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# In-Membrane Preconcentration/Membrane Inlet Mass Spectrometry of Volatile and Semivolatile Organic Compounds

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**The on-line determination of volatile and semivolatile organic compounds (SVOCs) is reported using membrane inlet mass spectrometry with in-membrane preconcentration (IMP-MIMS). Semivolatile organic compounds in aqueous samples are preconcentrated in a flow-through silicone hollow-fiber membrane inlet held in a GC oven. The sample stream is replaced with air, and the SVOCs are thermally desorbed into the mass spectrometer by rapid heating of the membrane. The method is evaluated for the on-line determination of 4-fluorobenzoic acid, 3,5-difluorobenzoic acid, 2-chlorophenol, *p-tert*-butylphenol, and dimethyl sulfoxide (DMSO) in water. The selectivity of the IMP-MIMS technique for SVOCs in the presence of VOCs is demonstrated. Cryotrapping and a rapid gas chromatographic separation step were added between the membrane and the mass spectrometer ion source for the determination of SVOCs in complex mixtures. The procedure is demonstrated for the determination of dimethyl sulfoxide (DMSO) in equine urine, using internal standardization with DMSO-$d_6$. Full-scan electron ionization (EI) mass spectrometric detection showed good linearity ($R = 0.998$) and RSDs, relative to the internal standard, of 2.2% for desorption only and 4.6% for desorption and cryotrapping.**

Membrane inlet (or introduction) mass spectrometry (MIMS) has been shown to be a rapid and sensitive technique for the determination of volatile organic compounds (VOCs) in aqueous streams,[1] air samples,[2,3] and process monitoring applications.[4] The principles and recent developments of MIMS have been discussed in a number of reviews[5,6] and have been shown by Ketola et al.[7] and Harland et al.[8] to be superior in many respects to other techniques, including purge and trap-GC/MS, for the determination of VOCs. The sensitivity of MIMS for VOCs is generally high, and detection limits in the parts per billion (ppb) range are possible for many compounds, with less polar, low molecular weight analytes showing the lowest detection limits. MIMS has been combined with tandem mass spectrometry (MS/MS)[9] and on-line cryotrapping and rapid GC separation[10] to improve selectivity and reduce detection limits to the low-ppt (parts per trillion) range for selected VOCs.

The observation that MIMS interfaces perform better for nonpolar, low molecular weight VOCs than for more polar, less volatile, compounds, particularly with the use of silicone membranes, limits the range of analytes amenable to the technique. While the determination of some VOCs at very low levels is now attainable by MIMS, the determination of more polar, less volatile, compounds has received less attention.[11−16] Lauritsen et al.[11] described an in-source membrane inlet system for the detection of semivolatile organic compounds (SVOCs) in aqueous solution, in which the sample was passed through a hollow-fiber membrane positioned in a modified EI mass spectrometer source. Interruption of the sample flow led to rapid heating of the membrane by the EI filament situated close to the membrane surface. This approach reduced limits of detection for a range of phenols, phenanthrene, and phenoxyacetic acid, showing gains in sensitivity up to 250 times compared to conventional MIMS. A second-generation

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system employing the same principles was also devised,[12] but instead of the sample flow being interrupted, an air plug was passed through the membrane while heating took place. This resulted in a more rapid heating rate, giving a narrower desorption profile, and the determination of caffeine in tea and coffee samples was demonstrated with good precision. In the configurations adopted by Matz et al.[13] desorption was facilitated by resistive heating of an adapted membrane interface, allowing determination of a mixture of organic compounds in water. A second configuration used in the analysis of fermentation suspensions[14] contained a pneumatically driven membrane probe on which analytes were preconcentrated before desorption at 180 °C.

The use of laser desorption in the determination of SVOCs by MIMS was reported by Soni et al.[15] A low-power carbon dioxide laser was used to irradiate the vacuum side of a sheet membrane held in a direct-insertion (in-source) membrane probe, resulting in desorption of the permeate molecules with little fragmentation. The probe was mounted either in a machined housing connected to a transfer line or directly into the spectrometer ion source region. The technique was demonstrated for the determination of a group of polyaromatic hydrocarbons (PAHs) at the low-ppb level. A development of laser desorption MIMS reported by the same group used resonance-enhanced multiphoton ionization[16] for the determination of PAHs in water at a much lower (ppt) levels than previously possible. The increase in sensitivity was attributed to the selectivity of the MPI process for the PAHs over the membrane material and residual background compounds present in the spectrometer vacuum chamber.

All the above methods are effective in the determination of SVOCs in water but require elaborate and often lengthy modifications to either the membrane interface or the spectrometer ion source, or both. In this paper, we describe a simple technique for the determination of SVOCs in water at the parts per billion to parts per million (ppm) levels, requiring no modification of the spectrometer ion source or the membrane interface used for conventional MIMS. SVOCs are preconcentrated in a flow-through silicone hollow-fiber membrane inlet,[17] located in a GC oven connected by a capillary transfer line to the mass spectrometer ion source, and thermally desorbed by rapid heating of the interface. The procedure is demonstrated for the on-line determination of 4-fluorobenzoic acid, 3,5-difluorobenzoic acid, 2-chlorophenol, *p-tert*-butylphenol, and dimethyl sulfoxide (DMSO) in water and of DMSO in equine urine.

## EXPERIMENTAL SECTION

**IMP-MIMS Configuration.** Analyses were carried out using a Hewlett-Packard (Waldbronn, Germany) HP5970B MSD mass spectrometer coupled to a Hewlett-Packard HP5890A gas chromatograph (GC) oven. The membrane interface was of a hollow-fiber silicone flow over design,[10] which was located inside the GC oven (Figure 1a). The interface was constructed from a conditioned silicone hollow-fiber membrane (0.635 mm o.d. × 0.305 mm i.d.; Dow Corning Silastic 602-105, Sanitech) mounted coaxially inside a short length of stainless steel tubing ($^1/_8$ in. o.d. × 40 mm; SGE, Milton Keynes, U.K.) and connected to two lengths of uncoated, deactivated fused silica capillary column (0.25 mm i.d.; SGE, Milton Keynes, U.K.). The whole unit was made vacuum and water tight by stainless steel compression fittings ($^1/_8$ in. × $^1/_{16}$ in. × $^1/_{16}$ in.; SGE, Milton Keynes, U.K.), and the capillary column was held in place within the membrane by radial compression using graphite ferrules (OGF 16/16, SGE, Milton Keynes, U.K.). Aqueous flow was directed over the outside of the membrane at a rate of 5 mL min$^{-1}$, using a peristaltic pump (Watson Marlow, Cornwall, U.K.) to pull the sample through the interface, and a helium purge of 1 mL min$^{-1}$ was directed through the inside of the fiber to transfer analytes permeating the membrane into the mass spectrometer source. A new hollow-fiber membrane was conditioned by pumping laboratory-purified water through the interface for 30 min. The aqueous flow was then switched to air for 15 s, and the interface was heated to 200 °C at 30 °C/min and held at that temperature for 130 min. The oven was then cooled at the same rate to 40 °C, and the aqueous flow was switched back to purified water.

Analyte preconcentration was effected by pumping the sample over the exterior membrane surface for a fixed period of time (10 min) at a low temperature (40 °C), allowing the analyte to dissolve in the membrane wall. The aqueous flow was then interrupted, and air was pumped through the interface for 15 s. The preconcentrated SVOCs were thermally desorbed using a rapid (40−200−40 °C) heating/cooling cycle of the GC oven. The aqueous flow through the membrane interface was then resumed by using laboratory-purified water. Electron ionization (EI) spectra were recorded in the full-scan mode ($m/z$ 45−250) at 0.34 scan s$^{-1}$.

**IMP-MIMS with Cryotrapping.** The determination of dimethyl sulfoxide in equine urine was carried out using a modified interface incorporating a short chromatographic column (Carbowax, 0.25 mm i.d. × 5 m length × 25 $\mu$m film thickness; Alltech) between the membrane and the mass spectrometer ion source (Figure 1b). The fused-silica capillary on the downstream side of the membrane interface was passed through a cryotrap, consisting of a simple stainless steel T-piece ($^1/_{16}$ in. o.d. × 6 cm gas inlet tube and $^1/_8$ in. o.d. × 13 cm gas exit tube), placed at the head of the coated GC column, for on-line preconcentration of the analytes desorbed from the membrane surface. The cryotrap was cooled by nitrogen gas directed through a heat exchanger consisting of coiled copper tubing ($^1/_8$ in. o.d. × 1 m length) immersed in a liquid nitrogen bath. The cryotrap was cooled for 1 min when the oven temperature reached 150 °C during the thermal desorption step, to trap analytes desorbed from the membrane surface within the cooled section of the GC capillary. The desorption peak maximum (Figure 2) lay within this 1 min trapping window. Remobilization of the condensed analytes was achieved by diverting the gas flow through a heat exchanger coil held in hot water at a controlled temperature of 70 °C (±0.1 °C), for 2 min. This released trapped analytes onto the short length of coated chromatographic column with the oven temperature held at 200 °C, allowing rapid chromatographic separation of the analytes. The outlet of the capillary GC column was connected directly to the mass spectrometer source via a heated transfer line (280 °C). Electron ionization spectra were recorded in the full-scan mode ($m/z$ 45−250) at 1.4 scans s$^{-1}$ to ensure a minimum of six data points over each eluting peak.

**Standard MIMS Operation.** The performance of the IMP-MIMS system was compared with that for the hollow-fiber

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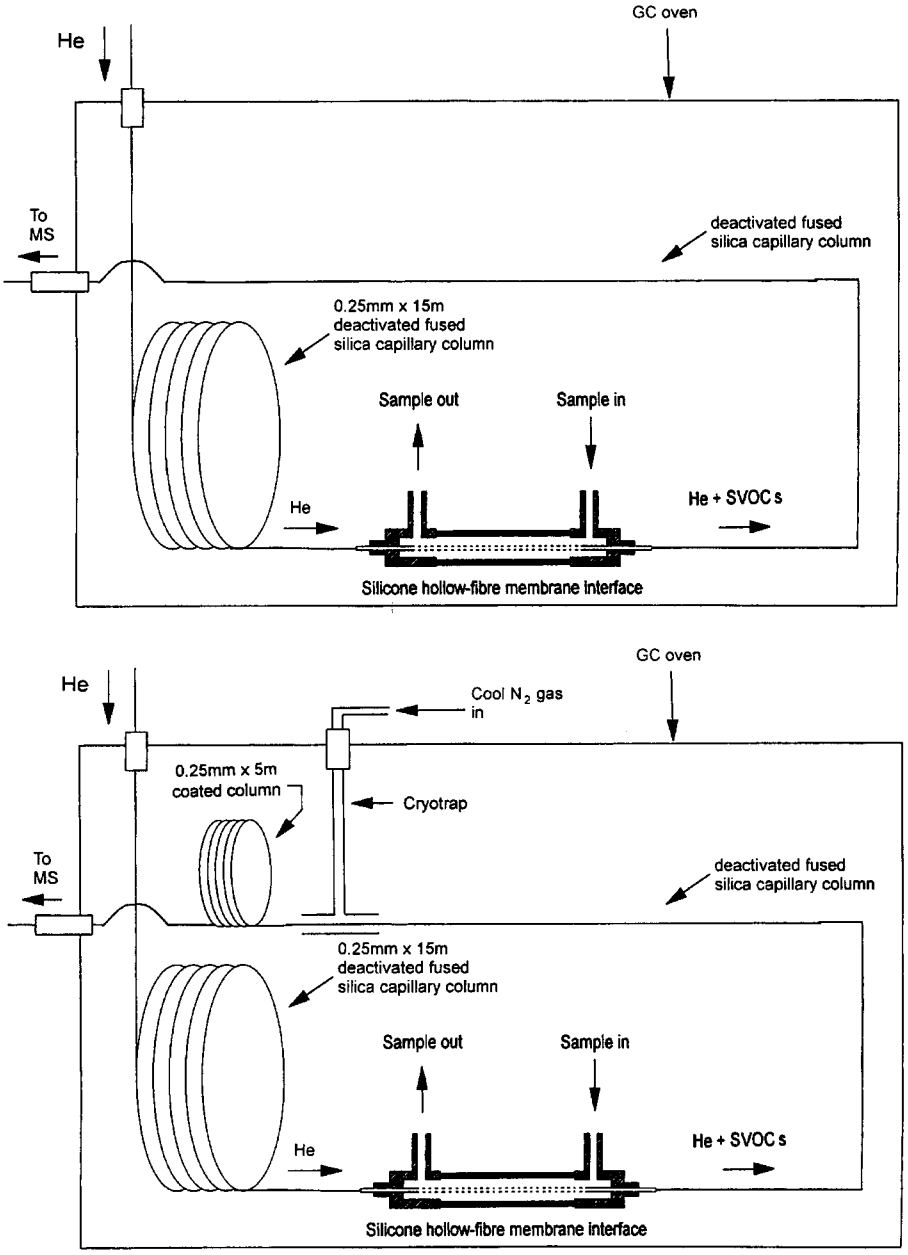


Figure 1. Schematic diagram of IMP-MIMS interface configurations.

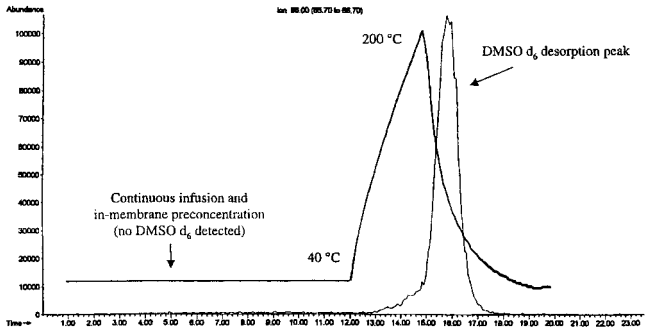


Figure 2. GC oven temperature and analyte desorption profiles for the IMP-MIMS analysis of DMSO.

membrane interface used in standard MIMS with the gas chromatograph oven maintained at an isothermal temperature of 70 °C. Aqueous flow was directed over the outside of the membrane at a rate of 5 mL $min^{-1}$, using a peristaltic pump (Watson Marlow, Cornwall, U.K.) connected to the outlet of the interface. The analyte was allowed to diffuse through the membrane wall into the countercurrent helium purge flow, directed toward the ion source, until steady-state conditions had been reached. The analyte response was defined as the difference in ion intensity between the average background signal and the average steady-state analyte signal.

**Standard Solutions and Samples.** 4-Fluorobenzoic acid, 3,5-difluorobenzoic acid, 2-chlorophenol, *p-tert*-butylphenol, dimethyl sulfoxide (DMSO), and hexadeuteriodimethyl sulfoxide (DMSO-$d_6$) were obtained from Sigma Aldrich. Standard solutions were prepared using serial dilutions of individual stock solutions, made by dissolving the neat SVOCs in purified water (concentration ranges: 4-fluorobenzoic acid and 3,5-difluorobenzoic acid, 2.4−240 mg $L^{-1}$; 2-chlorophenol, 0.001−1.2 mg $L^{-1}$; *p-tert*-butylphenol,

0.6−215 mg $L^{-1}$; dimethyl sulfoxide and hexadeuteriodimethyl sulfoxide, 50−1000 mg $L^{-1}$). Equine urine samples obtained from the Horseracing Forensic Laboratory Ltd. (Fordham, U.K.) were adjusted to pH 7, and a 25 mL aliquot was diluted to 100 mL prior to IMP-MIMS analysis. Spiked samples were prepared by adding 10 mL of a standard solution containing DMSO and DMSO-$d_6$ (100 mg $L^{-1}$ of each) to 25 mL of urine and diluting the mixture to 100 mL.

## RESULTS AND DISCUSSION

The interface configuration (Figure 1) used for in-membrane preconcentration membrane inlet mass spectrometry (IMP-MIMS) was similar to that described for direct MIMS analysis[17] and MIMS with on-line cryotrapping and rapid GC separation.[10] VOCs in aqueous samples pumped through the interface rapidly pervaporate through the membrane and are transferred to the mass spectrometer source. In contrast, semivolatile and nonvolatile organic analytes tend to accumulate in the membrane at temperatures below 100 °C, resulting in a weak mass spectrometric response. The analytical procedure was therefore adapted for SVOCs in this work by controlling the GC oven temperature to allow analyte preconcentration in the membrane at 40 °C, followed by removal of water from the interface and rapid cycling of the oven temperature (40−200−40 °C) to desorb the SVOCs into the helium flow directed toward the ion source. Typical oven temperature and analyte desorption profiles are shown in Figure 2, for the IMP-MIMS analysis of dimethyl sulfoxide (DMSO) in water. The oven temperature requires over 7 min to cycle from 40 to 200 to 40 °C, but DMSO desorbs in a narrow band with a peak width at half-height of approximately 1 min.

**In-Membrane Preconcentration.** The effect of in-membrane preconcentration time on analyte response was investigated using a mixture of 4-fluorobenzoic acid ($m/z$ 140) and 3,5-difluorobenzoic acid ($m/z$ 158), each at a concentration of 15 mg $L^{-1}$, under the IMP-MIMS conditions described for DMSO. The membrane was exposed to the sample solution for periods of 1−10 min followed by a 15 s air purge and thermal desorption. The analyte desorption profile response was observed to increase initially with preconcentration time but leveled out at times greater than 5 min, indicating that a steady-state had been reached. A preconcentration time of 10 min was used for all subsequent analyses. Repeating the preconcentration/desorption cycle with laboratory-purified water after several runs using the fluorobenzoic acid standard mixture gave a response below the limit of detection (S/N = 2/1), confirming that there are no significant memory effects from run to run for these analytes.

The effect of increasing the air purge time between the sample preconcentration and thermal desorption steps was investigated for DMSO using purge times from 15 to 120 s at an interface temperature of 40 °C. The ion intensity for a DMSO solution (200 mg $L^{-1}$) did not change significantly with purge time, indicating that SVOCs may be retained in the membrane even at extended purge times. Standard solutions of DMSO demonstrated good linearity ($R$ = 0.998, $n$ = 5) across the range 50−1000 mg $L^{-1}$ using an air purge time of 15 s and a preconcentration time of 10 min. The total run time per sample was less than 22 min.

**Membrane Conditioning and Lifetime.** The use of an unconditioned hollow-fiber silicone membrane in the IMP-MIMS interface resulted in a high background level of silicon-containing ions (e.g., $m/z$ 73, 77, 147, 207, 221, and 251) derived from the dimethylsiloxane membrane by thermal desorption. Some of these fragments have been observed in previous work[11,12] where long heating times were used. This background was reduced to manageable levels by prior conditioning of each new membrane, much like a new chromatographic column, before sample analysis. However, continuous temperature cycling of the membrane interface reduces the life of the silicone hollow-fiber membrane[12] compared to the standard MIMS technique, which relies upon constant infusion of the analyte sample at an isothermal temperature below 100 °C until steady-state diffusion has been reached.[18] The ballistic heating cycle used to desorb SVOCs in this work reduced the useful life of the interface to around 60−70 analyses before a new membrane was required. This is a shorter lifetime than that reported by Lauritsen et al.[11] for a silicone membrane, due to the longer heating times in this work, but is equivalent to the number of analyses (50−100) possible using a poly(dimethylsiloxane)-coated SPME fiber undergoing similar temperature-cycling conditions.[19]

**Selectivity for SVOCs and VOCs.** A limiting factor for in-source MIMS configurations[12] is that, while high sensitivity is possible, there is no direct control over the temperature of the desorption process for preconcentrated analytes once the sample stream, which keeps the membrane cool, has been switched to an air plug. In this work, we demonstrate the ability of the IMP-MIMS method to separate VOC from SVOC responses through control of the interface temperature during the purge and desorption processes. This is possible because the membrane interface is located in the GC oven, remote from the spectrometer ion source, allowing a separate and controllable heating cycle to be used. This is illustrated in Figure 3 for the IMP-MIMS analysis of a solution containing DMSO (200 mg $L^{-1}$), which is retained in the membrane at 40 °C, and diethyl ether (50 $\mu$g $L^{-1}$), which permeates readily at this temperature. The response for the volatile diethyl ether ($m/z$ 59) rises rapidly to a steady state when the sample is introduced into the interface (Figure 3a), while the DMSO response ($m/z$ 63) remains unchanged (Figure 3b), as this analyte is preconcentrated inside the membrane. The diethyl ether ion intensity falls off quickly when the sample flow is stopped and the membrane is purged with air for 60 s before thermal desorption of the DMSO as a sharp band.

Even when the VOCs present in a sample containing SVOCs are not pumped away before the desorption step, there is still a degree of selectivity in the IMP-MIMS procedure. This is because the GC oven heating rate for the membrane is not as rapid as heating by the filament in in-source configurations, or by resistive heating, and hence analytes with different boiling points may be desorbed sequentially into the ion source. For example, Figure 4 shows the resolved desorption peaks for toluene and DMSO-$d_6$ and the corresponding peak top mass spectra (without background subtraction) for the IMP-MIMS analysis of a solution of DMSO-$d_6$ in water (400 mg $L^{-1}$) containing a toluene spike (100 $\mu$g $L^{-1}$). The spectra are free of spectral overlap, demonstrating the selectivity of the IMP-MIMS method.

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Table 1. Limits of Detection for MIMS with and without In-Membrane Preconcentration

| analyte | bp (°C) | quantitation ion ($m/z$) | std MIMS detection limit[a] (mg $L^{-1}$) in full-scan mode | IMP-MIMS detection limit[a] (mg $L^{-1}$) in full-scan mode | gain factor for IMP-MIMS |
|---|---|---|---|---|---|
| toluene | 110 | 91 | 0.007 | 0.0007 | 10 |
| 4-fluorobenzoic acid | 183[b] (mp) | 140 | 240 | 0.5 | 480 |
| 3,5-difluorobenzoic acid | 122[b] (mp) | 158 | 240 | 0.5 | 480 |
| 2-chlorophenol | 63 | 128 | 0.3 | 0.006 | 50 |
| *p-tert*-butylphenol | 237 | 135 | 320 | 0.030 | 10500 |
| DMSO | 189 | 63 | >1000[c] | 6 | >170 |
| DMSO-$d_6$ | 189 | 66 | >1000[c] | 6 | >170 |

[a] S/N = 3/1. [b] Melting point. [c] A concentration of 1000 mg $L^{-1}$ gave no response above the noise level under standard MIMS conditions.

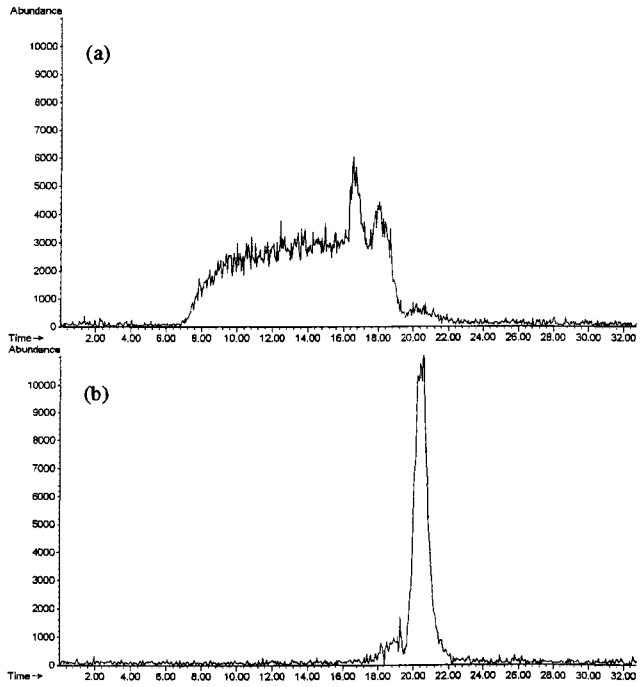


Figure 3. IMP-MIMS single-ion chromatograms of (a) diethyl ether ($m/z$ 59) and (b) DMSO ($m/z$ 63) for the analysis of a mixture of DMSO (200 mg $L^{-1}$) and diethyl ether (50 $\mu$g $L^{-1}$).

**Sensitivity and Limits of Detection.** Table 1 shows the sensitivity gains obtained for the analytes investigated using IMP-MIMS. In all cases, in-membrane preconcentration led to a reduction in the limit of detection of 50 to >10 000 times compared to continuous-infusion MIMS procedures. These gains are much higher than those previously reported for membrane preconcentration MIMS analysis (vide infra). The gain observed for the analysis of an aqueous solution of 4-fluorobenzoic acid (240 mg $L^{-1}$) is shown in Figure 5. MIMS with continuous sample infusion (i.e., without preconcentration) gave a response at the detection limit for the system (S/N of 3/1) as shown in Figure 5a. However, a diluted solution of the 4-fluorobenzoic acid (2.4 mg $L^{-1}$) gave a signal-to-noise ratio of 15/1 when analyzed by IMP-MIMS (Figure 5b). This corresponds to a detection limit of 0.5 mg $L^{-1}$ (500 ppb), approximately a 500-fold improvement in detection limit over standard MIMS.

The determination of 2-chlorophenol by MIMS without preconcentration gives a detection limit in the mid-ppb range (300 $\mu$g $L^{-1}$), which is enhanced by a factor of 50 using IMP-MIMS, to give a detection limit of 6 $\mu$g $L^{-1}$. This limit of detection for 2-chlorophenol is comparable with that for MIMS with cryotrapping[10] and is significantly lower than those for previously reported preconcentration/thermal desorption techniques.[11] Alternative methods for the analysis of a mixture of phenols using membrane

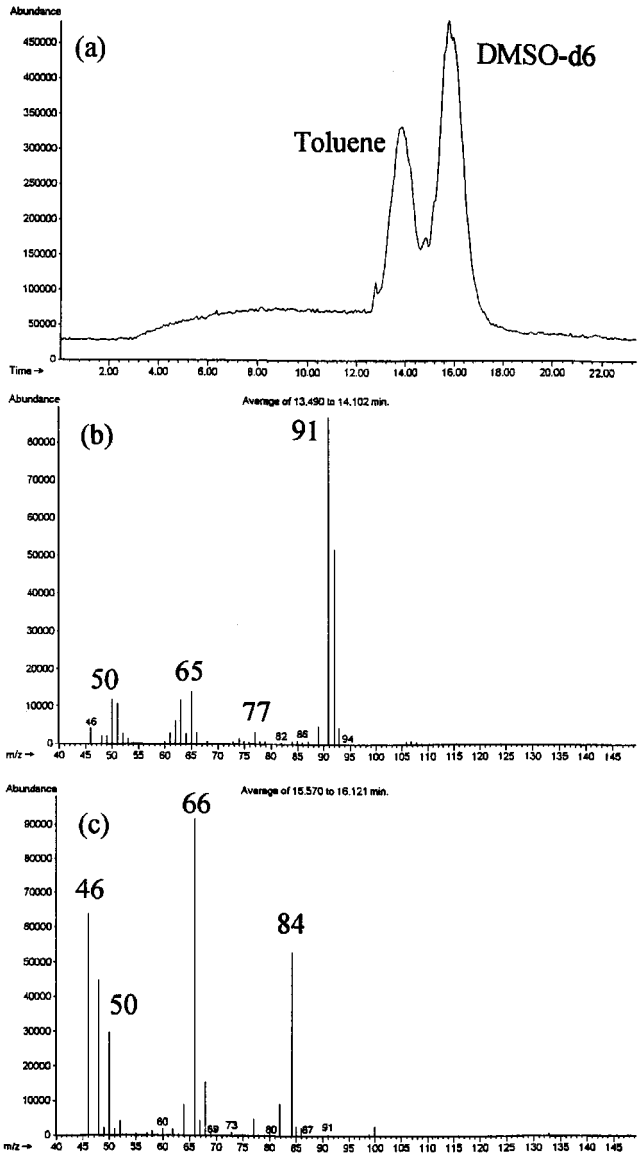


Figure 4. Desorption peak profiles for a mixture of toluene (100 $\mu$g $L^{-1}$) and DMSO-$d_6$ (400 mg $L^{-1}$) and mass spectra recorded at the peak maxima.

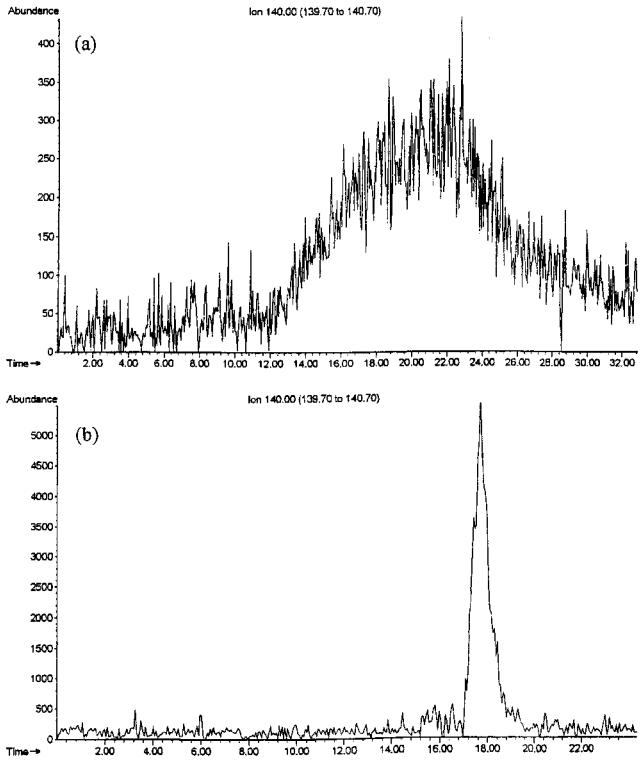


Figure 5. Single-ion chromatograms (*m*/*z* 140) obtained for the MIMS analysis of an aqueous solution of 4-fluorobenzoic acid (a) with continuous sample infusion (240 mg $L^{-1}$) and (b) with in-membrane preconcentration (2.4 mg $L^{-1}$).

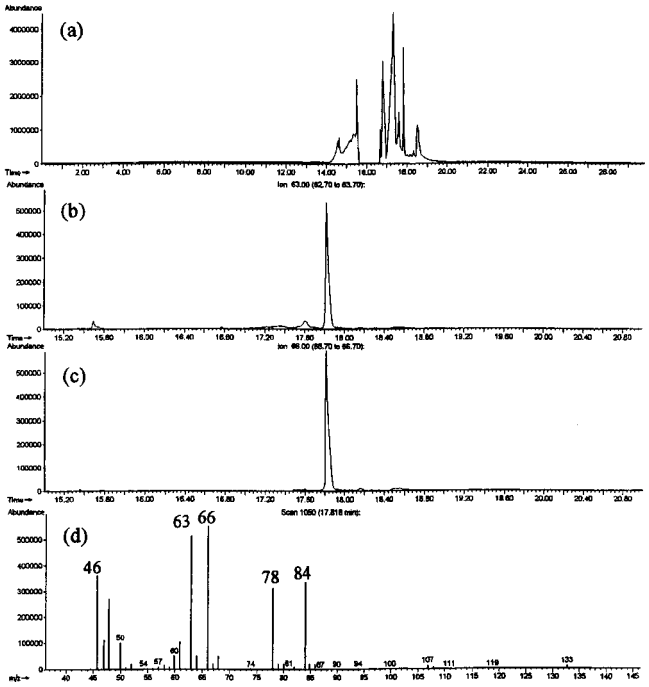


Figure 6. Determination of DMSO in a spiked equine urine sample by IMP-MIMS with cryotrapping and rapid GC separation: (a) total-ion chromatogram; (b) single-ion chromatogram for DMSO (*m*/*z* 63); (c) single-ion chromatogram for DMSO-$d_6$ (*m*/*z* 66); (d) mass spectrum recorded at the peak maximum.

liquid extraction and LC separation have previously been reported.[20]

The detection of alkylphenol ethoxylates (APEs) in water has received much attention recently, as their role as estrogen mimics, or endocrine disrupters, has been reported widely.[21] Methods for the detection of APEs usually rely on the detection of the corresponding alkylphenols (APs) by reverse-phase HPLC, gas chromatography, or liquid chromatography/mass spectrometry.[22−24] A solution of *p-tert*-butylphenol (0.6 mg $L^{-1}$) analyzed by IMP-MIMS gave a strong response from which a detection limit of 30 $\mu$g $L^{-1}$ was determined (Table 1). This is a significant improvement on the standard MIMS detection limit, where a solution of *p-tert*-butylphenol (215 mg $L^{-1}$) gave a signal-to-noise response of 2/1. The limit of detection was further improved by the addition of an organic modifier (50% methanol) to the aqueous sample phase, using the approach of Ouyang et al.,[25] as a result of better permeation of the analyte through the membrane.

MIMS using a nonpolar hydrophobic membrane material, such as poly(dimethylsiloxane), usually shows a poor response for polar analytes. This is evident for the determination of DMSO and DMSO-$d_6$ in water, where there was no observed analyte signal for the standard MIMS techniques even at concentrations in excess of 1000 mg $L^{-1}$. However, DMSO can be easily detected down to a detection limit of 6 mg $L^{-1}$ by IMP-MIMS, with a % RSD of 2.2 ($n = 6$). The detection limits given in Table 1 may be decreased further by the use of IMP-MIMS with cryotrapping, together with an appropriate choice of the capillary column stationary phase.[10] This extended technique is discussed below for the determination of DMSO in equine urine, using isotope dilution with DMSO-$d_6$, with minimal sample pretreatment.

**Determination of DMSO in Equine Urine.** Dimethyl sulfoxide is classed as a low-effect substance, which requires determination at a threshold of 15 mg $L^{-1}$ in equine urine.[26] This concentration corresponds to a level sufficiently higher than that of the endogenous level in the horse to indicate abuse of the substance. The few published methods for the monitoring of DMSO in racing forensic analysis are both time consuming and labor intensive, using liquid−liquid extraction followed by TLC and subsequent detection and quantitation by GC/MS.[27] We have therefore investigated the determination of DMSO in equine urine by IMP-MIMS with on-line cryotrapping and rapid gas chromatographic separation (Figure 1b).

Figure 6a shows the total ion chromatogram of an equine sample spiked with DMSO and DMSO-$d_6$ (each at 10 mg $L^{-1}$) and analyzed by IMP-MIMS with cryotrapping and gas chromatography. The single-ion chromatograms for DMSO (*m*/*z* 63) and DMSO-$d_6$ (*m*/*z* 66) in the range 15−21 min are shown in Figure 6b,c, together with the mass spectrum recorded at the peak maxima (Figure 6d). The single-ion responses for DMSO (RT = 17.8 min) and DMSO-$d_6$ are free of interferences from the complex

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urine matrix as a result of the combined selectivity of the membrane and the chromatographic separation. Precision was slightly lower (% RSD = 4.6; $n = 6$) than that for the direct IMP-MIMS method. Benzoic acid, methyl benzoate and *p*-cresol, all present at high concentrations in equine urine, were observed to preconcentrate in the membrane under standard IMP-MIMS conditions. A blank run was therefore required to prevent carryover between samples. However, the only sample pretreatment for the urine sample was adjustment of the pH and dilution, and the use of DMSO-$d_6$ as an internal standard allowed quantitation of DMSO in a equine urine by isotope dilution.

## CONCLUSIONS

In-membrane preconcentration/membrane inlet mass spectrometry (IMP-MIMS) has been demonstrated for the on-line determination of a range of SVOCs in aqueous samples with significant gains in sensitivity and selectivity compared to continuous-sample-infusion MIMS techniques. Good precision is shown for IMP-MIMS, giving % RSDs of 4.6 and 2.2 with and without cryotrapping, respectively. VOC and SVOC responses may be resolved by control of the interface temperature during the purge and desorption processes. The inclusion of a GC separation step facilitates the application of IMP-MIMS to the analysis of complex biological samples, such as the determination of DMSO in equine urine.

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