Polyetherimide–silicone: a 10 μm ultrathin composite membrane for faster and more sensitive membrane introduction mass spectrometry analysis

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A polyetherimide (polyester)/silicone (PEI/S) composite membrane with a 10 μm thick cross-linked silicone layer is found to display the required mechanical properties to work efficiently as the solution/high vacuum interface in membrane introduction mass spectrometry (MIMS) analysis of volatile organic compounds (VOC) in water. Owing to much shorter response and recovery times, the PEI/S membrane allows much faster analysis and calibration procedures as compared to the 250 μm silicone membrane usually used in MIMS. When using EI, owing to excessive water permeation, responses (signal intensity) for the PEI/S membrane are not always superior, being analyte-dependent. For the more polar VOCs, however, the PEI/S membrane shows 2–3 times greater responses, improving their relatively poor MIMS detection limits. When water–methane chemical ionization is applied, the problem of excessive water permeation is attenuated, and the PEI/S membrane displays greatly superior responses.

Introduction

Membrane introduction mass spectrometry (MIMS)[1] is a relatively simple, fast and very sensitive technique for VOC analysis,[2] showing outstanding performance for on-site monitoring and process control.[3,4] In MIMS, as the result of selective transport through the membrane (most often of silicone polymer), VOCs are introduced, without any extraction or pretreatment, from the matrix directly into a mass spectrometer. The hydrophobic membrane also works as the interface between the matrix and the high-vacuum mass spectrometer. The VOCs migrate from the solution to the membrane, concentrate in and diffuse through the membrane, and evaporate from the membrane surface directly into the high vacuum ion-source region of the mass spectrometer, in which they are ionized and further detected at the low ppb level or less.[2]

A major, most attractive feature of MIMS is the rapid full screening of VOCs.[1] The most used 250 μm thick silicone membrane displays, however, response times of 20–60 s or more,[5] thus compromising performance when very fast responses are needed, such as for near real-time monitoring or kinetic measurements of fast reactions.[6] To reduce response and recovery times, and to improve sensitivity, thinner (than 250 μm) silicone membranes have been tested.[1,5b] However, the decreased mechanical resistance of thin silicone membranes compromises their effectiveness and reliability as the high/low pressure, sample/mass spectrometer interface; their performance is also limited by lower VOC enrichments as measured by the analyte–water permeation ratio.

To overcome the decreased mechanical resistance of thin silicone membranes, composite membranes have been tested. Recently,[7] the use of a cross-linked polyacrylonitrile–polyether/25 μm silicone composite membrane was reported. Owing to excessive water permeation the composite membrane showed, however, in normal (aqueous) phase experiments, performance inferior than that of a 125 μm silicone membrane, with no significant difference in response times. Conversely, for reverse-phase experiments, response times for the thin composite membrane improved by a factor of two. When using an ion trap mass spectrometer, the water permeating the thin composite membrane was efficiently used to protonate the analytes.[7]

For gaseous samples, excessive water permeation is eliminated, and much improved performances for thinner silicone membranes are obtained.[5b] Recently,[8] much improved response and recovery times for several semi-VOCs in gaseous samples, and for 2-chlorophenol in aqueous samples, has been reported for a polypropylene/(0.5 μm) silicone tubular composite membrane.

We now report on the use of a cross-linked polyetherimide (polyester)/silicone (PEI/S) sheet composite membrane with a 10 μm ultra-thin silicone layer for MIMS analysis of VOCs, and compare its speed (response and recovery times) and sensitivity (response) in both EI and CI modes to that for a 250 μm silicone membrane.

Experimental

Fig. 1 shows a diagram of the membrane probe,[9] and a schematic of the PEI/S composite membrane; it consists of a 10 μm cross-linked silicone layer formed on a 10 μm polyetherimide asymmetric membrane prepared on a polyester fabric by the phase inversion process.[10] A 250 μm silicone sheet
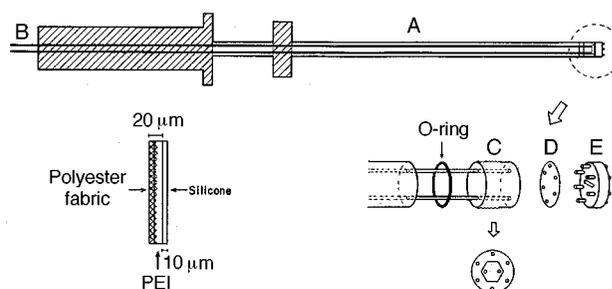

Fig. 1 Diagram of the MIMS probe and a schematic of the PEI(PE)/S composite membrane. The highlighted items are: A, ¼" stainless external probe; B, ⅛" stainless internal tube for sample pumping; C, probe head with the 100 μm deep hexagonal sample reservoir; D, membrane; E, membrane holder.

membrane (Silastic 500-3 from Dow Corning Co.) was used for comparison.

An Extrel (Pittsburgh, PA, USA) pentaquadrupole mass spectrometer[11] was used for detection. The analyte solutions were pumped, at room temperature (23 ± 1 °C), through the membrane interface by an eight-roll peristaltic pump at the rate of 2 mL min⁻¹.

Results and discussion

EI responses

Using Fick's diffusion equations (A = membrane surface area, D = diffusion coefficient, S = solubility constant, P_s = vapour pressure of the analyte on membrane surface on the analyte side), and assuming that constants for solvation and diffusion are independent of partial pressure, the steady-state flow (I_{ss}) of the analyte is preducted (eqn. 1) to be inversely proportional to the membrane thickness (I).[1a,5b]

$$I_{ss} + ADS(P_s/I) \qquad (1)$$

Therefore, neglecting any blocking effect of the 20 μm fibre support membrane, and not considering yet the loss of selectivity resulting from greater water permeation (analyte dilution effect), a near 25 times greater response (signal height) is predicted by using eqn. 1 for the 25 times (silicone-layer) thinner PEI/S membrane.

Table 1 compares, for aqueous solutions of several VOCs, both the responses and response times of the 10 μm PEI/S membrane with those of the 250 μm silicone membrane when 70 eV electron ionization (EI) is applied; Fig. 2 exemplifies, for butan-2-one, the MIMS-selective ion monitoring (MIMS-SIM) profiles for both membranes. The amount of water that permeates both membranes was also measured: for the PEI/S membrane, the $H_2O^{+\cdot}$ ion of m/z 18 was near 20 times more intense. Hence as, most likely, a result of excessive water permeation (loss of membrane selectivity), the response of the PEI/S membrane was not as superior as predicted by eqn. (1); in fact, lower responses are seen for toluene, xylene, dichloromethane, and carbon tetrachloride.

However, for benzene, butan-2-one (Fig. 2), acetone, tetrahydrofuran and *tert*-butyl methyl ether, the PEI/S membrane shows two to three times greater responses; hence, the performance of the PEI/S membrane, in terms of response, is analyte-dependent, having no direct correlation with the polarity of the VOC. Yet for all the more polar compounds (acetone, butan-2-one, THF, MTBE) the PEI/I membrane shows considerable improvement in response, reducing significantly the relatively poor MIMS detection limits of such compounds.[1]

CI responses

Excessive water permeation, a disadvantage for EI monitoring, should, however, be less prejudicial when using chemical ionization (CI) as the water vapour can act as the CI gas. The amount of water that permeates the PEI/S membrane was found insufficient for water-'only' CI, but combined water–methane CI worked adequately: the water is near-totally protonated in the water–methane plasma; hence, some of the H_3O^+ ions protonate the analyte.

Fig. 3 compares the CI responses when monitoring protonated butan-2-one with both membrane. As water no longer competes with the analyte during ionization, but H_3O^+ assists
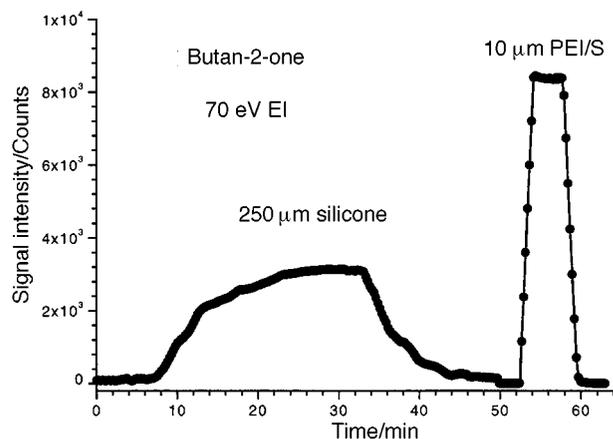

Fig. 2 MIMS 70 eV EI selective ion monitoring analysis of a 500 ppb aqueous solution of but-2-one using both membranes. Solutions were run at room temperature (23 ± 1 °C).
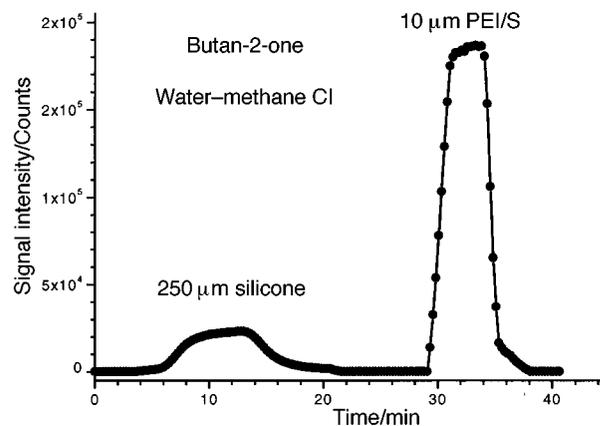

Fig. 3 MIMS water–methane CI selective ion monitoring analysis of an aqueous solution of butan-2-one using both membranes.

Table 1 Responses for the 10 μm PEI/S composite membrane and response times for both the 10 μm PEI/S composite membrane and the 250 μm silicone membrane for several 500 ppb aqueous VOC solutions

| VOC | Response (arbitrary units)[a] 10 μm PE/S | Response time $[t_{(50)}]^{b,c}$/s | | |
		250 μm silicone	10 μm PEI/I	$t_{(50)}^{PEI/S}/t_{(50)}^{Silicone}$
CCl₄	0.65	128	75	1.7
CH₂Cl₂	0.87	90	68	1.3
Benzene	2.8	176	38	4.6
Toluene	0.67	210	55	3.8
Xylene	0.55	205	91	2.3
Acetone	2.6	325	55	5.9
Butan-2-one	2.7	460	75	6.1
Tetrahydrofuran	2.6	345	48	7.2
tert-Butyl methyl ether	2.3	280	42	6.7

[a] The responses of the 10 μm PEI/S composite membrane is reported relative to that of the 250 μm silicone membrane, set arbitrarily to 1. [b] $t_{(50)}$ is the response time required to achieve 50% steady-state permeation. [c] Solutions were run at room temperature (23 ± 1 °C).
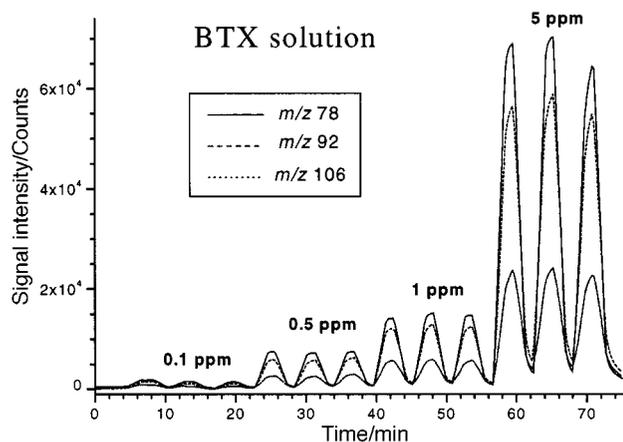
Fig. 4 MIMS 70 eV selective ion monitoring analysis of aqueous solutions of benzene, toluene and xylene using the PEI/S membrane.

the chemical ionization of the analyte, the PEI/S membrane response for butan-2-one is nearly seven times better than that with the 250 μm membrane. This compares with the 2.7 times signal enhancement obtained using EI (Fig. 2).

Response (and recovery) times

As Figs. 2 and 3 exemplify, much improved response times and recovery times are major advantages of the PEI/I membrane (Table 1). For the 250 μm silicone membrane, considerably long time intervals are often needed (except only for dichloromethane) until the signal levels off, and for rinsing the membrane probe after sample analysis. For the PEI/S membrane, however, the signal raises and levels off quickly after sample introduction; the signal disappears as quickly after sample removal.

MIMS calibration

The much faster response and recovery times of the PEI/S membrane drastically reduce the time consumed by calibration. As Fig. 4 shows, when using the PEI/S membrane, calibration by simultaneous monitoring of the ions of *m/z* 78 (benzene), *m/z* 92 (toluene) and *m/z* 106 (xylene), performed at room temperature for three consecutive injections of 0.1, 0.5, 1.0 and 5.0 ppm BTX solutions, took 1.5 h; when using the 250 μm silicone membrane, nearly 5 h are required.

Conclusions

The 10 μm ultra-thin PEI/S composite membrane displays the required mechanical properties to work efficiently as the solution/high vacuum interface in MIMS analysis, offering much shorter response and recovery times than those of thick silicone membranes. Much faster analysis with the PEI/S membrane should therefore benefit MIMS' near real-time process monitoring and fast kinetic measurements. When using EI, owing to excessive water permeation, responses for the PEI/S membrane are not always superior, being analyte-dependent. For the more polar compounds tested (acetone, butan-2-one, THF and TBME), however, 2–3 times greater sensitivity is obtained, reducing considerably their relatively poor MIMS detection limits. When combined water–methane CI is used, the problem associated with excess water permeation is attenuated, and the PEI/S composite membrane displays its best performance, offering much improved sensitivity.

References

1 (a) T. Kotiaho, F. R. Lauritsen, T. K. Choudhury and R. G. Cooks, *Anal. Chem.*, 1991, **63**, 875A; (b) F. R. Lauritsen and T. Kotiaho, *Rev. Anal. Chem.*, 1996, 237; (c) N. Srinivasan, R. C. Johnson, N. Kasthurikrishnan, P. Wongs and R. G. Cooks, *Anal. Chim. Acta*, 1997, **350**, 257.

2 (a) M. Soni, S. Bauer, J. W. Amy, P. Wong and R. G., *Anal. Chem.*, 1995, **67**, 1409; (b) A. A. Rivlin, *Rapid Commun. Mass Spectrom.*, 1995, **9**, 397; (c) J. A. Shoemaker, T. A. Bellar, J. W. Eichelberger and W. L. Budde, *J. Chromatogr. Sci.*, 1993, **31**, 279; (d) M. Leth and F. R. Lauritsen, *Rapid Commun. Mass Spectrom.*, 1995, **9**, 591; (e) M. A. Mendes, R. S. Pimpim, T. Kotiaho and M. N. Eberlin, *Anal. Chem.*, 1996, **68**, 3502.

3 (a) Jorgensen, L. and H. Degn, *Biotechnol. Lett.*, 1987, **9**, 71; (b) T. M. Kana, C. Darkengelo, M. D. Hunt, J. B. Oldham, G. E. Bennett and J. C. Cornwall, *Anal. Chem.*, 1994, **66**, 4166; (c) P. S. H. Wong, N. Srinivasan, N. Kasthurikrishnan and R. G. Cooks, *J. Org. Chem.*, 1996, **61**, 6627; (d) S. Bohatka, *Rapid Commun. Mass Spectrom.*, 1997, **11**, 656; (e) R. F. P. Nogueira, R. M. Alberici, M. A. Mendes, W. F. Jardim and M. N. Eberlin, *Ind. Eng. Chem. Res.*, 1999, **38**, 1754.

4 (a) M. A. LaPack, J. C. Tou and C. G. Enke, *Anal. Chem.*, 1991, **63**, 1631; (b) P. S. H. Wong, R. G. Cooks, M. E. Cisper and P. H. Hemberger, *Environ. Sci. Technol.*, 1995, **29**, 215A; (c) M. Ojala, R. A. Ketola, H. Sorsa and T. Kotiaho, *Talanta*, 1997, **44**, 1253; (d) G. Matz, M. Loogk and F. Lennemann, *J. Chromatogr. A*, 1998, **819**, 51.

5 (a) M. J. Hayward and A. R. Dongré, *Anal. Chim. Acta*, 1996, **327**, 1; (b) R. A. Ketola, M. Ojala, H. Sorsa, T. Kotiaho and R. K. Kostiainen, *Anal. Chim. Acta*, 1997, **349**, 359.

6 (a) K. C. Calvo, C. R. Weisenberger, L. B. Anderson and M. H. Klapper, *J. Am. Chem. Soc.*, 1983, **105**, 6935; (b) F. R. Lauritsen and S. Gylling, *Anal. Chem.*, 1995, **67**, 1418; (c) R. Augusti, A. O. Dias, L. L. Rocha and R. M. Lago, *J. Phys. Chem. A*, 1998, **102**, 10 723.

7 N. Kasthurikrishnan, R. G. Cooks and S. Bauer, *Rapid Commun. Mass Spectrom.*, 1996, **10**, 751.

8 M. E. Cisper and P. H. Hemberger, *Rapid Commun. Mass Spectrom.*, 1997, **11**, 1449.

9 M. A. Mendes, R. S. Pimpim, T. Kotiaho, J. S. Barone and M. N. Eberlin, *Quim. Nova*, 1996, **19**, 480.

10 K. Ohlrogge, K.-V. Peinemann, J. Wind and R.-D. Behling, *Sep. Sci. Technol.*, 1990, **25**, 1375.

11 V. F. Juliano, F. C. Gozzo, M. N. Eberlin, C. Kascheres and C. L. Lago, *Anal. Chem.*, 1996, **68**, 1328.

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