/T$ is in good agreement with the experimental data (with regression coefficients above 0.99).

for those compounds for which enrichment occurs inside the membrane with respect to the air matrix.

Finally, besides having a high sensitivity, MI-PTRMS was shown here to have also a linear response over a wide dynamic range for all the compounds studied. Fig. 5 shows as an example a response curve for toluene demonstrating a linear response over four orders of magnitudes.

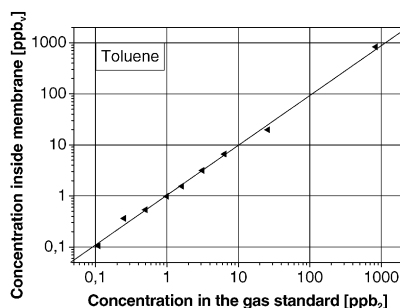


Fig. 5. log–log plot of concentration of toluene inside the membrane (response toward the membrane, calculated as shown in the experimental part) vs. concentration of toluene in the sample air. The regression coefficient for the linear fit is above 0.99.

4. Conclusions

MI-PTRMS is confirmed to be a very suitable tool to characterise membrane materials. Fundamental properties, i.e., diffusion and partition coefficients, describing the interaction between membrane and several classes of chemical compounds can be investigated over a wide range of concentrations. Permeability was confirmed to exhibit Arrhenius behaviour in the range of temperate studied (25–65 °C).

Acknowledgements

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