

**SPECIAL FEATURE:
PERSPECTIVE****Environmental applications of membrane introduction mass spectrometry****Raimo A. Ketola,^{1*} Tapio Kotiaho,² Mary E. Cisper³ and Todd M. Allen⁴**¹ VTT Processes, P.O. Box 1401, FIN-02044 VTT, Finland² Department of Pharmacy, Viikki Drug Discovery Technology Center (DDTC), P.O. Box 56, FIN-00014 University of Helsinki, Finland³ Chemistry Division, Los Alamos National Laboratory, Los Alamos, New Mexico 87545, USA⁴ Isotag Technology, Inc., Los Alamos, New Mexico 87544, USA

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The purpose of this review is to highlight the versatility of membrane introduction mass spectrometry (MIMS) in environmental applications, summarize the measurements of environmental volatile organic compounds (VOCs) accomplished using MIMS, present developments in the detection of semi-volatile organic compounds (SVOCs) and forecast possible future directions of MIMS in environmental applications. Copyright © 2002 John Wiley & Sons, Ltd.

KEYWORDS: membrane introduction mass spectrometry; water analysis; soil analysis; air analysis; environmental analysis; organic compounds; permanent gases

INTRODUCTION

The use of mass spectrometry (MS) for the measurement of organic contaminants in environmental samples is one of its largest areas of application.¹ In waste reduction activities and treatment and remediation of contaminated sites, compounds such as polyaromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), dioxins and volatile organic compounds (VOCs) are measured using routine MS methods. Recent developments in environmental mass spectrometry have focused on the determination of possible new chemical pollutants (e.g. pharmaceuticals, natural and synthetic estrogens and water disinfection by-products) and on the development of new methods for on-line/on-site measurements minimizing environmental pollution, energy and raw material usage. One of the emerging methods for on-line/on-site measurements is membrane introduction mass spectrometry (MIMS).

In MIMS, introduced for the first time in 1963,² organic compounds are separated from water or air by a thin membrane (typically polydimethylsiloxane, also known as silicone) installed between the sample and the ion source of a mass spectrometer.^{3–9} Organic compounds dissolve in the membrane, diffuse through it and finally evaporate directly into the ion source (Fig. 1).³ Because the flow of the analyte matrix, usually water or air, through the membrane is proportionally smaller than the flow of the desired organic

analytes, analyte enrichment is obtained. This facilitates very sensitive levels of detection, as low as ng l⁻¹ levels in water and ng m⁻³ levels in air. Other important advantages offered by MIMS are (i) the method is fast, (ii) pretreatment of samples is not necessary, (iii) the cost per sample is low, (iv) solvents are not used and (v) most importantly, MIMS can be used for long-term continuous monitoring of environmental, biochemical and chemical processes.

Environmental monitoring of air, water and soil by MIMS is expanding. A number of reviews of the technique have been published;^{3–9} however, a comprehensive environmental review is lacking.

WATER ANALYSIS**Environmental water analysis: background**

Two factors contribute to the importance of water purity: around the world there is a shortage of pure drinking water and legislation controlling both ground water and waste water has become more stringent, especially in Europe and the USA (EU Directive 98/83/EC, Safe Drinking Water Act of 1974, amended in 1986 and 1996).^{10,11}

Static or dynamic headspace methods are the primary methods currently used to extract VOCs from water samples. The theory and construction of headspace methods have been reviewed by Koester and Clement,¹² Crompton,¹³ Soniassy *et al.*¹⁴ and Poole and Schuette¹⁵. These techniques provide a clean matrix-free sample, and are best suited for the determination of low molecular mass, slightly water-soluble VOCs. Theoretical considerations of purge-and-trap gas

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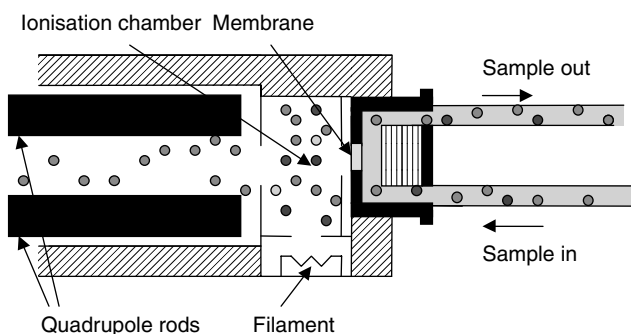


Figure 1. Schematic diagram of a membrane introduction mass spectrometer. The water or air sample is circulated over the membrane and the analytes pass through the membrane into the ionization chamber of the mass spectrometer. Reprinted with permission from Kotiaho T, Lauritsen FR, Choudhury TK, Cooks RG, Tsao GT. Membrane introduction mass spectrometry. *Analytical Chemistry* 1991; **63**: 875A.

chromatography/mass spectrometry (P&T-GC/MS) have been studied in detail.^{16–18} Researchers have scrutinized an automated P&T-GC/MS method;¹⁹ parameter optimization for P&T-GC/MS²⁰ and static headspace gas chromatographic (HSGC) methods²¹ have also been examined.

Many different techniques have been developed for the determination of semi-volatile organic compounds (SVOCs) in water samples. The most common pretreatment method for liquid samples prior to analysis by chromatography is liquid–liquid extraction (LLE).²² The benefits of the LLE technique are simplicity, low cost and the fact that the method is well known and understood. Concentration factors >10 000 have been achieved with micro-LLE.²³ Furthermore, LLE is a very useful technique for eliminating interfering inorganic compounds present in aqueous samples. Although LLE is a versatile technique and requires only simple equipment, it is time consuming, labor intensive, not easily automated, typically non-selective and it consumes solvents. For GC analysis, the analytes can be derivatized to increase their volatility but derivatization is also time consuming and some of the analytes may be lost during the procedure.

If more selectivity is desired, solid-phase extraction (SPE) can be a good alternative to LLE. Large enrichment factors (typically 100–1000) are possible, and selectivity can be achieved by choosing an appropriate sorbent material for analytes that do not adsorb impurities and/or matrix compounds or, alternatively, allows their desorption by a different solvent. SPE can be performed off-line or on-line; the off-line experiment is simple and highly flexible, whereas on-line SPE can be automated and provides a high sample throughput.²⁴ The greatest disadvantage of the SPE technique is that it is time consuming.

Solid-phase microextraction (SPME) has been used primarily for the determination of VOCs, but it can also be applied to the determination of SVOCs.²⁵ SPME can be performed manually or by means of an autosampler. Because it is an equilibrium sampling technique, the limits of detection are higher than those of LLE and SPE. The time to reach equilibrium depends on the nature of the

analytes and ranges from 2 to 60 min. In the case of semi-volatile compounds, the fiber coating must be inserted into the sample (not in the headspace above the sample), and general experience shows that if reliable quantification is desired, the technique is only applicable to relatively pure samples.²²

High-performance liquid chromatography (HPLC) is not only a powerful analytical method as such, but also allows effective sample preparation for GC. Semi-volatile compounds can be separated directly by HPLC without any sample preparation with a very short analysis time of only a few minutes. The disadvantages are higher limits of detection than with extraction techniques (LLE, SPE) and difficulty of qualitative measurement of unknown samples unless the technique is used with mass spectrometry. HPLC can be combined with GC on-line for the determination of some target compounds in highly complex matrices. This LC/GC method is highly specific but requires a complex instrument.²⁶

MIMS does not replace the above-mentioned techniques but rather complements the repertoire of analytical techniques when faster responses are needed or on-line/on-site capabilities are desired.

Development of different membrane inlet methods for water analysis

Determination of volatile organic compounds in water

MIMS, with a hollow fiber probe membrane, was first used by Westover *et al.*²⁷ to monitor reacting systems containing VOCs such as chloroform, hexane and methanol in aqueous solution and air. Permeation of organic compounds across different membrane materials was studied; it was found that silicone rubber was the most useful membrane material for the separation of VOCs from aqueous solution. Hydrogen bonding between a compound molecule and the aqueous matrix was believed to be the most important reason for the detection limit of methanol (1 ppm) being higher than that of chloroform (10 ppb). Low ppb levels of VOCs were detected with response times of a few seconds. An enrichment factor of 1.1×10^4 was determined for chloroform.

Tetler *et al.*²⁸ introduced the first sheet membrane system for detecting VOCs in estuarine water. A silicone rubber membrane supported by wire mesh and sealed Teflon collar was interfaced directly to the vacuum chamber of a mass spectrometer. Minimum detection limits of $1\text{--}7 \mu\text{g l}^{-1}$ and a few hundred $\mu\text{g l}^{-1}$ were achieved for non-polar and polar compounds, respectively. A high concentration of sodium chloride (35 g l^{-1} ; sea concentration) reduced the toluene signal only slightly (6%).

The use of the flow-through technique (Fig. 2), in which the analyte solution passes across the inner surface of the membrane while the outer surface is exposed to the vacuum of the mass spectrometer, improves response times and lowers detection limits.^{29–33} This technique also permits the use of flow injection analysis (FIA) procedures that allow precise repetitive sampling of flow streams. On-line monitoring and quantification can be performed by injecting aliquots of the sample mixture into the continuous water stream supplied by a peristaltic pump. The FIA technique reduces the amount of sample used.^{34–38} Weaver

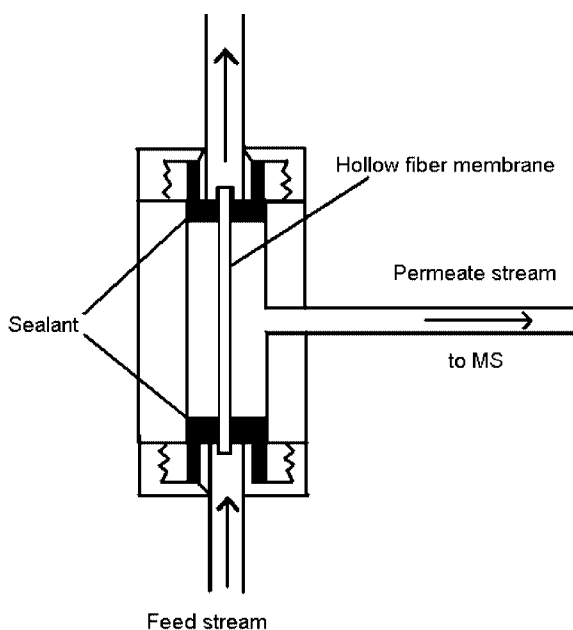


Figure 2. In the flow-through geometry, the sample flows across the inner surface of the membrane while the outer surface is exposed to the mass spectrometer vacuum. Reprinted with permission from LaPack MA, Tou JC, Enke CG. Membrane mass spectrometry for the direct trace analysis of volatile organic compounds in air and water. *Analytical Chemistry* 1990; **62**: 1265. Copyright 1990 American Chemical Society.

and Abrams³⁴ developed a simple FIA related system that allowed pH adjustment of the sample solution on-line before MIMS measurement. For example, acetic acid, which cannot be measured at pH 6, can be easily measured with MIMS when the pH is lowered below 2. In the FIA/MIMS system, the membrane is exposed to the sample for a short period, i.e. sample flow is interrupted by pure water before steady-state permeation is reached. The height of the FIA peak can be used for quantification because the total flux through the membrane at any time is linearly dependent on the sample concentration in the feed liquid. Owing to short sampling times, the FIA/MIMS technique is a very rapid method for determining organic compounds in aqueous solutions, and it can be automated very easily.

During the past few years the standard MIMS method has seen a number of modifications. Chemical ionization (CI) with tandem mass spectrometry, which was introduced to MIMS by Brodbelt and Cooks²⁹ in 1985, is a very powerful tool for analyzing mixtures. CI simplifies the mass spectrum of a mixture when compared with one obtained with electron ionization (EI). Analyte identification is enhanced with mass spectrometry/mass spectrometry (MS/MS). When a microporous polypropylene membrane is used, the solvent flux is high enough for the vaporized solvent to be used as a chemical ionization gas.³⁹ Instead of a filament, a glow discharge was used to ionize the reagent gas, since the high water pressure was found to shorten the filament lifetime. Response times were short, ~10 s, but limits of detection (low- or sub-ppm) were higher than with a non-porous silicone membrane because the enrichment step is

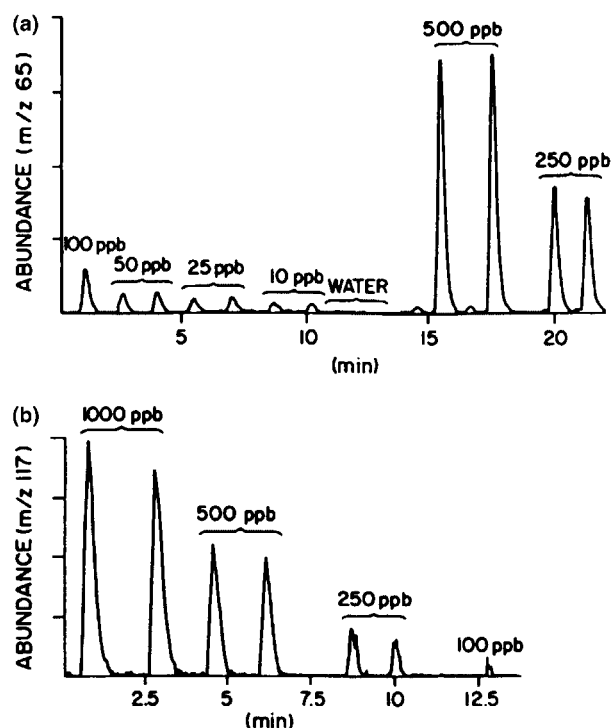


Figure 3. Single ion monitoring data of successive duplicate injections of low concentration samples of aqueous (a) ethanol and (b) tetrachloromethane. Measurements were made with a microporous membrane and solvent chemical ionization. Ethanol was measured by recording the abundance of the $[(M + H_2O)H]^+$ ion (m/z 65) and tetrachloromethane was measured as the protonated molecule minus HCl $[M + H - HCl]^+$ (m/z 117). Reprinted with permission from Lauritsen FR, Choudhory TK, Dejarne LE, Cooks RG. Microporous membrane introduction mass spectrometry with solvent chemical ionization and glow discharge for the direct detection of volatile organic compounds in aqueous solution. *Analytica Chimica Acta* 1992; **266**: 1. Copyright 1992 Elsevier Science.

missing. On the other hand, polar compounds were easily measured. Figure 3 shows an example of this technique, in which ethanol can be measured at low levels paralleling tetrachloromethane measurement.³⁹ Wong and Cooks used a microporous membrane to separate more polar compounds, such as 5-hydroxymethylfurfuraldehyde and lactic acid, in aqueous samples.⁴⁰

Slivon *et al.*³⁵ introduced the idea of pneumatically assisted transport of the membrane permeate. In this system the permeate is transported to the mass spectrometer with the help of a carrier gas, usually helium. The flow direction of the carrier gas is normally opposite that of the sample stream. The carrier gas can be enriched further by a jet separator which reduces the carrier gas and water concentration before the permeate reaches the mass spectrometer.⁴¹ In this way it is possible to obtain two-stage analyte enrichment and achieve low parts per trillion (ppt) levels of detection.

The mass spectrometer of choice in the early history of MIMS was usually a simple linear quadrupole instrument; however, the membrane inlet can also be interfaced to an ion trap mass spectrometer (ITMS).^{42,43} Under controlled

conditions, CI is also possible in ion trap MIMS experiments when using a silicone membrane. A simple direct insertion membrane probe was designed for use with an ion trap. This combination produces a compact, rapid and sensitive system for environmental analysis, e.g. organic compounds can consistently be determined at low-ppb levels and MS/MS experiments are facilitated. Membrane inlets have also been connected to time-of-flight instruments (TOFMS) to obtain rapid mass scans.^{44,45}

Detection limits at parts-per-quadrillion (10^{15}) (ppq = pg l^{-1}) levels have been achieved by using stored waveform inverse Fourier transformation (SWIFT) and an ion trap mass spectrometer (ITMS).⁴⁶ In this technique, broad-band waveforms, notched at the resonance frequencies of analyte ions, are applied during long ionization periods to eject unwanted ions and store only analyte ions. Figure 4 shows the detection of toluene in pure water at sub-ppq level.⁴⁶

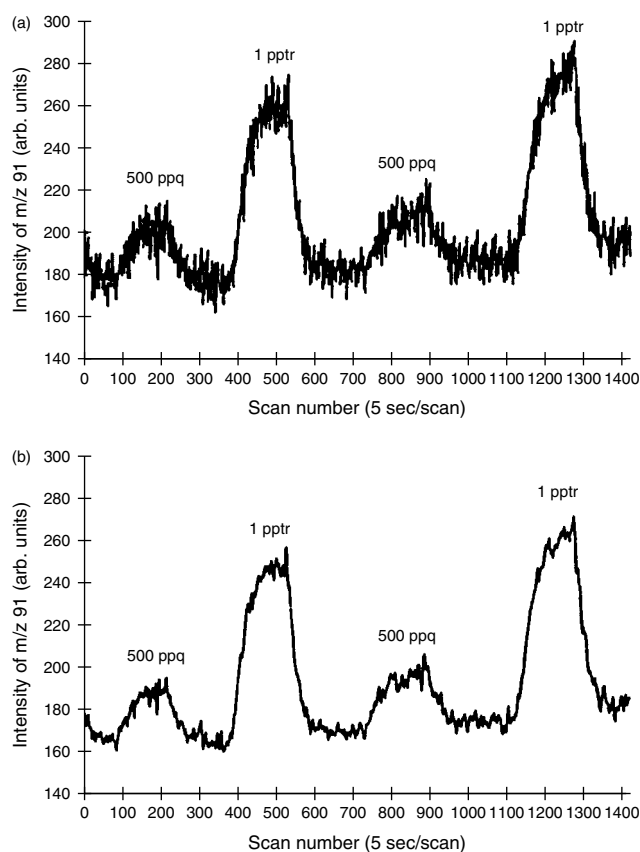


Figure 4. (a) Ion chromatogram showing the signal (m/z 91) recorded for 1 ppt and 500 ppq samples of toluene in pure water using MIMS. Signal-to-noise ratios of 16.0 and 3.4 (average for both replicates in each case) are calculated from these data. (b) Ion chromatogram from (a) after post-acquisition signal averaging performed using a five point moving average routine using Microsoft Excel. The Signal-to-noise ratios increased to 41.6 and 11.0 for the 1 ppt and 500 ppq samples, respectively. Reprinted with permission from Soni M, Bauer S, Amy JW, Wong P, Cooks RG. Direct determination of organic compounds in water at parts-per-quadrillion levels by membrane introduction mass spectrometry. *Analytical Chemistry* 1995; **67**: 1409. Copyright 1995 American Chemical Society.

An improvement factor of 100 is achieved by a cryotrap-MIMS (CT-MIMS) method compared with a standard MIMS method, and typical limits of detection for VOCs are 10–20 ppt.⁴⁷ In this technique analytes are cryotrapped after crossing the membrane; rapid heating of the trapped compounds releases them into the ion source of a quadrupole MS.

The purging technique has been applied in purge-and-membrane (PAM) methods, where the detector is either an electron-capture detector (PAM-ECD) or a mass spectrometer (PAM-MS).^{48,49} In these methods the sample (water or soil) is purged with an inert gas and the purged compounds are collected from the gas phase through a silicone membrane inlet to the analytical system. This method facilitates the application of MIMS to soil samples. Detection limits are $\text{sub } \mu\text{g l}^{-1}$ for water samples and at the $\text{low-}\mu\text{g kg}^{-1}$ level for soil samples.

The membrane itself can be modified to trap organic molecules. In this method, called affinity MIMS, a chemically modified membrane is used to adsorb selectively analytes bearing a particular functional group and concentrate them from solution.⁵⁰ An alkylamine-modified cellulose membrane was used to trap aldehydes at high pH through imine formation. Acid hydrolysis of the surface-bound imine at low pH released the bound aldehyde. Benzaldehyde was measured with excellent specificity from a mixture containing various organic compounds (Fig. 5).⁵⁰

In sorption MIMS, the analytes permeating the membrane inlet are adsorbed on a trap prior to MS detection.^{51,52} In all cases a relatively long trapping period combined with a rapid release of the analytes resulted in analyte enrichment. A disadvantage of the sorption MIMS technique is that real-time monitoring can no longer be conducted. Rivlin introduced a system in which the trap was mounted in the vacuum between the membrane inlet and the ion source.⁵² A heating wire mounted inside the trapping material allowed the trapped sample to be thermally released into the mass spectrometer. Major drawbacks were degradation of the sorbent material (Tenax) during the thermal desorption step and a considerable pressure increase inside the mass spectrometer when the large amount of water trapped by the sorbent was released.

Beyond VOCs

While the MIMS measurement of VOCs in aqueous samples has become routine, that of SVOCs (boiling-points $>250^\circ\text{C}$) has not. Water analysis with membrane inlets cannot be operated at temperatures much higher than 70°C before bubble formation in front of the membrane causes highly unstable signals (this is not true with air samples). At temperatures above 100°C the signals fall almost to baseline because of the large volumetric expansion of water as it starts to boil.⁵³ The low inlet temperature limits the vaporization of the SVOCs from the membrane surface and results in long membrane response times (>5 min) for such compounds. Until recently, compounds with a boiling-point between 200 and 300°C were best detected by the so-called direct insertion membrane probes (DIMP), in which the membrane is mounted inside³¹ or in the immediate vicinity of the ion source region.^{53,54} Using these inlets,

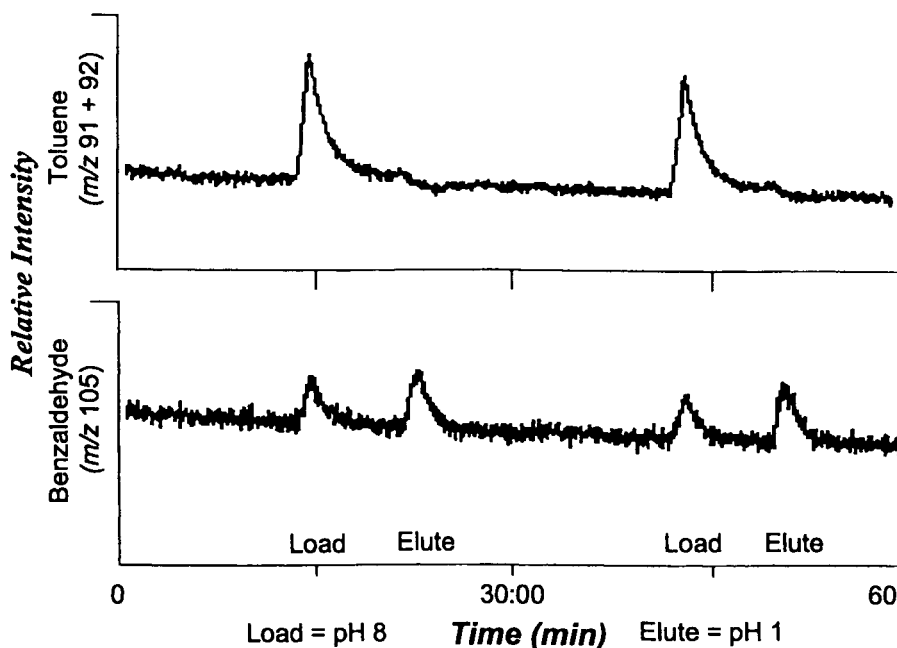


Figure 5. A comparison of two loading and elution peaks to demonstrate reproducibility of Schiff base formation occurring within the affinity liquid membrane. A stock binary solution of 100 ppb toluene (m/z 91 + 92) and benzaldehyde (m/z 105) was introduced to the affinity membrane for 5 min (1 ml min^{-1}). Reprinted with permission from Johnson RC, Koch K, Cooks RG. Affinity liquid membrane introduction mass spectrometry. *Analytica Chimica Acta* 1999; **395**: 239. Copyright 1999 Elsevier Science.

problems with chromatographic effects on vacuum surfaces due to a 'cold' membrane surface are almost eliminated. The measurement of polar compounds is also limited with MIMS because the widely used polydimethylsiloxane membrane is hydrophobic and polar compounds do not easily diffuse through it at room temperature.

Recently, the so-called trap-and-release MIMS (T&R-MIMS) technique was introduced.^{55–57} In this method, SVOCs are preconcentrated inside the tubular membrane that passes directly through the ion source. A slit in the source parallel to both the membrane and the filament allows heat radiation from the filament to bombard the membrane surface continuously. During aqueous sampling, the membrane is cooled by the liquid flowing through the inside of the tube. However, during a short interruption of the liquid flow, the membrane is rapidly heated to more than 300°C and organic compounds dissolved in the membrane are released into the ion source. In this way a desorption peak is obtained. In T&R-MIMS the trapping can also be done with an external interface.⁵⁸ A recently introduced technique, desorption chemical ionization MIMS, combines T&R-MIMS and CI, making it possible to detect compounds with high boiling-points, e.g. acids and steroid hormones, in aqueous solutions.^{59–61}

Using a similar MIMS system, Matz's group reported on a thermal membrane desorption application (TMDA) for the on-line GC/MS determination of organics in water or fermentation suspension.^{62,63} With TMDA, a membrane separator was used to extract VOCs from the sample for direct analysis by GC/MS. Compounds which did not diffuse through the membrane during sampling but which accumulated in the membrane were then thermally desorbed and transported to a GC/MS system for the analysis. The

major difference between TMDA and T&R-MIMS is that in the latter the inlet is an integral part of the ion source, whereas in TMDA the inlet forms a separate unit mounted at a short distance from the ion source.

A significant feature of MIMS is the simultaneous introduction of all analytes into the mass spectrometer, resulting in a rapid analytical method suitable for on-line measurements, but making the analysis of complex mixtures more difficult. To overcome this problem and preserve the on-line feature of the method, some mathematical techniques have been applied to mixture analysis. Overney and Enke⁶⁴ reported mathematical sample modulation for mixture analysis where temporal resolution of analytes was achieved. Ohorodnik *et al.*⁶⁵ used multivariate, univariate and principal component analysis (PCA) methods to analyze a solution containing monoaromatic compounds. Another chemometric method, a non-linear asymmetric error least-squares method, was also applied successfully to solve multicomponent mass spectra containing up to eight different analytes.⁶⁶ Other versions of mathematical methods have been used to solve multicomponent mass spectra.^{67–69}

On-line/on-site applications

Harland and Nicholson utilized MIMS for the continuous monitoring of volatile compounds in canal and estuarine water.^{70,71} A transportable MIMS system was constructed and mounted in a boat, and measurements were made continuously while the boat was travelling along the canal. MIMS has also been used on-site for the analysis of ground water⁷² and during waste water monitoring.⁷³ Figure 6 presents results of continuous on-line monitoring of a waste water stream of an oil refinery,⁷³ clearly showing the advantage of MIMS in on-line measurements when the

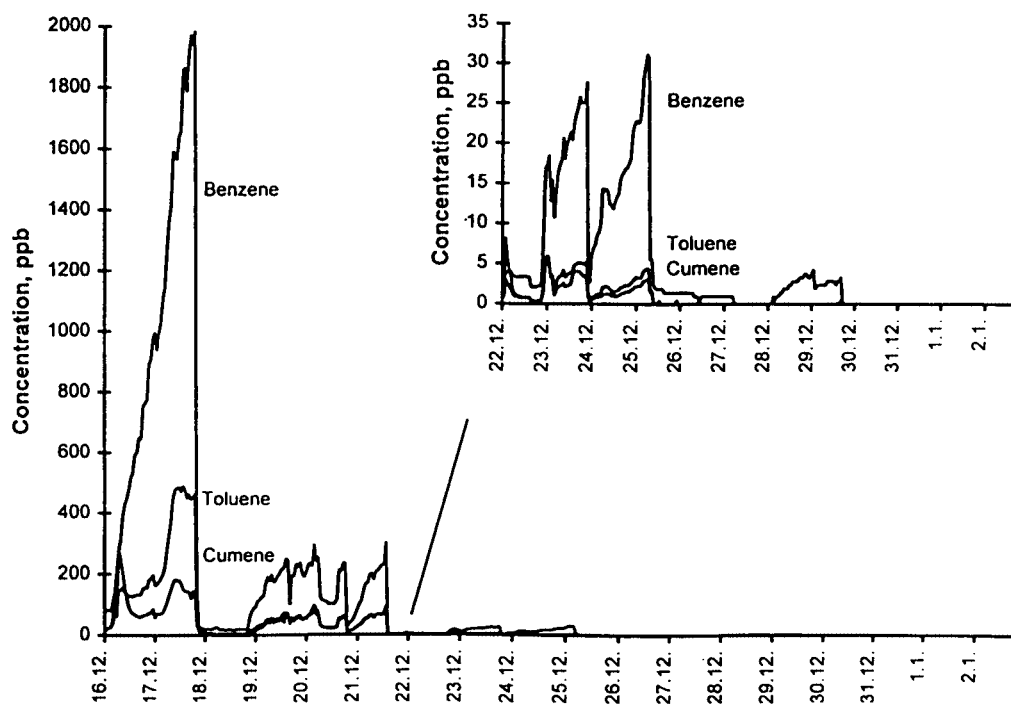


Figure 6. Measurements made over an 18 day period of the waste water stream of an oil refinery. The ions measured were m/z 78 for benzene, m/z 92 for toluene and m/z 120 for cumene (isopropylbenzene). The results show daily variations in concentrations of these compounds which correlated well with the off-line gas chromatographic measurements, which were performed once a day. Reprinted with permission from Kotiaho T, Kostianen R, Ketola RA, Mansikka T, Mattila I, Komppa V, Honkanen T, Wickström K, Waldvogel J, Pilviö O. Development of a fully automatic membrane inlet mass spectrometric measurement system for on-line industrial waste water monitoring. *Process Control and Quality* 1998; **11**: 71. Copyright 1998 VSP International Science Publishers.

compounds are well known beforehand. Other applications in the field are underwater mass spectrometry for direct *in situ* detection of volatile organic compounds and dissolved gases in oceans, lakes, rivers and waste water streams^{74–76} and site characterization by detecting contaminants in the subsurface.⁷⁷

Comparisons with other methods

Harland and Nicholson compared the MIMS method with two purge-and-trap methods (GC/FID and GC/MS), in which six volatile halogenated hydrocarbons were determined in five environmental samples using the selected ion monitoring mode.⁷¹ The concentration levels of the hydrocarbons ranged from $<0.1 \mu\text{g l}^{-1}$ to $90 \mu\text{g l}^{-1}$ in the samples, and the analytical results were in good agreement. However, the comparison was not a profound study of the characteristics of the methods. MIMS has also been compared with other analytical methods, such as static headspace gas chromatography (HSGC) and purge-and-trap GC/MS,⁷⁸ with HSGC and GC using a Hall electrolytic conductivity detector in the determination of volatile organic sulfur compounds,⁷⁹ with HPLC in the analysis of phenolic compounds,⁸⁰ with DPD/FAS titration and UV/visible spectrophotometry,⁸¹ with P&T and SPME⁸² and with P&T-GC/MS in the determination of MTBE.⁸³ In general, agreement between MIMS and the other methods was good, indicating the suitability of MIMS for the measurement of organic compounds in water.

Table 1 shows the performance characteristics of various MIMS methods which have been applied to the analysis of environmental water samples.

AIR ANALYSIS

Environmental air analysis: background

Hundreds of VOCs from anthropogenic sources have been identified in air samples.¹²² Conventional air analysis for contaminants uses GC, a mature method that has proved very suitable for the determination of VOCs at trace levels, often in combination with a mass spectrometric detector.¹²³

Air sample collection, storage and transport can be plagued by cross-contamination, degradation and loss. Difficulties with conventional air analysis methods include water absorption, compound breakthrough, artifact formation, long-term storage, canister cleaning and sample humidity.^{124,125}

Portable and transportable mass spectrometers developed for on-site screening and analysis support cost-effective sampling modifications and eliminate sample degradation.^{5,126,127} Direct sampling techniques include small diameter orifice leaks, adjustable leak valves, capillary inlets with two-stage pressure reduction, atmospheric pressure ionization and atmospheric sampling glow discharge ionization.^{5,128} With MS/MS and deconvolution methods, direct sampling MS compares very well with standard laboratory GC/MS methods while meeting EPA criteria.¹²⁷

Although membrane inlets do not offer direct sampling capabilities because of the enrichment step they provide, their simplicity places them near the top of the above spectrum of techniques. Membrane inlets are a low-cost, rugged interface between air and instrument vacuum and may be placed within or outside the MS ion source.

Table 1. Water analysis: selected applications of membrane introduction mass spectrometry (the table is sorted by the name of the first compound mentioned in the first column)

Compound	Method	Detection limit	Notes	Ref.
Acrolein, acrylonitrile	Sheet membrane	10 ppb	MS/MS	84
Aldehydes				85
Aldehydes	Affinity liquid membrane	50 ppb	Jet separator Ion trap MS	50
Benzene, ethanol	Sheet membrane	10–50 ppb	CI	86
BTEX, ethanol	Sheet membrane		FIA, water solubilization of ethanol and BTEX from gasoline	87
BTX	DIMP		Multivariate calibration, ion trap	65
BTX, VOC, polar compounds such as butan-2-one	PEI/S membrane		Comparison with silicone, pentaquadrupole	88
Chemical agents	Flow-through			89
Chlorine, chloramines	Flow-through	0.02–0.1 mg l ⁻¹	Comparison with DPD/FAS and UV/VIS	81
Deuterated water	Sheet membrane	0.1 M		90
Dicarboxylic acids	Flow-through		Desorption CI	59
Biomolecules		High ppb		60
Steroid hormones				61
Disinfection by-products, VOCs	Flow-through	0.05 µg l ⁻¹	Comparison with EPA 524.2	91
Dissolved gases	Sheet membrane			92
Dissolved gases, VOCs	DIMP	0.1 ppb	Underwater, ion trap	75, 76
Gases	Flow-through			93
Inorganic chloramines, chlorobenzenes	Trap and release	Low- or sub-ppb	External interface	58
Kathon CG	Membrane probe		Cosmetic emulsions	94
Methanol	Helium purged	2–5 ppm	PDMS and allyl alcohol membrane, jet separator	95
Naphthalene	Hollow fiber membrane extraction	Concentration factor 166		96
Nitrogen trichloride	Hollow fiber membrane		Wastewater treatment	97
Organic compounds	DIMP	10 ⁻⁶ M	Tandem MS, CI	29
Organohalogen and BTEX compounds	Helium purged	8 ppt	Membrane extraction	98
Organohalogen compounds	Helium purged	0.5–1 ppb		99
PAHs, estrogenic compounds, pesticides	Flow-through	20 ppt–300 ppb	Desorption CI	100
<i>p</i> -Cresol, 2-methyl-2-pentanol, trichloroethene	Flow-through	Low ppm		101
Phenolic compounds	Sheet membrane	1–1000 µg l ⁻¹	FIA	102
Semivolatiles	Trap and release	0.5–600 µg l ⁻¹		55, 56
Terpenes	Sheet membrane	0.2–2 µg l ⁻¹	Comparison with static headspace GC	103
Trihalomethanes	Helium purged	2–8 ppt	MIMS with fast GC	104
VOCs	Cryotrap	10–20 ppt	Pentaquadrupole	47
VOC	DIMP	35–56 ppt		105

(continued overleaf)

Table 1. (Continued)

Compound	Method	Detection limit	Notes	Ref.
MTBE		0.1 ppb	Automated, comparison to P&T-GC/MS	83
VOCs	DIMP	0.003–10 ppb	EPA 524.2, ion trap	106, 107
VOCs	DIMP	0.03–5 ppb	Jet separator	41
VOCs	DIMP	0.5 ppt	SWIFT	46
VOCs	Flow-through	1–30 ppb		30
VOCs	Flow-through	15 ppb		108
VOCs	Flow-through	190 ppt	Seawater, ion trap	109
VOCs	Flow-through	0.1 ppm		110
VOCs	Flow-through	1–100 ppb	MS/MS	43
VOCs	Flow-through		Underwater, ion trap	74
VOCs	Flow-through		FIA, methane CI, 3D MS ²	111
VOCs	Flow-through, flow-over		On-line, process streams	32, 33
VOCs	Helium purged	Sub-ppb		35
VOCs	Helium purged	Low ppb	Ion trap, CI	112
Benzene		0.2 µg l ⁻¹	Comparison with P&T and SPME	82
VOCs	Helium purged	0.1–0.7 µg l ⁻¹	On-site	72
VOCs	Helium purged	ppb	Jet separator	113
VOCs	Hollow fiber membrane	10 ppb		27
VOCs	Membrane probe	250 µg l ⁻¹	Subsurface	77
VOCs	Microporous	100 ppb	CI, glow discharge	39
VOCs	Purge and membrane	0.1–10 µg l ⁻¹	Also soil samples	49
VOCs	Sheet membrane	0.7–5 ppb		114
VOCs	Sheet membrane	0.1–10 ppb	Headspace, comparison with headspace GC/MS	115
VOCs	Sheet membrane	1–10 µg l ⁻¹	On-site	70, 71, 116
VOCs	Sheet membrane	1–120 µg l ⁻¹	Field monitoring	117
VOCs	Sheet membrane	ppm	Backpack-portable	118
VOCs	Sheet membrane	Low µg l ⁻¹	On-line monitoring	73
VOCs	Sheet membrane	0.1–50 µg l ⁻¹	Comparison with static headspace GC and P&T-GC/MS	78
VOCs	Sheet membrane	1 µg l ⁻¹		28
VOCs	Sheet membrane	2–3 ppb	Portable TOF	44
VOCs, nitrogen	Sheet membrane	3 µg l ⁻¹	TOFMS	45
VOCs, polar compounds	DIMP	10 µg l ⁻¹	CI	31, 53
VOCs, semivolatiles	Flow-through	0.04 ppb	Jet separator, ion trap	40
VOCs, semivolatiles	Flow-through	0.7 µg l ⁻¹ –6 mg l ⁻¹	In-membrane concentration	119
VOCs, semivolatiles	Trap and release		DIMP, headspace	57
VOCs, semivolatiles	DIMP		On-line monitoring of photocatalytic degradation	120
VOCs, semi-volatiles, organometallics	Helium purged		Simultaneous analysis of all compounds	121
Volatile sulfur compounds	Sheet membrane	0.1–0.5 µg l ⁻¹	Comparison with GC/FID and GC/ELCD	79
Phenolic compounds		0.5–10 µg l ⁻¹		80

Development of different membrane inlet methods for air analysis

Determination of volatile organic compounds in air

Table 2 lists key accomplishments in air sampling using membrane inlets combined with mass spectrometry. In 1969, the dual-stage membrane gas separator was patented as an enrichment interface for carrying GC effluent into an MS instrument.¹²⁹ Soon after, a sheet membrane inlet system was used alone with a quadrupole MS system, permitting direct organic vapor sampling.¹³⁰ The majority of applications have

used silicone membranes, quadrupole mass spectrometers and electron ionization.

Different membrane configurations and materials other than silicone have also been investigated for air analysis. In studies using single or multiple hollow fiber probes, Westover *et al.*²⁷ demonstrated that silicone's performance exceeded that of the other polymers in response time comparisons. A dramatic response time difference for VOCs in air and water samples reflected the degree of hydrogen bonding occurring for polar compounds in water.

Table 2. Air analysis: selected applications of membrane introduction mass spectrometry (the table is sorted by the name of the first compound mentioned in the first column)

Compound	Method ^a	Detection limit	Notes ^b	Ref.
Aromatic VOCs including BTEX	Sheet	1 ppm	On-line measurement of exhaust gases (engine test stand, dynamometer, on the road); 1 s cycle rate	152
Atmospheric isoprene	Hollow fiber, ion trap MS	80 ppt	Vinyl methyl ether as alkene-selective CI reagent; 0.5–10 ppb calibration curve; membrane transfer efficiency measured at 10%	150
Dynamite effluent	Llewellyn separator		Characterization of prototype portable MS for explosives detection	156
Methanol	Allyl alcohol hollow fiber, jet separator, ion trap MS	3.3 ppmv	Allyl alcohol membrane enhanced sensitivity to methanol by a factor of 8.5 over silicone; CE using H ₃ O ⁺ ; 30 s sampling periods	95
Organometallics	Ultra-thin fiber, jet separator, ion trap MS		Oxygen CE more efficient than EI	147
PAHs, also sulfur-containing cmpds.	Glass-fiber filter tape, fast GC, sheet		On-line measurement of emission gases at several emission sources; 6 min analysis cycle	143
Polar VOCs	Hollow fiber, jet separator, ion trap MS	pptv–ppbv	4–20-fold improvement with charge exchange using air when compared with EI	138
SVOCs	Hollow fiber, ion trap MS	ppt	Adsorption and desorption of analytes from same side of membrane; fast rise and fall times; 1 min cycle time	145
SVOCs	Ultra-thin fiber, jet separator, ion trap MS	pptv–ppbv (lowest concentrations analyzed)	0.5 μm thick membrane; CE using membrane-transported oxygen more efficient than EI	144
VOCs		ppt	CI using H ₃ O ⁺ , response dependent on functional group and molecular backbone	139
VOCs	Hollow fiber	ppb	Investigation of flow geometry, dimensions, temperature, flow rate; steady-state response with flow-through inlet 50× greater than flow-over inlet	32
VOCs	Hollow fiber		On-line analysis at wastewater treatment plant	33
VOCs	Hollow fiber, ion trap MS	Non-polar 1–11 ppbv Polar 31–104 ppbv	Comparison of MIMS with ASGDI; water CI	137
VOCs	Hollow fiber, jet separator, ion trap MS	pptv–ppbv (lowest concentrations analyzed)	Response times 60–90 s; minimal memory effects; membrane transfer efficiency measured at 10–20%	131
VOCs	Hollow fiber, sorbent tube/Peltier cell, ion trap MS	0.1 μg m ⁻³	Cryotrapping inside Peltier cell	98

(continued overleaf)

Table 2. (Continued)

Compound	Method ^a	Detection limit	Notes ^b	Ref.
VOCs	Llewellyn separator	ppb	Portable monitor for explosives, degreasing operations, pesticides, chemical agent monitoring	148, 149
VOCs	Sheet	0.1 ppm Freon	Development of membrane inlet for MS	130
VOCs	Sheet	0.02–0.5 mg m ⁻³	Transportable MS for direct breath monitoring; 2 s response time; response inhibited by water vapor	155
VOCs	Sheet	ppm	Mobile MS using 500 W power; very fast rise times	157
VOCs	Sheet	40–300 ppb	Higher sensitivity with membrane inlet compared with direct sampling	41
VOCs	Sheet	0.5–4 µg m ⁻³	Comparison of MIMS analysis of paintshop air with FID; characterization of membrane thickness, temperature, sample flow-rate	153
VOCs	Sheet	0.04–4 mg m ⁻³	Passive sampling of room air on sorbent tubes followed by thermal desorption; good agreement with continuous monitoring method	154
VOCs	Sheet, ion trap MS	ppb–ppm	Five orders of magnitude dynamic range; MIMS detection limits enhanced 10–300 × over direct air sampling	141
VOCs	Sheet, time-of-flight MS	Low ppb	Portable battery-powered instrument using 40 W power	43
VOCs	Similar to Llewellyn separator	1–100 ppb	Calibration standards; response times seconds or less	140
VOCs	Sorbent tube, sheet	<1 ng l ⁻¹	Temperature programmed desorption to achieve fast separation of VOCs; 6–10 min analysis cycle	142
VOCs, also MeOH, dimethyl-Hg	Hollow fiber	10 ppb chloroform	Response time <1–3 s; comparison of silicone with other materials	27
VOCs, chemical weapons agents	Llewellyn separator	≥0.1 ppb	Portable MS (150 lb) for explosives, degreasing operations, pesticides, chemical agent monitoring; 10 ⁶ -fold sample enrichment; heated separator enhanced detection of less volatile compounds	148, 149
VOCs, SVOCs	Hollow fiber, ion trap MS	20–130 ppt	60 cm long capillary membrane; short rise and fall times	133
VOCs, SVOCs organometallics	Ultra-thin fiber, jet separator, ion trap MS		Oxygen CE; simultaneous detection of three different compound classes	121
VOCs	Sheet	3–20 µg m ⁻³	Custom-made gas calibrator used to produce gas standards; four orders of magnitude dynamic range	146

^a Unless noted otherwise, the methodology uses quadrupole MS and a silicone membrane.

^b The ionization technique is noted if it is other than EI.

Of the two membrane configurations—the flat sheet and the hollow fiber—the latter permitted more variation. In addition to flowing sample over the outside, workers introduced the sample through the inside of the fiber.³¹ The ‘flow-through’ configuration as shown in Fig. 2 was found to be more efficient, since higher linear sample velocities could be obtained and the surface area was used more effectively.³²

Toluene was detected in air at 20 ppt by volume with an ion trap mass spectrometer¹³¹ using a membrane inlet design incorporating a jet separator for a second enrichment stage.^{41,132} In this study, the helium flow through the silicone hollow fiber was countercurrent to the sample flow, and served as the sample transport and ion trap buffer gas. No evidence of long-term memory effects after membrane exposure to high concentrations was observed. Three sample

matrices—air, water and soil—containing 1 ppb of toluene were analyzed in close order by moving the sample inlet from one matrix to the other.

With a high surface area membrane that caused long rise and fall times for organic compounds in water, ppt limits for VOCs and SVOCs in air with brief rise and fall times (10 and 48 s for toluene) were achieved.¹³³ The 60 cm long silicone capillary gave linear responses over 3–4 orders of magnitude with optimized sample flow-rate and membrane temperature.

In the USA, exposure limits to methanol in air are set at 200 ppm by volume over an 8 h work period.¹³⁴ In 1974, MIMS was shown to produce linear calibration curves for airborne methanol.²⁷ Recent work using an ultra-thin allyl alcohol membrane generated linear responses extending beyond two orders of magnitude for air samples⁹⁵ typically analyzed for methanol by EPA methods TO-15¹³⁵ and TO-17.¹³⁶ The use of non-silicone membranes for MIMS has been a little-explored approach for selectivity enhancement.

Ionization by electron impact (EI) has been typically employed in the majority of MIMS experiments. As researchers looked for ways to improve sensitivity, especially for polar VOCs, chemical ionization using water or air as the reagent gas proved to be a useful tack. Taking advantage of the presence of water vapor in the samples or using supplemental water, Gordon *et al.*¹³⁷ implemented CI in the MIMS experiment. Detection limits for airborne polar VOCs at 50% relative humidity ranged from 31 ppb by volume (ppbv) for methyl *tert*-butyl ether to 104 ppbv for methyl ethyl ketone.

In other work, a charge exchange ionization (CE) technique using membrane-diffused oxygen as the reagent gas led to enhanced signals over EI.¹³⁸ The CE/EI response ratio ranged from 2 for benzene to 22 for cyclohexanol. CE ionization proved suitable for SVOCs and with reduced mass spectral fragmentation.

Membrane introduction was combined with proton transfer mass spectrometry that uses H_3O^+ as a chemical ionization agent in an ion flow-drift tube reactor for real-time environmental air monitoring of VOCs.¹³⁹ The time it took for analytes to permeate through the silicone membrane was found to depend on both the functional group and molecular backbone.

A dedicated trace gas analyzer was developed which interfaced a quadrupole MS system with a membrane inlet constructed of stainless steel and PTFE parts to minimize sticking of organic compounds.¹⁴⁰ Chlorinated hydrocarbons diffused very quickly with a 90% signal rise time of ~ 0.5 s, whereas alcohols were much slower. A linear calibration for toluene from the ppb level to 100 ppm was obtained, above which saturation occurred.

Using ITMS, researchers found membrane introduction to be more sensitive than direct air sampling by orders of magnitude with detection limits in the low-ppb range.^{41,141} The membrane inlet discriminated against unmediated air background that reduced sensitivity and affected fragmentation mechanisms in the ion trap when direct sampling was employed.¹⁴¹

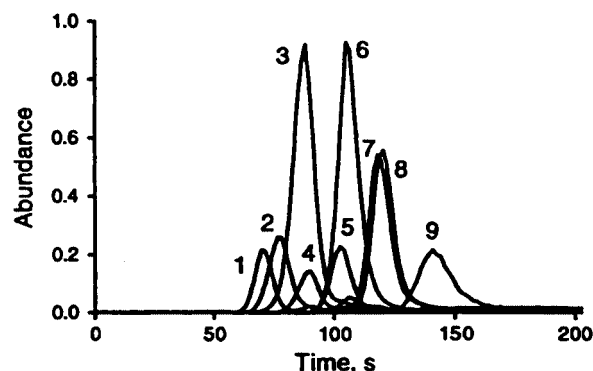


Figure 7. Trapped compounds are released from an adsorbent at different temperatures depending on the strength of the interaction of the individual compound and the sorbent. The temperature-programmed desorption profile of a gas sample analyzed by MIMS shows nine compounds in the mixture: 1-*trans*-1,2-dichloroethene; 2-chloroform; 3-carbon tetrachloride; 4-trichloroethene; 5-toluene; 6-tetrachloroethene; 7-xylenes; 8-styrene; 9-1,2-dibromo-1,2-dichloroethene. Reproduced with permission from Ketola RA, Grøn C, Lauritsen, FR. Temperature-programmed desorption for membrane inlet mass spectrometry. *Rapid Communications in Mass Spectrometry* 1998; **12**: 773. Copyright 1998 John Wiley & Sons Limited.

A MIMS technique used temperature-programmed desorption to obtain analyte separation.¹⁴² The sorbent tube was heated at a controlled rate, releasing analytes into a helium stream entering a membrane inlet, resulting in good peak separation with 10 s desorption profiles at half-height. Figure 7 shows desorption profiles of nine compounds obtained from analysis of a mixture containing a few micrograms of each contaminant.¹⁴²

The development of low power consumption fieldable instruments enhances the on-site capabilities of MIMS. A transportable time-of-flight mass spectrometer incorporating a membrane inlet system was tested.⁴⁴ Converging annular geometry of the mass spectrometer allowed for lower source pressure, smaller pumps, lower power consumption (40 W) and more efficient design. A sampling configuration whereby two membranes operated in series provided a secondary enrichment stage with enrichment factors as high as 15 600.

A Tenax cryotrap inside a Peltier cell, inserted between a silicone membrane and an ITMS system, permitted the detection of $0.1 \mu\text{g m}^{-3}$ of aromatics in air;⁹⁸ the Peltier device would be more suited to field applications than cryocooling with liquid N_2 . Figure 8 compares signal shapes obtained by this method and the conventional MIMS technique.⁹⁸

Beyond VOCs

Munchmeyer *et al.*¹⁴³ developed a portable system for on-site combustion gas measurement, which was tested at several emission sources for analysis of PAHs. After sampling, a HEPA glass-fiber filter tape sampler was then desorbed into a membrane inlet through a GC column. In tests at an oil combustion plant, a production plant for coal tar-based electrodes and a motor test site, a good correlation was

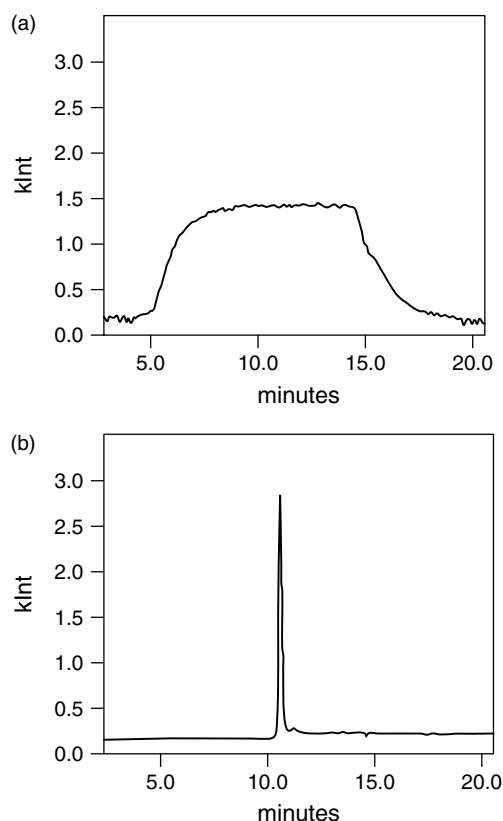


Figure 8. The analysis of a 5 ppb chloroform solution using a conventional MIMS technique (a) and a cryo-focused Tenax trap after the membrane (b). Rapid release of trapped organics in the Tenax trap results in a higher signal-to-noise ratio and a narrower peak shape as shown in (b) than obtained using a conventional MIMS technique ($kInt = \text{ionic intensity}/1000$). Reprinted with permission from Bocchini P, Pozzi R, Andalò C, Galletti GC. Experimental upgrades of membrane introduction mass spectrometry for water and air analysis. *Analytical Chemistry* 2001; **73**: 3824. Copyright 2001 American Chemical Society.

found between the on-site method and literature-derived data. In addition to PAHs, sulfur-containing compounds were detected.

Other MIMS workers focused efforts on airborne SVOCs. Using an ultra-thin composite membrane for on-line SVOC analysis, very high permeation rates resulted.¹⁴⁴ The ultra-thin fiber reduced the amount of membrane-dissolved analyte present, an advantage for compounds with slow diffusion rates and high solubilities. SVOCs from several compound classes were tested including nitrobenzene, methyl salicylate, 2-chlorophenol and malathion, an organophosphate pesticide.

Using a technique termed single-sided membrane introduction mass spectrometry (SS-MIMS), Riter *et al.* determined SVOCs including lindane (a pesticide), dimethyl methylphosphonate (DMMP), naphthalene and hexahydro-1,3,5-trinitro-1,3,4-triazine (RDX, an explosive) in air.¹⁴⁵ To counter the slow diffusion through PDMS that hampers timely SVOC analysis in the conventional MIMS setup, the method utilized adsorption and desorption from the same side of the membrane. Rise times of 4–7 s and fall times

of 12–36 s were achieved with cycle times from sampling to data acquisition of ~1 min. Limits of detection were in the ppt range with linear response over four orders of magnitude.

Industrial sources including the pulp and paper industry and natural sources such as oceans, soil and volcanoes release toxic volatile organic sulfur compounds (VOSCs) into the environment, contaminants typically analyzed by GC and GC/MS methods. MIMS provided sensitivity high enough for real-time monitoring of many VOSCs, including carbon disulfide, ethanethiol, dimethyl sulfide, thiophene and dimethyl sulfoxide.¹⁴⁶ Mixed VOSC samples containing three compounds were analyzed using a deconvolution program. The average of the absolute differences between calculated and measured concentrations was 6.1%.

An early MIMS paper reported the determination of organometallic dimethylmercury in air.²⁷ Over 20 years later that work was expanded upon with the rapid detection of ferrocene and molybdenum hexacarbonyl vapors using an ultra-thin membrane fiber and ITMS.¹⁴⁷ A charge exchange ionization reaction with O_2^+ resulted in intense molecular ion fragments for both species.

A broad spectrum characterization technique has yet to be developed that can address highly complex samples such as those that might be found at waste sites. MIMS is promising, however, because it has shown applicability across a range of compounds and sample types. Methyl ethyl ketone, toluene, 1-methylnaphthalene and ferrocene were detected simultaneously in an air sample using MIMS.¹²¹

On-line/on-site applications

The US Army Environmental Hygiene Agency investigated a portable vapor detection quadrupole analyzer incorporating a silicone membrane separator for pollution monitoring, solvent detection in degreasing operations, identification of pesticides and monitoring of cholinesterase-inhibiting chemicals.^{148,149} The instrument weighed less than 70 kg and occupied 68 dm³. The separator was pumped using evacuated canisters containing zeolite, eliminating mechanical pumping of this stage in the field. Detection limits for organics in ambient air ranged from 0.1 ppb of tetrachloroethene to 5 ppb of phosdrin, an organophosphate compound.

Real-time or near real-time analytical techniques allow the full characterization of environmental chemical reactions or waste streams. LaPack *et al.*³³ analyzed gas streams from a wastewater treatment biodegradation process using a single analyzer incorporating a silicone membrane fiber and a quadrupole MS system. Twelve compounds, including chlorinated compounds and substituted benzenes, were detected in air effluent at concentrations ranging from 0.003 to 0.07 mg l⁻¹ (3–70 ppb). Detection of organic vapor emissions in the air effluent tracked the influx of solids in the wastewater stream.

Atmospheric monitoring calls for analysis cycle times capable of resolving fast reactions. Investigators combined a membrane inlet, cryogenic focusing, and CI in the ITMS system for the determination of isoprene (2-methyl-1,3-butadiene),¹⁵⁰ a highly reactive short-lived species emitted in significant amounts in the environment. An automated membrane sampler was devised to collect permeate in a

cryogenic sample loop. Ballistic heating under a helium stream delivered the sample plug to the mass spectrometer. Vinyl methyl ether, a selective CI reagent for alkenes, was leaked into the mass spectrometer and allowed to react with a preconcentrated sample, providing linear isoprene calibrations over a range typical in deciduous forest environments¹⁵¹ and a detection limit of 80 ppt. In studies of isoprene emission from greenhouse velvet bean plants, the isoprene response peaked after 12 h and could be correlated with a rise in greenhouse temperature. Soon after the sun lamps had been turned off, isoprene decay followed first-order kinetics and could not be detected.

Time-resolved measurements of auto exhaust are critical for correlating engine state with auto emissions. Matz *et al.*'s 1996¹⁵² study measuring aromatic compounds in automobile exhaust gases used a membrane inlet quadrupole MS system with a cycle rate of one analysis per second for on-site evaluation on an engine test stand, a dynamometer and in automobile traffic. PAHs up to anthracene and phenanthrene were detected on-line.

An optimized MIMS method analyzed paintshop air exhaust using a quadrupole MS system and a silicone sheet membrane inlet.¹⁵³ Linear dynamic ranges for 14 VOCs extended over four orders of magnitude; detection limits (DLs) ranged from 0.5 to 5 $\mu\text{g m}^{-3}$ with higher DLs for more polar or heavier compounds. Paintshop air samples were measured by both MIMS and an on-line flame ionization (FID) analyzer. The results from the two different methods were comparable with differences in VOC totals ranging from -6.7 to 15.0%. Throughput in MIMS as high as 150 samples per hour was possible.

Air in five laboratory rooms was analyzed using a membrane inlet and a quadrupole MS system.¹⁵⁴ Activities included ion source cleaning, vacuum pumping, glassware cleaning and MS operation. Samples were collected twice a day in passive sampling tubes which were then desorbed into a silicone sheet membrane interface. A continuous monitoring method providing averaged concentrations over 7 days resulted in good agreement with the MIMS technique. The room containing cleaning and washing operations was found to be the most contaminated with a sum VOC concentration measured at nearly 158 $\mu\text{g m}^{-3}$ (158 ppt) with acetone as the major constituent. Laboratory air was observed to improve after 2–3 days with good ventilation.

Breath analysis can be used to monitor solvent exposure in workers non-invasively. Researchers combined a silicone membrane inlet and gas handling system with a transportable quadrupole MS instrument for direct measurement of VOCs in breath.¹⁵⁵ Selected ion monitoring tracked the decay of a chlorinated solvent in a volunteer's breath for 168 h, as shown in Fig. 9.

SOIL ANALYSIS

Contamination of soils with volatile organic compounds, semi-volatile organic compounds and metal-containing compounds is frequently encountered in developed countries. Potential sources of chemicals that can contaminate soils (and groundwater and drinking water) include leaking

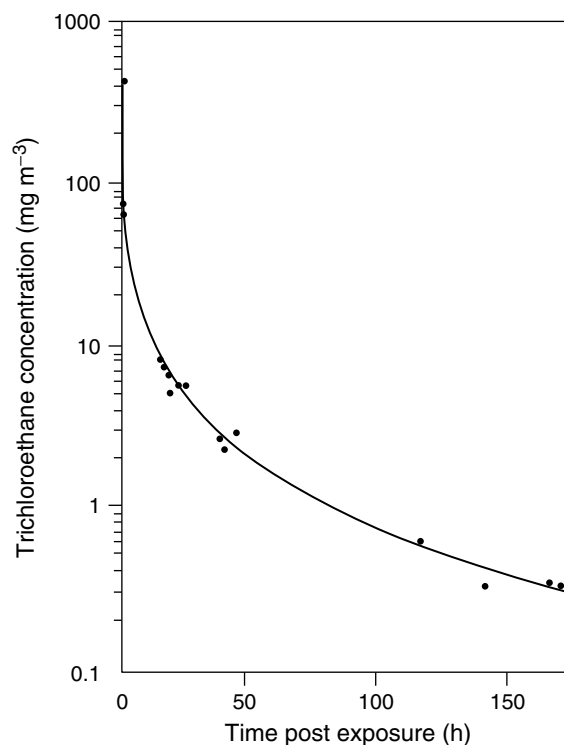


Figure 9. 1,1,1-Trichloroethane was tracked in alveolar breath (m/z 61) for 168 h after a volunteer had been exposed to 750 mg m^{-3} of solvent for 4 h. Reproduced with permission from Wilson HK, Ottley TW. The use of a transportable mass spectrometer for the direct measurement of industrial solvents in breath. *Biomedical Mass Spectrometry* 1981; **8**: 606. Copyright 1981 John Wiley & Sons Limited.

storage tanks, improper disposal of spent solvents and inadequately designed landfills. Major soil contaminants, such as VOCs, can easily diffuse from the source into nearby soil and groundwater.¹⁵⁸ Conventional GC or GC/MS methods, such as dynamic and static headspace or purge-and-trap analysis,^{159–161} focus on improving recovery and quantification of VOCs in soil and/or water samples, and generally require time-consuming sample collection, storage and extraction procedures.

The increasing demand for efficient on-site monitoring has spurred the development of more rapid and direct analytical techniques to detect and quantify multiple chemical contaminants in diverse environmental matrices. MIMS has been developed for the rapid, selective and sensitive determination of VOCs and SVOCs in water and air samples, and is emerging as an efficient method for the direct measurement of ambient gases in soil, peat and sediment.^{162–168}

Very little work with MIMS has been done on the determination of contaminants in soils, primarily because of the difficulty in extracting organics from soil and introducing them to the membrane. Thus, the main focus has been on permanent gases and contaminant compounds with relatively high vapor pressures. Thermal desorption of contaminants from soil has taken on two forms—purge-and-membrane MS and headspace MS—both of which work very well on spiked samples and moderately well on authentic soil samples.^{49,169–171} When it comes to real-world environmental

samples, the soil matrix, humidity and temperature level play very important roles in the relative ease of removal and detection.¹⁵⁹ Often, an internal standard (IS) is required, but there is much controversy over the adsorption and binding of the IS compared with real contamination. Environmental scientists await the development of an *in situ* membrane probe for detecting VOCs, SVOCs and metal-containing compounds in soil. Table 3 summarizes the recent applications of MIMS in soil analysis.

One of the first examples of soil analysis involving MIMS was the on-line detection of 1 ppb of toluene spiked in air, water and soil samples.¹³¹ Little effort was made to optimize the experiment for the best peak shape and analyte response; however, the experiment demonstrated the potential of using MIMS for the rapid and direct determination of VOCs in different matrices, including soils. Since that time, improvements and alterations have been made to membrane introduction methods for soil analysis.

In situ soil, peat and sediment techniques provide environmental and ecological data related to gas exchange and bacterial growth without disturbing natural processes. Concentration profiles of dissolved gases indicate the point of detection rather than the site of production, and are subject to change with upward and lateral diffusion. A

spatial resolution of 1 mm (vertical) has been demonstrated in the determination of dissolved O₂ and CO₂.¹⁶⁶ Needles capped with silicone served as *in situ* membrane inlets for quadrupole mass filters when monitoring dissolved gases (e.g. N₂, O₂, CO₂, Ar, CH₄, N₂O) in peat and sediment samples. Monitoring VOCs in soil is considerably more challenging than ambient gases since heating or purging is not easily accomplished with *in situ* analysis.

Ex situ techniques provide environmental data related to VOC contamination location and transport. Greater sensitivity for VOCs is observed with *ex situ* MIMS methods because efficient heating and purging of samples can be done prior to analysis. Sheet silicone membranes are often coupled with soil sampling devices that can be heated or purged. Purge-and-membrane mass spectrometry (PAM-MS)^{49,169,170} and headspace MIMS (HS-MIMS)¹⁷¹ are two *ex situ* techniques that combine the major advantages of headspace methods and membrane pervaporation for the direct determination of VOCs in soil samples.

In PAM-MS and HS-MIMS, volatile compounds are thermally purged from low humidity ($\leq 25\%$) soil samples, pervaporated through a sheet membrane and rapidly transported to the ion source region of a quadrupole mass filter. *Ex situ* techniques are characterized by short analysis times, no

Table 3. Soil analysis: selected applications of membrane introduction mass spectrometry (the table is sorted by the name of the first compound mentioned in the first column)

Compound	Method ^a	Detection limit	Notes ^b	Ref.
Permanent gases N ₂ , O ₂ , Ar	Capillary		Dissolved gases in sediment core water	165
Permanent gases CH ₄ , CO ₂ , O ₂	Inlet probe		Dissolved gases in peat cores	162
Permanent gases CH ₄ , CO ₂ , O ₂	Inlet probe		Dissolved gases in freshwater sediment and peat cores	166
Permanent gases CH ₄ , CO ₂ , O ₂	Inlet probe		Gases in peat cores	168
Permanent gases CH ₄ , CO ₂ , O ₂	Inlet probe		Dissolved gases in peat cores	167
Permanent gases N ₂ , N ₂ O, O ₂	Inlet probe		Dissolved gases in sediment cores	163
Permanent gases N ₂ O, O ₂ , Ar, CO ₂	PTFE (30 μ m) on silicone		Dissolved gases in sediment core water	164
VOCs	Custom sheet membrane inlet	≥ 1 ppb	Purge-and-membrane technique, commercial and authentic soil samples; moisture content effect preheating, desorption temperature, MeOH, purge gas effects	169
VOCs	Custom sheet membrane inlet		Improved version of purge-and-membrane device	170
VOCs	Hollow fiber, ion trap MS		Proof-of-principle, spiked soil sample	131
VOCs	Sheet	≥ 1 ppb	Soil, water: purge-and-membrane technique, 'authentic soil sample,' LODs below guidelines	49
VOCs	Sheet	50–100 ppt	Soil, dry or wet solids: headspace technique	171

^a Unless noted otherwise, the methodology uses quadrupole MS and a silicone membrane.

^b The ionization technique is noted if it is other than EI.

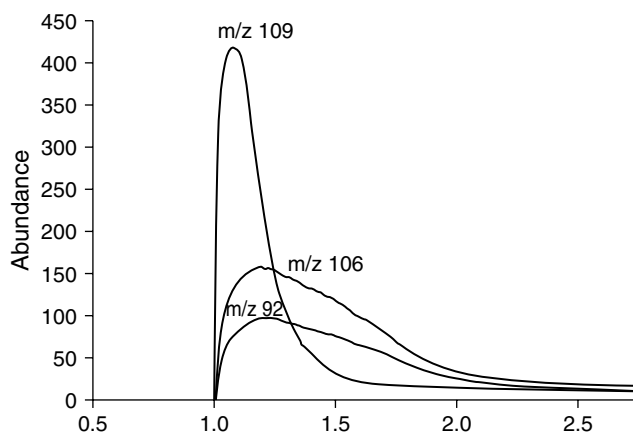


Figure 10. PAM-MS of 5 g of an authentic soil sample contaminated with toluene (m/z 92) and xylenes (m/z 106) and spiked with fluorotoluene (20 mg kg⁻¹, m/z 109). The soil sample was heated to 80 °C in a water-bath. The slow decline in the contaminant signals indicates the VOCs were more tightly bound than the spike. Reprinted with permission from Kostianen R, Kotiaho T, Mattila I, Mansikka T, Ojala M, Ketola RA. Analysis of volatile organic compounds in water and soil samples by purge-and-membrane/mass spectrometry. *Analytical Chemistry* 1998; **70**: 3028. Copyright 1998 American Chemical Society.

pretreatment of samples, high sensitivity and selectivity and elimination of solvent extraction. Real soil samples, containing only a few VOCs, were analyzed with electron ionization. Chemical ionization, as demonstrated for MIMS,^{137,138} would improve the selectivity for samples contaminated with complex VOC mixtures. Excellent reproducibility, linearity and VOC detection limits in the low-ppb ($\geq 1 \mu\text{g kg}^{-1}$) and low-ppt ($\geq 50 \text{ ng kg}^{-1}$) ranges were obtained for PAM-MS and HS-MIMS, respectively. Results from the PAM-MS of a spiked authentic soil sample are shown in Fig. 10.⁴⁹ The internal standard's more rapid signal decline compared with that of the VOCs is an indication that it was less tightly bound to the matrix than the contamination.

FUTURE PERSPECTIVES

The need for rapid, near real-time analytical measurement methods has increased with the demand for waste reduction and treatment, less industrial pollution and remediation of contaminated sites. MIMS has been shown to be a very versatile method for environmental monitoring of water, air and soil samples. Detection limits are suitable for many applications; however, there is always the opportunity to reduce these further. MIMS will be used more and more for on-line/on-site measurements (industrial, environmental applications), especially when miniaturized (and cheap) mass spectrometers are available commercially, and may even be used in homes to monitor food, water and air quality. It should be noted that MIMS instruments are already commercially available from several different companies.¹⁷² New application areas will include monitoring emerging contaminants, biological samples, pharmaceutical and cosmetic products and less volatile and more polar

compounds, and developing alternative membranes (i.e. other than silicone) for specific and sensitive environmental analyses.

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