The Use of MIMS-MS–MS in Field Locations as an On-Line Quantitative Environmental Monitoring Technique for Trace Contaminants in Air and Water

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Abstract

Membrane introduction mass spectrometry (MIMS) is emerging as an important technique for on-line, real-time environmental monitoring. Because MIMS interfaces are simple and robust, they are ideally suited for operation in MS instrumentation used for in-field applications. We report the use of an on-line permeation tube to continuously infuse an isotopically labeled internal standard for continuous quantitative determinations in atmospheric and aqueous samples without the need for off-line calibration. This approach also provides important information on the operational performance of the analytical system during multi-day deployments. We report measured signal stability during on-line deployments in air and water of 7% based on variation of the internal standard response and have used this technique to quantify BTEX (benzene, toluene, ethylbenzenes, and xylenes), pinenes, naphthalene and 2-methoxyphenol (guaiacol) in urban air plumes at parts-per-billion by volume levels. Presented are several recent applications of MIMS-MS–MS for on-line environmental monitoring in atmospheric and aqueous environmental samples demonstrating laboratory, remote and mobile deployments. We also present the use of a thermally assisted MIMS interface for the direct measurement of polyaromatic hydrocarbons, alkylphenols, and other SVOCs in the low ppb range in aqueous environmental samples and discuss improvements in both the sensitivity and response times for selected SVOCs. The work presented in this paper represents significant improvements in field deployable mass spectrometric techniques, which can be applied to direct on-site analytical measurements of VOC and SVOCs in environmental samples.

Introduction

Advances in the assessment of human exposures to airborne toxic chemicals have highlighted the value of time resolved chemical information in order to effectively evaluate the impacts on human and environmental health as well as identify point sources of pollution. At the same time, an increased concern for security has emphasized the need for analytical methods that can detect multiple chemical, biological, and radiological agents in real time, in both air and water samples. Membrane introduction mass spectrometry (MIMS) has been employed for over thirty years as an on-line analytical technique (1). This approach typically uses a semi-permeable polymer membrane to reject the sample matrix and enrich certain analytes from gaseous or liquid samples. These separated analytes are then directly transferred as a mixture (often using a helium carrier gas acceptor phase) to a mass spectrometer for their subsequent resolution and measurement. Analytes amenable to MIMS are those that can readily permeate the membrane, often made from silicone (polydimethylsiloxane, PDMS). Typically this includes volatile organic compounds (VOCs) as well as some semi-volatile organic compounds (SVOCs). In the mid 1990s, there was a resurgence in the use of MIMS for "real-time" trace analytical measurements in air (2) and water (3), possibly because of advances in mass spectrometer technology and also because of an increased interest in continuous and direct measurement strategies for environmental applications. Excellent reviews of MIMS appeared in 2000 (4) and specifically for its environmental uses in 2002 (5). In general, there has been a progression of development in MIMS techniques to allow the analysis of a greater range of analytes (from VOCs to SVOCs) and to improve the analytical capabilities for the direct resolution of complex mixtures; most notably by the increased use of tandem mass spectrometry (MS–MS).

Recent applications of MIMS have continued to examine VOC/SVOC molecules that readily permeate silicone membranes, predominately using hollow fiber membrane (HFM) geometries. These studies include the analysis of analytes in a variety of aqueous, air, or headspace samples. This work includes applications that range from monitoring molecular emissions from biological systems (e.g., microbial denitrification, etc.) (6–12) to investigations of reaction kinetics for a variety of aqueous systems (13–17). Early approaches to describe permeation kinetics in MIMS data used Cartesian coordinate transport models (18–20) or numerical analysis (21–23). We have recently developed an analytical solution in cylindrical coordinates and data fitting algorithms that yield both permeant diffusion and partition coefficients from experimental non-steady state signal behaviour (24).

Efforts to improve the analytical performance of MIMS have included the development of in-line cryo-focusing between the

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membrane and the mass spectrometer (25), cyclic sudden sampling with multiple membranes to allow pre-concentration of analytes in the acceptor phase before MS analysis (26), the application of chemical ionization techniques (27–31), photoionization techniques (32), the use of proton transfer reaction MS (33,34), supported liquid membranes (13), the study of non-PDMS membranes (35,36) and reversed phase non-aqueous MIMS techniques (35). In addition, the miniaturization of MIMS systems for portability and remote operation has been explored by several researchers (37–39), including on-line monitoring of dissolved gases in seawater onboard a research vessel (40) and the development of an underwater MIMS system (41–43).

To address the long-standing sensitivity limitations of MIMS for SVOC molecules, several researchers have developed new methodologies based upon thermal modulation of membranes. Simple heating of the MIMS interface affords some improvements (27), but for aqueous samples, is of limited use because of bubble formation (5,44) and increased water permeation through the membrane (45,46) both lead to degraded analytical sensitivity as the membrane temperature approaches the boiling temperature of water. As an alternate approach, Creaser et al. developed in-membrane pre-concentration techniques as a means of improving SVOC sensitivity (47). The Lauritsen group investigated desorption chemical ionization using a HFM mounted directly in a methane CI plasma within the MS to detect fat soluble bio-molecules (48), estrogenic compounds, and polycyclic aromatic hydrocarbons (49). The Eberlin and Cooks groups used thermally assisted trap-and-release MIMS as a means of pre-concentrating analytes in the membrane to improve sensitivity (50–52). Nayar et al. used a CO_2 laser to thermally probe a sheet PDMS membrane as a means of rapidly evaluating an array of heterogeneous catalysts (53). Our group has recently developed a versatile, co-axially heated HFM interface for MIMS, which improves the sensitivity and response time for SVOCs in both continuous and pulsed heating modes, yet retains its sensitivity for VOCs when the heater is not actuated (54). As an alternate approach, SVOCs can be pre-derivatized to form more volatile analyte species for MIMS measurement, although this requires additional sample handling and/or dilution (50,52,55). To detect molecules with low volatility that do not permeate PDMS membranes (e.g., ionic species), we demonstrated the first use of an enzyme modified membrane (56). This approach employs a covalently immobilized lipase that competitively binds with a non-volatile ester substrate and releases detectable volatile hydrolysis products at the membrane surface. This strategy holds great promise for the selective detection of bio-molecules via specific enzyme-substrate pairs. There is growing interest in the use of condensed acceptor phases (e.g., liquids) with MIMS as an on-line method to detect less volatile analytes (57,58). This methodology uses a membrane to transfer analytes from aqueous samples into a liquid acceptor phase. In this manner, analytes not amenable to MIMS with gas phase acceptor can be determined. Direct MS analysis of the condensed acceptor phase is subsequently achieved by spray ionization techniques such as electrospray and/or atmospheric pressure chemical ionization.

To successfully employ MIMS as a quantitative on-line analytical tool, the analyst must use some form of calibration. This can be done by using standard solutions of analytes (e.g., external calibration curve or standard additions) or by using internal standard(s). Although external calibrations are simple and convenient, they can be problematic for long-term continuous on-line monitoring deployments, as they require that no instrumental drift occurs after calibration. Instrumental drift can be compensated for by measuring a calibration verification standard periodically, however this requires that the instrument be taken off-line. As an alternative to off-line calibration, internal standards can be added to the sample stream at regular intervals to evaluate analytical performance, or can be continuously infused in the environmental sampling stream. We have chosen to use on-line permeation tubes to continuously infuse deuterated internal standards (IS) in gaseous and aqueous on-line environmental sampling scenarios. The advantages of this approach are that it is simple (permeation tubes are installed upstream of the membrane in the sampling train), does not dilute the sample stream, provides continuous quantitation (via pre-determined relative response factors) and allows an on-line evaluation of the analytical performance of the system (via the stability of the IS signal). Although permeation tubes have been successfully used to prepare on-line gas phase standards for rapid gas chromatography (59,60), we are not aware of their use for MIMS in this mode.

Our group has been targeting fundamental and applied MIMS research with the aim of developing an improved on-line analytical tool for quantitative environmental measurements. In general, these improvements consist of an on-line continuous calibration technique to account for any potential measurement drift during multi-day monitoring deployments as well as interface modifications that increase sensitivity and decrease response times for a wider range of environmentally relevant analytes. In the following work, the authors highlight recent advances using MIMS–MS as a quantitative on-line environmental monitoring strategy in both air and water sample streams from mobile, fixed remote and laboratory-based locations. We describe the use of an on-line permeation tube to continuously infuse a deuterated internal standard into the sampling stream and MIMS–MS techniques for the quantification of BTEX (benzene, toluene, ethylbenzene, and xylenes), pinene, naphthalene, and guaiacol (2-methoxyphenol) in urban air plumes. The on-line internal standard approach has been extended to monitor chloroform production during the chlorination of a drinking water sample. Also discussed are the improved analytical response characteristics of a thermally-assisted MIMS (TAMIMS) interface for several representative SVOCs in aqueous environmental samples.

Experimental

The MIMS system used for this work has been described elsewhere (17,54). Briefly, a capillary hollow fibre polydimethylsiloxane (Silastic tubing from Dow-Corning) membrane was mounted co-axially inside 0.25" o.d. stainless steel flow cell interface. Helium carrier gas was continuously passed through the center of the membrane (1.0 mL/min) for all experiments to transfer analytes to the mass spectrometer. The MIMS interface was mounted inside a temperature controlled oven (70°C). In addition, a 5.0 m × 0.25" o.d. stainless steel sample pre-heating

coil and a small permeation cell (mounted in a glass flow through cell) were also placed in the oven, connected in-line and upstream of the interface. The permeation cell provided a continuous, trace infusion of toluene-d8 internal standard, allowing continuous, on-line quantitation throughout all real-time measurement runs. A 5 µm in-line air filter (Model 225-802SC, SKC Inc., Fullerton, CA) was used to remove particulate matter from the air samples prior to analysis by MIMS. Air samples were drawn through the apparatus at a rate of 4.0 L/min through 0.25" o.d. Teflon tubing. A quadrupole ion trap tandem mass spectrometer (Thermo-Fisher GCQ, Austin, TX) was used to obtain the presented MIMS data. Figure 1 gives a schematic diagram of the MIMS apparatus. For the field studies, this system was installed in a mobile laboratory equipped with on-board AC power (provided at cost by Cantest Ltd., Burnaby, BC) to allow measurements from both static and mobile remote locations. The sample inlet stream was positioned on the exterior of this vehicle at 2.5 m height, opposite the exhaust to minimize inadvertent sampling of the emissions from the vehicle during motion and the generator when at fixed locations. To further reduce any potential contamination from the generator exhaust, a 5 m flexible exhaust line was used to direct these emissions downwind during fixed location deployments.

Target analytes and internal standards were ACS grade or better, and predominantly obtained from Sigma Aldrich Ltd. (Oakville, ON, Canada). Common solvents (benzene, toluene, xylenes and chloroform, also ACS grade or better) were obtained from Fisher Scientific (Ottawa, ON, Canada). Analytes and internal standards studied include benzene (CAS# 71-43-2), benzene-d_6 (1076-43-3), toluene (108-88-3), toluene-d_8 (2037-26-5), ethylbenzene (100-41-4), the xylenes (ortho 95-47-6, meta 108-38-3, para 106-42-3), guaiacol (2-methoxyphenol, 90-05-1), pinenes (80-56-8), naphthalene (91-20-3), chloroform, (67-66-3), 2,4,6-trichloroanisole (87-40-1), 8:2 fluorotelomer alcohol (perfluorooctyl ethanol, 678-39-7) biphenyl (92-52-4), 4-ethylphenol (123-07-9), 4-nonylphenol (104-40-5), and diethylphthalate (84-66-2). Analytes were chosen to be representative of a range of physico-chemical properties and their relevance as known determinants of human and environmental health (e.g., in indoor/outdoor air or surface/drinking water). Most analytical signals for the target analytes described in this work were quantified by obtaining instrumental relative response factors (versus toluene-d8) using the described system. Gaseous standards of the analytes were prepared (except where noted) by using gravimetrically calibrated permeation tubes diluted in high purity air using a Dynacalibrator system (Model 450, VICI Metronics Ltd, Poulsbo, WA). Relative response factors were calculated in the standard manner (Equation 1) at several ppbv concentration levels using steady state MIMS-MS–MS signals and then averaged to give overall relative response factors.

$$RF = \frac{Signal_X / [X]}{Signal_{Toluene\text{-}d8} / [Toluene\text{-}d_8]} \quad \text{Eq. 1}$$

Two approaches were used for calibration of the MIMS system for use with aqueous samples. In the first approach, direct calibration (e.g., a calibration curve) was determined by using dilute aqueous standards of the respective analytes. Solutions of these standards were directly circulated through the MIMS system (Figure 1) at 250 mL/min. using a peristaltic pump (Model 77200-62 Masterflex Easy-Load II with LS-25 Viton pump tubing; Cole-Parmer Ltd., Montreal, QC, Canada) and flushing

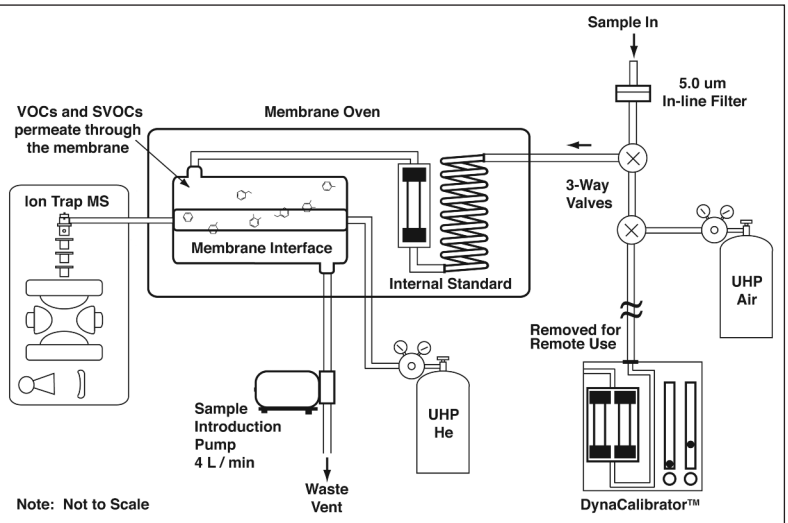

Figure 1. Schematic MIMS apparatus.

Table I. Analyte MS–MS Transitions and/or SIM *m/z*, Permeation Tube Emission Rates, and Experimentally Determined Relative Response Factors for Target Analytes

Target analytes	MS–MS transitions or SIM *m/z*	Permeation rate (ng/min @ 50°C)	Relative response factors*	
Toluene-d_8 (Internal Standard)	100 → 70	589	1.00	
Benzene	78 → 50, 51, 52	321	1.28 ± 0.09	
Toluene	91 → 65	189	2.36 ± 0.07	
Ethylbenzene/Xylenes	106 → 77, 79, 91	838†	5.1 ± 0.4	
Guaiacol	124 → 81, 109	31.1	2.8 ± 0.2	
Pinenes‡	93 → 77	0.5§	1.6 ± 0.3	
Naphthalene	128 → 102	–	1.5 ± 0.1**	
Chloroform††	83, 85, 87	–	5.1 ± 0.1	
2,4,6-Trichloroanisole	210 → 195, 197, 199	–	–	
8:2 Fluorotelomer Alcohol	127 → 77	–	–	
4-Nonylphenol	107,121,135,149	–	–	
4-Ethylphenol	107,122	–	–	
Biphenyl	153, 154	–	–	
Diethylphthalate	149,177	–	–	

* Relative to Toluene-d_8 internal standard (n = 3 to 5 runs in each case).
† Xylene permeation tube used; these isomers not resolvable by MS–MS.
‡ Pinenes (30% a / 70% b, v:v).
§ A-type Diffusion Vial used.
** Approximate relative response factor determined for aqueous standards.
†† Toluene-d_8 permeation tube used online in an aqueous feed stream.

the system with deionized water between analytes until baseline signals were observed. Further details regarding the use of our MIMS system for measuring aqueous samples have been published elsewhere (17). Water for this work was deionized and purified for trace organics (Model MQ Synthesis A10, Millipore Corp., Billerica, MA). Natural water samples were obtained from the Nanaimo River watershed (Nanaimo, BC, Canada) or directly from the municipal distribution system (Nanaimo, BC, Canada) and used without additional filtration in either case.

We also evaluated the use of permeation tubes as on-line internal standards for quantitative calibration of the MIMS system via relative response factors when used with aqueous samples. The experimental apparatus was similar to that illustrated in Figure 1, except that an aqueous sample flow of 250 mL/min was used with the permeation tube (mounted in an in-house constructed flow chamber) downstream from a 15-meter long 0.25" o.d. Teflon tubing sample pre-heating loop. The permeation tube and pre heating loop were immersed in a water filled constant temperature water bath (Model SW23, Julabo Corporation, Seelbach, Germany) to ensure stable temperatures for these experiments (± 0.02°C). Permeation rates for the internal standard permeation tube in aqueous flows were determined by direct calibration with external aqueous toluene-d8 standards. All compressed gases used for this work were UHP grade (99.999% pure) and obtained from a local supplier (Praxair Ltd., Nanaimo, BC, Canada). Table I summarizes the relevant MS–MS transitions and/or selected ion monitoring (SIM) *m/z* used by the mass spectrometer, the permeation rates of the analyte tubes and experimentally determined response factors. In addition to the MS–MS and SIM scans, full mass scans (*m/z* = 50 to 250) were also conducted for all experiments. All atmospheric monitoring analytical signals were background subtracted using a baseline signal determined for UHP (99.999% pure) air. Because a suitable naphthalene permeation tube was not available at the time of the study, surrogate standards prepared in aqueous solution (naphthalene and toluene-d8) were used to determine an approximate response factor for naphthalene. All aqueous solutions of target analytes and standards used in this work were prepared by diluting concentrated stock solutions (prepared in methanol). Care was taken so that final methanol concentrations in aqueous solutions were < 0.1 % to eliminate any potential for co-solvent effects. Optical nephelometry measurements (for particulate matter) were made using an optical nephelometer (Model M903, Radiance Research, Seattle, WA) calibrated for $PM_{2.5}$.

A series of aqueous standard solutions were prepared to evaluate analyte response times and sensitivity improvements of TAMIMS as a method for the direct analysis of trace SVOCs in aqueous samples. Full details of the operation of TAMIMS interfaces as used for this work are given elsewhere (54).

Results and Discussion

The work presented herein illustrates representative case studies where MIMS has been used for on-line monitoring of trace environmental contaminants from mobile, fixed remote and laboratory based locations. The presented results are grouped into three categories: atmospheric monitoring, aqueous monitoring, or the use of TAMIMS. To examine the variation of the internal standard (IS) signal due to the presence of multiple co-analytes over a multi-day period, we have assessed the reproducibility of calibration data for a series of binary mixtures. The results of this work (Figure 2) suggest multi-day calibration can be achieved for a variety of analytes, with a signal relative standard deviation of ± 12% regardless of the molecules present in a given calibration mixture. The similarity of the calibration slopes for toluene-d_8 regardless of the co-analyte present suggests that for the molecules examined, there is no significant interference with the IS response. We have analyzed the stability of the toluene-d_8 signals for the data presented in this work (obtained during on-line atmospheric and aqueous environmental monitoring). The relative standard deviation of the measured IS signal was determined to be 7% (or less) based upon data in Figure 3 (urban airshed monitoring), Figure 5 (atmospheric monitoring of cruise ship emission plume) and Figure 6 (aqueous dis-infection byproduct formation).

We have observed that measurement of toluene (*m/z* = 91)

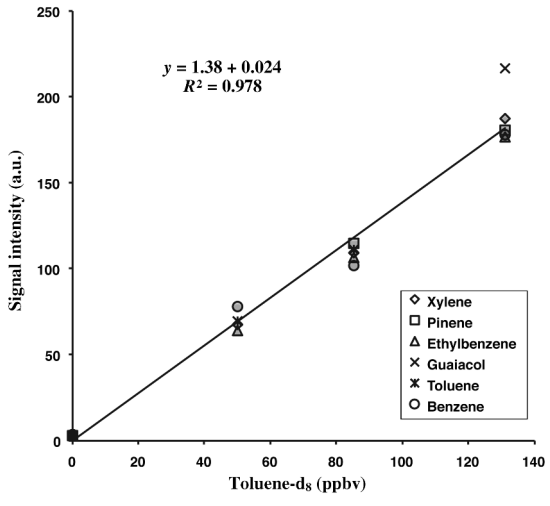

Figure 2. Toluene-d_8 calibration curves for standard gas phase solutions containing a variety of co-analytes present at similar concentrations (e.g., ppbv levels) to check reproducibility and potential interferences.

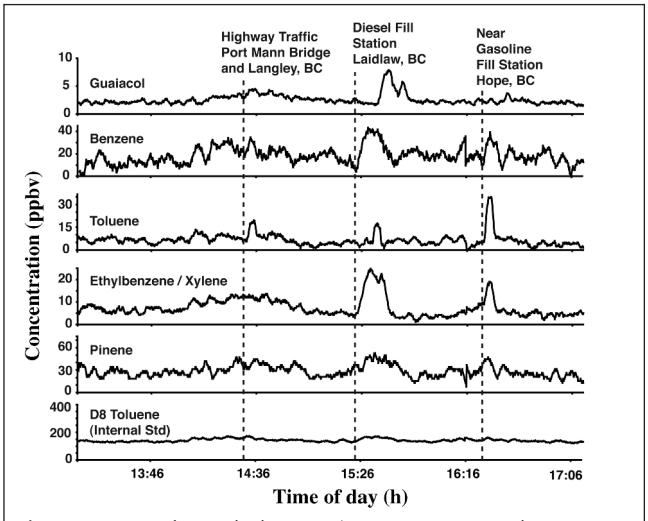

Figure 3. Portion of an airshed transect (Vancouver, BC, Canada, Nov. 21st, 2005) obtained with the mobile MIMS system demonstrating on-line, multi-analyte quantitation in a field deployment scenario.

and/or benzene (m/z = 78) by both SIM and MS–MS methods in the presence of ethylbenzene, xylene and pinenes can yield a positive analytical bias (e.g., these molecules produce identical fragment ions that also occur at m/z = 91, 78). This positive interference can be addressed to some extent by using softer chemical ionization (CI) methods in the mass spectrometer (resulting in less fragmentation of the interfering molecules) (30), or through numeric deconvolution via experimentally determined interference factors (61). Because the work presented here was designed to examine temporal variations in analyte concentration rather than absolute quantitation, we have not attempted to resolve these potential interferences. Since other terpenoid species could also produce a positive bias, the reader is cautioned to use the observed trends rather than specific concentrations, especially in the case of benzene and toluene.

Atmospheric monitoring

To assess the applicability of MIMS for on-line atmospheric contaminant monitoring, the described system (Figure 1) was deployed in a number of field locations, including operation in a moving vehicle.

In Figure 3, a portion of a time series of MIMS data collected during a transect of the Georgia Basin airshed (Vancouver, BC Canada) is presented. The MIMS system was operated in a continuous mode, monitoring a variety of contaminants and tracer molecules on-line from a moving (vehicle based) system. With signal averaging (10 scans/point), we achieve ~1 measurement per second, although the actual response time for all analytes are limited by their membrane transport times (54) which are on the order of minute(s) and vary dependent upon the diffusivity of the specific analyte (small, volatile analytes, e.g., toluene, have faster response times). From this study (Figure 3), we observe numerous concentration excursions for the BTEX suite (benzene, toluene, ethylbenzene, and xylenes). Although no direct correlation with most point sources (e.g., individual automobiles etc.) is attempted, a few observations are noted below. Sharp increases in concentration for BTEX were recorded during stops at a diesel fill station and a gasoline fill station (Figure 3), an expected result given that these are point sources for hydrocarbon emissions. A unique spike in toluene levels at ~1440 h correlates with traveling past a large industrial park where it is speculated that fugitive toluene emissions may have been occurring. The broad, low-level BTEX signals observed from 1400–1500 h correlates with traveling on a four lane highway in heavy traffic that progressively reduced over the time course of the data presented in Figure 3 as our mobile unit traveled East on an transect away from metropolitan centre of Vancouver, British Columbia. To illustrate the significance of the results obtained by MIMS-MS–MS in this study, a comparable experiment conducted using an on-line chromatographic separation technique (e.g., trap-and-purge gas chromatography–mass spectrometry) operated from a mobile laboratory would have a temporal resolution limited by both analyte trapping and chromatographic separation steps. The data obtained in this alternate scenario would be sub-optimal by underestimating contaminant levels at "hot spots" by temporally integrating them with background levels during the trapping step or missing them entirely during the chromatographic resolution step. MIMS-MS–MS provides an elegant alternative with a faster duty cycle, limited only by the rate of analyte transfer through the membrane.

Our group and others (62–67) have been evaluating the use of a variety of different compounds including guaiacol and related molecules as atmospheric tracer molecules for wood smoke, a substantial source of atmospheric pollution where wood burning for domestic heating is used (68). Guaiacol is formed during pyrolysis of the wood polymer lignin, and its presence in atmospheric samples is a unique tracer for biomass combustion. The minor guaiacol signal rise between 1400–1500 h in Figure 3 may reflect an increased prevalence of domestic wood burning heat sources and other wood combustion sources in outlying suburbs (the study was conducted on a cold November day when it is presumed that people would be using their woodstoves), although no direct correlation can be inferred. At ~1540 h, two distinct guaiacol signal excursions were recorded (Figure 3) in a rural village location where several active domestic wood burning heat

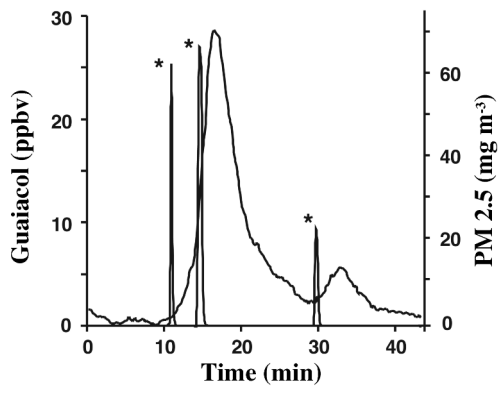

Figure 4. Comparison of the on-line guaiacol response by MIMS-MS–MS and on-line PM 2.5 nephelometric measurements (signals denoted by *) for several point source woodsmoke samples from a small mixed softwood fire (Western Red Cedar, Douglas Fir and Balsam Fir).

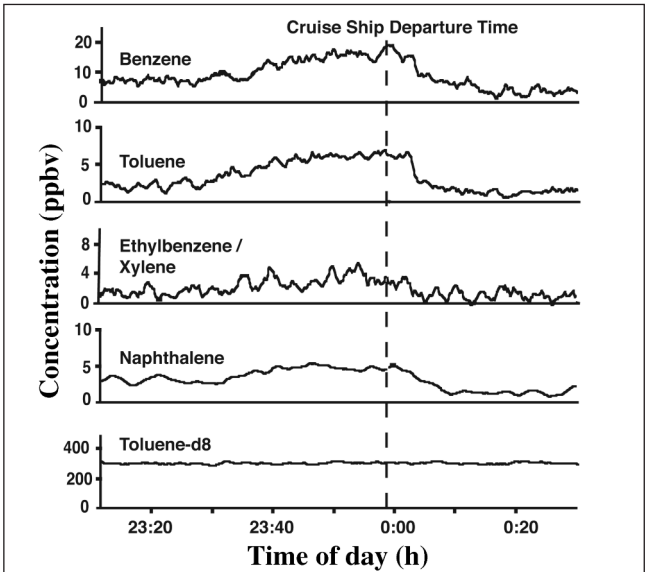

Figure 5. Static deployment of the mobile MIMS system on a waterfront pier (Victoria, BC, Canada, July 19, 2007) showing the on-line detection of the emission plume from a cruise ship during departure from port.

sources were observed (e.g., visible domestic flue emissions). This data suggests that MIMS was successful in the on-line detection of these point source emissions. As a follow up study, small, non-quantitative portions of the atmospheric emissions from a small wood fueled fire were tested with an on-line MIMS experiment in the laboratory (Figure 4). This experiment clearly shows that guaiacol is readily detectable at ppbv levels by MIMS in the atmospheric samples. In addition, an on-line measure of particulate matter was simultaneously conducted using optical nephelometry (Figure 4), showing spikes in $PM_{2.5}$ levels when the point source wood fire smoke plume was sampled. The three wood types used in this test fire were Western Red Cedar, Douglas Fir and Balsam Fir, which represent a major percentage of the wood fuels used for domestic heating in western British Columbia, Canada. In the case of the SVOC guaiacol, the signal response time is slower than the $PM_{2.5}$ nephelometric response, yielding a slightly delayed and smoothed response (Figure 4). Although not addressed in this particular study, methods for improving the MIMS analytical response time for SVOCs, such as guaiacol are possible (47,48,54,69–71) and are presented in the last section of this work.

In a separate remote on-line application of MIMS for atmospheric monitoring, the system was deployed at numerous fixed locations as well as from a moving vehicle over 8 days (two separate trips of four days each) in and around the inner harbour of Victoria, British Columbia, Canada. The goal of this work was to assess the temporal variations in MIMS detectable atmospheric contaminants in the inner harbour area, especially during the arrival and departure of oceanic cruise ships. Although we encountered unfavorable meterological conditions (e.g., off shore winds) for the detection of emissions from most cruise ships, we were successful in the on-line detection of departure emission events during favorable conditions (Figure 5). As depicted in Figure 5, atmospheric concentrations of BTEX and naphthalene increase at ~ 11:30 h as ships engines warm up prior to departure. Levels of these compounds show a marked decrease after the cruise ship left port around mid-night.

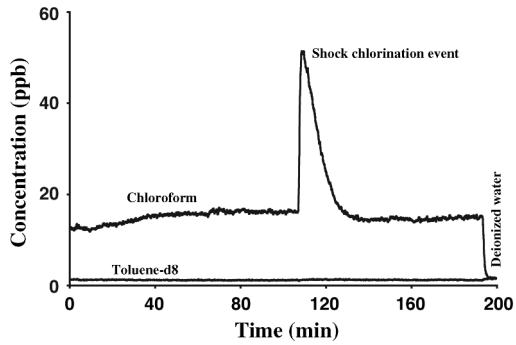

Figure 6. The use of toluene-d_8 from a permeation tube as an on-line internal standard for monitoring chloroform levels in municipal water (May 22nd, 2008, Nanaimo, BC) at point of use. The large spike of chloroform signal is for a shock chlorination performed in the lab in a 12 L reservoir. At 192 min, the system was flushed with deionized water.

Table II. Comparison of Aqueous Chloroform Concentrations Determined using Direct Calibration via Aqueous Standards and Response Factors Relative to Online Internal Standards

Time (min)	Baseline corrected $CHCl_3$ signal (a.u.)	$[CHCl_3]$ via direct calibration* (ppb)	$[CHCl_3]$ via response factor† (ppb)	Percent difference (%)‡
15	1060	10.67	10.96	3
109	4760	48.20	49.32	2

* Where $y = 98.59x + 8.107$, $r^2 = 0.998$; y = the baseline corrected signal; x = the chloroform concentration (ppb).
† Determined using Equation 1 and Table I.
‡ Based upon percent difference from direct calibration method.

Aqueous monitoring

As described previously, for atmospheric monitoring experiments we use an on-line calibration procedure to ensure reliable quantification of analytes. This is achieved by continuously infusing deuterated internal standard (IS) from a permeation tube into the gaseous sample stream. This yields a stable signal (Figures 3 and 5), verifying the proper operation of the system, as well as allowing continuous quantitation of analytes via relative response factors (Table I).

To facilitate a parallel experiment in aqueous environmental samples, we employed a similar strategy, using an analogous apparatus except that a 15.0 meter long 0.25" o.d. Teflon tube was used as a sample pre-heating loop to ensure a stable sample temperature as it flowed over the permeation cell (permeation rates are dependent upon temperature). The advantage of the direct infusion of internal standard from a permeation tube is that it eliminates additional solution preparation and provides a 100% on-line duty cycle for analytical measurements. In cases where environmental samples may cause fouling of the permeation cell, a bypass system that allows internal standard measurement in a clean matrix (e.g., deionized water) may be necessary. This would either reduce the on-line duty cycle (the system would be off-line when measuring the internal standard), or reducing sensitivity (by dilution), if a separate calibrant stream was continuously mixed with the sample stream.

To evaluate the effectiveness of the use of the permeation tubes for on-line quantitation in aqueous flows, chloroform in municipal water was monitored using toluene-d_8 as an internal standard (Figure 6). Chloroform (a known dis-infection byproduct) is produced when active chlorine dis-infection treatments are used (72,73). Municipal tap water was sampled with the MIMS system (250 mL/min) from the bottom of an open 12 L benchtop flow-through reservoir (water residence time of 3.0 mins). The stability of toluene-d_8 IS signal in this single pass system (analogous to the air sampling system) is very good over a > 3 h period, with an RSD of 7.1%. We have observed that the same permeation tubes are somewhat less emissive in water than air (e.g., for deuterated toluene 258 ng/min in water and 382 ng/min in air, both at 35°C). Similar results (not shown) were also observed for a deuterated benzene permeation tube measured in the same system. At this point, we do not speculate on a reason for the discrepancy, other than that it would be expected that different phenomena may be controlling mass transport processes from the permeation tube

in condensed phases as compared to the gas phase. Chloroform levels remained relatively constant between 10–20 ppb over a 2-h time course of on-line monitoring, at which point we simulated a "shock" chlorination event at 107 min (Figure 6). Spiking the reservoir to a level of c.a. 200 ppm active chlorine (as calcium hypochlorite) produced additional chloroform (in-situ) which persisted for over 20 min while the reservoir water is exchanged with additional tap water. The concentrations of chloroform obtained by using the on-line internal standard method were within 3% of those obtained by using a direct chloroform calibration curve. This is presented in Table II, where representative concentrations at baseline and peak chloroform concentrations are compared. This case study illustrates that the on-line IS method using permeation tubes in aqueous sample flows produces acceptable on-line monitoring results.

Thermally assisted MIMS

To address the need for improved analytical response for SVOCs by MIMS, a variety of membrane heating strategies have been employed (47,48,54,69–71). Heating the membrane interface increases the diffusivity of analytes through the polymer and aids in the desorption of SVOCs into the helium carrier gas, resulting in modest improvements in sensitivity and response times for SVOC compounds. However, when the entire interface is heated beyond ~ 60°C, analytical performance is degraded due higher water vapour transport across the membrane (45,46) and bubble formation as the temperature approaches 100°C (5,44). Alternative thermally assisted strategies have been employed to circumvent this problem. For example, MIMS methods have been developed in which a drying gas flow is introduced after an aqueous sample is flowed over the membrane, followed by rapid heating (47,48). Thermal desorption of "trapped" analytes improves their detection, but longer duty cycles are introduced because of the drying steps. We have developed a co-axially heated membrane assembly to address this issue that performs well for both VOC and SVOC analytes and allows for continuous real-time monitoring (54,74).

The premise for our design was to heat one side of the membrane to create a thermal gradient counter to the concentration gradient across the membrane. For aqueous samples, the outer surface of the hollow fiber membrane is cooled by the continuous water flow while an interior surface is heated by a resistive wire heating element. Hydrophobic SVOCs partition favourably into the cooler outer surface of the PDMS membrane, which remains relatively impermeable to water. The resulting concentration gradient drives the diffusion of analytes through the polymer which becomes progressively hotter and more permeable as analytes traverse the membrane. The heated interior surface of the membrane (~150°C) promotes thermal desorption of less volatile analytes into the acceptor helium gas. This interface can be operated in either a continuous heating or pulsed heating mode ("in-membrane" trap and release) and importantly retains its operational characteristics for VOC analytes when the heater is not actuated. Improvements in both the response time and the sensitivity of environmentally relevant SVOCs using the TAMIMS interface are illustrated below.

Table III. Physico-Chemical Properties (77) of Selected SVOC Target Analytes and Estimated Minimum Detection Limits in Aqueous Samples using TAMIMS

Target analytes	Log VP (atm @ 25°C)	Log K_{ow}	MDLs (pptr)
Hydrocarbons			
Toluene	–1.42	2.7	20
Naphthalene	–3.43	3.4	100
Biphenyl	–5.0	4.1	20
Alcohols			
2-Methoxyphenol	–3.86	1.3	40,000
4-Ethylphenol	–4.6	2.5	4000
4-Nonylphenol	–6.9	6.4	100
Miscellaneous			
Trichloroanisole	–4.9	4.1	100
Diethylphthalate	–5.08	2.4	5000

We have previously reported improvements of one to two orders of magnitude in both the response time and sensitivity of environmentally relevant SVOCs using TAMIMS (54). For example, the signal response time for atmospheric guaiacol measurements conducted at ambient temperature is roughly 20 min, which accounts for the lag time of the guaiacol signal noted above in Figure 4. This is reduced to ~ 2 min if the entire membrane interface is heated to 100°C and about 15 s using internal co-axial heating. Similar reductions in the signal response times are noted for aqueous guaiacol samples, although aqueous samples cannot be heated above 60°C without loss of signal intensity (54). Rapid signal rise times are noted after the membrane has been exposed to the sample and heated in pulsed mode. Table III summarizes a selection of these and other compounds (including polyaromatic hydrocarbons, alcohols and dialkylphthalates) along with selected physico-chemical properties and estimated detection limits using our TAMIMS interface. Since analyte partitioning between water and PDMS are known to correlate with octanol-water partition co-efficients (K_{ow}) (75,76), we use K_{ow} values as predictor for membrane enrichment factors. Examination of the results presented in Table III illustrates that we observe the lowest detection limits for analytes with low volatility that are more hydrophobic (e.g., log $K_{ow} > 3$). For example, although trichloroanisole and diethylphthalate have similar vapour pressures (~10^{-5} atms at 25°C), the MDL for trichloroanisole is observed to be about 50 times lower than that of diethylphthalate. Interestingly, the K_{ow} of trichloroanisole is 50 times greater than that of diethylphthalate. 4-Ethylphenol, which in spite of being considerably more volatile than 4-nonylphenol, has a minimum detection limit, which is some 40 times higher. We attribute this to a greater enrichment factor for 4-nonylphenol that arises as a result of its much larger octanol-water partitioning co-efficient. A similar, albeit less dramatic trend is also observed for naphthalene and biphenyl.

TAMIMS was applied to the analysis of mixtures of SVOC/VOC analytes in spiked environmental samples. Figure 7 illustrates TAMIMS for the simultaneous detection of a variety of VOC and SVOC contaminants in a natural water sample. When the TAMIMS heater is not activated (time period ~15–45 min) conventional performance of the MIMS system for VOCs is achieved (e.g., see toluene trace ~15–45 min). When the internal heater is

pulsed (three pulses from c.a. 45–80 min), in-membrane trap-and release occurs, enhancing sensitivity for the SVOCs. Figure 7B. depicts the detection of nonylphenol at 680 pptr in an aqueous sample in response to internal heating pulses applied after the solution had been re-circulated over the membrane interface for > 10 mins. Repeated heating pulses result in acceptable signal reproducibility (5% RSD) and much faster signal response times (< 1 min) for this environmentally relevant contaminant. By using pulsed activation of the TAMIMS heater, an on-line "trap-and-release" (from the membrane) is achieved that greatly improves sensitivity and response time for their direct measurement in aqueous samples over un-heated MIMS. Further demonstrations of the use of TAMIMS (e.g., pulsed and continuous mode operation in air and water samples) have been published elsewhere (54).

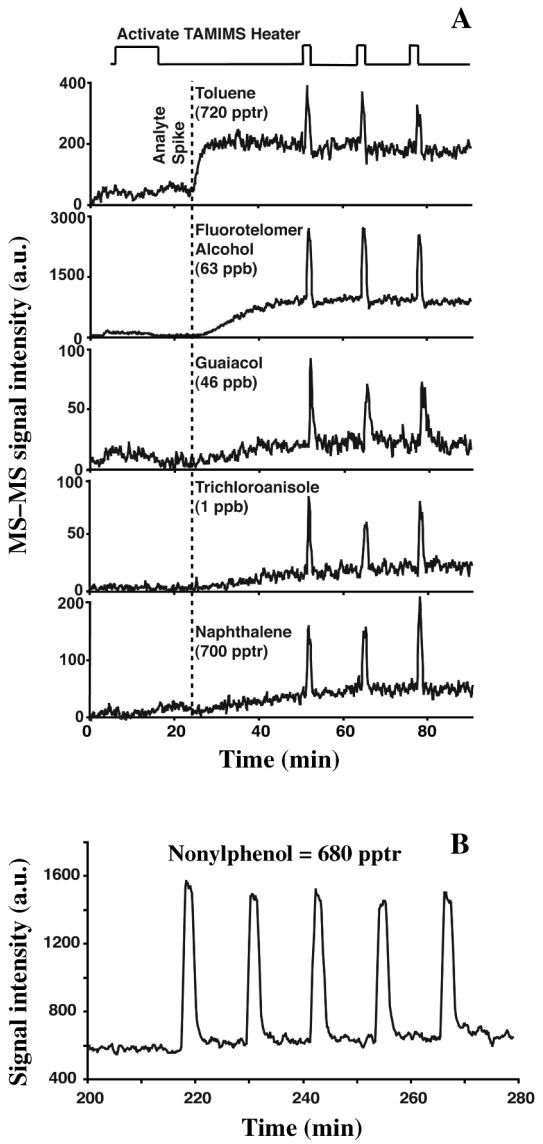

Figure 7. The use of TAMIMS to simultaneously detect a variety of VOC and SVOC contaminants in a natural water sample, comparing no heating and pulsed heating trap-and-release modes (A); Detection of aqueous 4-nonylphenol at environmentally relevant levels using pulsed co-axial heating with TAMIMS after membrane loading from a re-circulated sample in a closed loop (B).

Conclusions

MIMS is a simple and robust analytical method that can be adapted to virtually any mass spectrometer capable of gas chromatography, and as such provides an accessible alternative for the on-line measurement of VOC and SVOC contaminants in dynamic chemical systems. We have demonstrated the use MIMS-MS–MS for both laboratory and field deployment monitoring scenarios using a continuously infused internal standard. This approach yields on-line quantitation for multiple analytes and provides satisfactory analytical performance characteristics during long term monitoring deployments in both air and water samples. We also describe the use of TAMIMS methods for the analysis of SVOCs that improve both the sensitivity and signal response time over ambient temperature MIMS methods. In summary, MIMS-MS–MS provides environmental chemists with a rapid and sensitive on-line analytical tool filling a niche between hand-held sensors and conventional chromatographic analysis strategies (e.g., GC–MS). We continue to explore the development of MIMS as a viable analytical strategy for environmental monitoring, including the further examination and development of membrane interface geometries, the use of new membrane materials and improved mass spectrometric methodologies.

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References

1. L.B. Westover, J.C. Tou, and J.H. Mark. Novel mass spectrometric sampling device-hollow fiber probe. *Anal. Chem.* **46:** 568–71 (1974).
2. M.E. Cisper, C.G. Gill, L.E. Townsend, and P.H. Hemberger. On-line detection of volatile organic compounds in air at parts-per-trillion

levels by membrane introduction mass spectrometry. *Anal. Chem.* **67:** 1413–17 (1995).
3. M. Soni, S. Bauer, J.W. Amy, P. Wong, and R.G. Cooks. Direct determination of organic compounds in water at parts-per-quadrillion levels by membrane introduction mass spectrometry. *Anal. Chem.* **67:** 1409–12 (1995).
4. R.C. Johnson, R.G. Cooks, T.M. Allen, M.E. Cisper, and P.H. Hemberger. Membrane introduction mass spectrometry: Trends and applications. *Mass Spectrom. Rev.* **19:** 1–37 (2000).
5. R.A. Ketola, T. Kotiaho, M.E. Cisper, and T.M. Allen. Environmental applications of membrane introduction mass spectrometry. *J. Mass Spectrom.* **37:** 457–76 (2002).
6. J.R. Firth and C. Edwards. Effects of cultural conditions on denitrification by pseudomonas stutzeri measured by membrane inlet mass spectrometry. *J. Appl. Microbiol.* **87:** 353–58 (1999).
7. J.E. Baumgardner, I.C. Choi, A. Vonk-Noordegraaf, H.F. Frasch, G.R. Neufeld, and B.E. Marshall. Sequential v(a)/q distributions in the normal rabbit by micropore membrane inlet mass spectrometry. *J. Appl. Physiol.* **89:** 1699–1708 (2000).
8. J.R. Firth and C. Edwards. Analysis of denitrification by pseudomonas stutzeri under nutrient-limited conditions using membrane inlet mass spectrometry. *J. Appl. Microbiol.* **88:** 853–59 (2000).
9. S. An, W.S. Gardner, and T. Kana. Simultaneous measurement of denitrification and nitrogen fixation using isotope pairing with membrane inlet mass spectrometry analysis. *Appl. Environ. Microbiol.* **67:** 1171–78 (2001).
10. M.J. Bernot, W.K. Dodds, W.S. Gardner, M.J. McCarthy, D. Sobolev, and J.L. Tank. Comparing denitrification estimates for a texas estuary by using acetylene inhibition and membrane inlet mass spectrometry. *Appl. Environ. Microbiol.* **69:** 5950–56 (2003).
11. A.J. Thompson, J.M. Etzkorn, D.M. Van Pel, E.T. Krogh, D.R. Drakeford, and C.G. Gill. Membrane introduction tandem mass spectrometry (MIMS-MS/MS) as a real-time monitor for biogenic volatile organic compound (BVOC) emissions from plants. *Can. J. Anal. Sci. Spectrosc.* **53:** 75–81 (2008).
12. D. Lloyd, K.L. Thomas, G. Cowie, J.D. Tammam, and A.G. Williams. Direct interface of chemistry to microbiological systems: Membrane inlet mass spectrometry. *J. Microbiol. Methods* **48:** 289–302 (2002).
13. R.C. Johnson, K. Koch, and R.G. Cooks. On-line monitoring of reactions of epichlorohydrin in water using liquid membrane introduction mass spectrometry. *Ind. Eng. Chem. Res.* **38:** 343–51 (1999).
14. R.F.P. Nogueira, R.M. Alberici, M.A. Mendes, W.F. Jardim, and M.N. Eberlin. Photocatalytic degradation of phenol and trichloroethylene: On-line and real-time monitoring via membrane introduction mass spectrometry. *Ind. Eng. Chem. Res.* **38:** 1754–58 (1999).
15. R.V. Rios, L.L. da Rocha, T.G. Vieira, R.M. Lago, and R. Augusti. On-line monitoring by membrane introduction mass spectrometry of chlorination of organics in water. Mechanistic and kinetic aspects of chloroform formation. *J. Mass Spectrom.* **35:** 618–24 (2000).
16. R. Augusti, M. Turowski, and R.G. Cooks. Membrane introduction mass spectrometry for monitoring complexation equilibria of beta-cyclodextrin with substituted benzenes. *Analyst* **128:** 61–64 (2003).
17. J.H.L. Nelson, E.T. Krogh, C.G. Gill, and D.A. Friesen. Monitoring the TiO2-photocatalyzed destruction of aqueous environmental contaminants at parts-per-trillion levels using membrane-introduction mass spectrometry (MIMS). *J. Environ. Sci. and Health, Part A.* **39:** 2307–17 (2004).
18. M.A. LaPack, J.C. Tou, V.L. McGuffin, and C.G. Enke. The correlation of membrane permselectivity with hildebrand solubility parameters. *J. Membrane Sci.* **86:** 263–80 (1994).
19. F.L. Overney and C.G. Enke. A mathematical study of sample modulation at a membrane inlet mass spectrometer—potential application for the analysis of mixtures. *J. Am. Soc. Mass Spectrom.* **7:** 93–100 (1996).
20. M. Alexander, E. Boscaini, W. Lindinger, and T.D. Mark. Membrane introduction proton-transfer reaction mass spectrometry. *Int. J. Mass Spectrom.* **223-224:** 763–70 (2003).
21. A.A. Sysoev. A mathematical model for kinetic study of analyte permeation from both liquid and gas pahses through hollow fiber membranes into vacuum. *Anal. Chem.* **72:** 4221–29 (2000).
22. A.A. Sysoev, R.A. Ketola, I. Mattila, V. Tarkiainen, and T. Kotiaho. Application of the numerical model describing analyte permeation through hollow fiber membranes into vacuum for determination of permeation parameters of organic compounds in a silicone membrane. *Int. J. Mass Spectrom.* **212:** 205–17 (2001).
23. A. Urtiaga, D. Gorri, and I. Ortiz. Mass-transport modelling in the pervaporation of VOCs from diluted solutions. *AIChE J.* **48:** 572–81 (2002).
24. D.W. Janes, C.J. Durning, D.M. van Pel, M.S. Lynch, C.G. Gill, and E.T. Krogh. Modelling analyte permeation in cylindrical hollow fiber membrane introduction mass spectrometry. *J. Membrane Sci.* **325:** 81–91 (2008).
25. P. Bocchini, R. Pozzi, C. Andalo, and G.C. Galletti. Experimental upgrades of membrane introduction mass spectrometry for water and air analysis. *Anal. Chem.* **73:** 3824–27 (2001).
26. O.S. Viktorova, V.T. Kogan, S.A. Manninen, T. Kotiaho, R.A. Ketola, B.M. Dubenskii, S.P. Parinov, and O.V. Smirnov. Utilization of a multimembrane inlet and a cyclic sudden sampling introduction mode in membrane inlet mass spectrometry. *J. Am. Soc. Mass Spectrom.* **15:** 823–31 (2004).
27. T.M. Allen, M.E. Cisper, P.H. Hemberger, and C.W. Wilkerson, Jr. Simultaneous detection of volatile, semivolatile organic compounds, and organometallic compounds in both air and water matrices by using membrane introduction mass spectrometry. *Int. J. Mass Spectrom.* **212:** 197–204 (2001).
28. T.M. Allen, T.M. Falconer, M.E. Cisper, A.J. Borgerding, and C.W. Wilkerson, Jr. Real-time analysis of methanol in air and water by membrane introduction mass spectrometry. *Anal. Chem.* **73:** 4830–35 (2001).
29. F. Wedian and D.B. Atkinson. Ozone modulation of volatile hydrocarbons using membrane introduction mass spectrometry. *Environ. Sci. Technol.* **36:** 4152–55 (2002).
30. F. Wedian and D.B. Atkinson. Membrane introduction mass spectrometry of nonpolar hydrocarbons using nitric oxide chemical ionization. *Environ. Sci. Technol.* **37:** 4425–28 (2003).
31. T.A. Blake, X. Zheng, T. Aggerholm, F.R. Lauritsen, and R.G. Cooks. Determination of pentachlorophenol by negative ion chemical ionization with membrane introduction mass spectrometry. *Analyst* **127:** 1463–66 (2002).
32. H. Oser, M.J. Coggiola, S.E. Young, D.R. Crosley, V. Hafer, and G. Grist. Membrane introduction/laser photoionization time-of-flight mass spectrometry. *Chemosphere* **67:** 1701–1708 (2007).
33. M. Alexander, E. Boscaini, W. Lindinger, and T.D. Mark. Membrane introduction proton-transfer reaction mass spectrometry. *Int. J. Mass Spectrom.* **223:** 763–70 (2003).
34. E. Boscaini, M.L. Alexander, P. Prazeller, and T.D. Mark. Membrane inlet proton transfer reaction mass spectrometry (mi-ptrms) for direct measurements of vocs in water. *Int. J. Mass Spectrom.* **239:** 171–77 (2004).
35. C.S. Creaser, D.G. Lamarca, J. Brum, C. Werner, A.P. New, and D. Freitas. Reversed-phase membrane inlet mass spectrometry applied to the real-time monitoring of low molecular weight alcohols in chloroform. *Anal. Chem.* **74:** 300–304 (2002).
36. M.L. Stone and L.A. Polson. Chlorocarbon permeabilities of several polymeric membranes determined by membrane introduction mass spectrometry (MIMS). *Sep. Sci. Technol.* **38:** 3215–23 (2003).
37. L.S. Riter, B.C. Laughlin, E. Nikolaev, and R.G. Cooks. Direct analysis of volatile organic compounds in human breath using a miniaturized cylindrical ion trap mass spectrometer with a membrane inlet. *Rapid Commun. Mass Spectrom.* **16:** 2370–73 (2002).
38. L.S. Riter, Y. Peng, R.J. Noll, G.E. Patterson, T. Aggerholm, and R.G. Cooks. Analytical performance of a miniature cylindrical ion trap mass spectrometer. *Anal. Chem.* **74:** 6154–62 (2002).
39. C. Janfelt, H. Frandsen, and F.R. Lauritsen. Characterization of a mini membrane inlet mass spectrometer for on-site detection of contaminants in both aqueous and liquid organic samples. *Rapid Commun. Mass Spectrom.* **20:** 1441–46 (2006).
40. P.D. Tortell. Dissolved gas measurements in oceanic waters made by membrane inlet mass spectrometry. *Limnol. Oceanogr.*

Meth. **3:** 24–37 (2005).
41. R.T. Short, D.P. Fries, M.L. Kerr, and R.H. Byrne. Underwater mass spectrometers for in situ chemical analysis of the hydrosphere. *J. Am. Soc. Mass Spectrom.* **12:** 676–82 (2001).
42. D.P. Fries, R.T. Short, L.L. Langebrake, J.T. Patten, M.L. Kerr, G. Kibelka, D.C. Burwell, and J.C. Jalbert. In-water field analytical technology: Underwater mass spectrometry, mobile robots, and remote intelligence for wide and local area chemical profiling. *Field Anal. Chem. Technol.* **5:** 121–30 (2001).
43. R.J. Bell, R.T. Short, F.H.W. Van Amerom, and R.H. Byrne. Calibration of an in situ membrane inlet mass spectrometer for measurements of dissolved gases and volatile organics in seawater. *Environ. Sci. Technol.* **41:** 8123–28 (2007).
44. M.E. Bier, T. Kotiaho, and R.G. Cooks. Direct insertion membrane probe for selective introduction of organic compounds into a mass spectrometer. *Anal. Chim. Acta* **231:** 175–90 (1990).
45. M.A. LaPack, J.C. Tou, and C.G. Enke. Membrane mass spectrometry for the direct trace analysis of volatile organic compounds in air and water. *Anal. Chem.* **62:** 1265–71 (1990).
46. P.S.H. Wong and R.G. Cooks. Trace level analysis of volatile and semi-volatile organic compounds in water using a membrane/jet separator interfaced to an ion trap mass spectrometer. *Anal. Chim. Acta* **310:** 387–98 (1995).
47. C.S. Creaser and D.J. Weston. In-membrane preconcentration/membrane inlet mass spectrometry of volatile and semivolatile organic compounds. *Anal. Chem.* **72:** 2730–36 (2000).
48. F.R. Lauritsen, M.A. Mendes, and T. Aggerholm. Direct detection of large fat-soluble biomolecules in solution using membrane inlet mass spectrometry and desorption chemical ionization. *Analyst* **125:** 211–15 (2000).
49. T. Aggerholm and F.R. Lauritsen. Direct detection of polyaromatic hydrocarbons, estrogenic compounds and pesticides in water using desorption chemical ionisation membrane inlet mass spectrometry. *Rapid Commun. Mass Spectrom.* **15:** 1826–31 (2001).
50. R. Haddad, M.A. Mendes, N.F. Hoehr, and M.N. Eberlin. Amino acid quantitation in aqueous matrices via trap and release membrane introduction mass spectrometry: Homocysteine in human plasma. *Analyst* **126:** 1212–15 (2001).
51. L.S. Riter, L. Charles, M. Turowski, and R.G. Cooks. External interface for trap-and-release membrane introduction mass spectrometry applied to the detection of inorganic chloramines and chlorobenzenes in water. *Rapid Commun. Mass Spectrom.* **15:** 2290–95 (2001).
52. A.P. Vellasco, R. Haddad, M.N. Eberlin, and N.F. Hoehr. Combined cysteine and homocysteine quantitation in plasma by trap and release membrane introduction mass spectrometry. *Analyst.* **127:** 1050–53 (2002).
53. A. Nayar, R. Liu, R.J. Allen, M.J. McCall, R.R. Willis, and E.S. Smotkin. Laser-activated membrane introduction mass spectrometry for high-throughput evaluation of bulk heterogeneous catalysts. *Anal. Chem.* **74:** 1933–38 (2002).
54. A.J. Thompson, A.S. Creba, R.M. Ferguson, E.T. Krogh, and C.G. Gill. A coaxially heated membrane introduction mass spectrometry (MIMS) interface for the rapid and sensitive on-line measurement of volatile and semi-volatile organic contaminants in air and water at parts-per trillion levels. *Rapid Commun. Mass Spectrom.* **20:** 2000–2008 (2006).
55. R.M. Alberici, R. Sparrapan, W.F. Jardim, and M.N. Eberlin. Selective trace level analysis of phenolic compounds in water by flow injection analysis - membrane introduction mass spectrometry. *Environ. Sci. Technol.* **35:** 2084–88 (2001).
56. A.S. Creba, A.N.E. Weisfloch, E.T. Krogh, and C.G. Gill. An enzyme derivatized polydimethylsiloxane (PDMS) membrane for use in membrane introduction mass spectrometry (MIMS). *J. Am. Soc. Mass Spectrom.* **18:** 973–79 (2007).
57. R. Clinton, C.S. Creaser, and D. Bryant. Real-time monitoring of a pharmaceutical process reaction using a membrane interface combined with atmospheric pressure chemical ionization mass spectrometry. *Anal. Chim. Acta.* **539:** 133–40 (2005).
58. E. VanHassel and M.E. Bier. An electrospray membrane probe for the analysis of volatile and semi-volatile organic compounds in water. *Rapid Commun. Mass Spectrom.* **21:** 413–20 (2007).
59. E. Davoli, O. Rossi and R. Fanelli. Stable isotope permeation tubes for GC-MS analysis of VOC in air. *J. High Res. Chrom.* **16:** 626–28 (1993).
60. E. Davoli, M. Cappellini, M. Moggi, and R. Fanelli. Automated high-speed analysis of selected organic compounds in urban air by on-line isotopic dilution cryofocussing gas chromatography/mass spectrometry. *J. Am. Soc. Mass Spectrom.* **5:** 1001–1007 (1994).
61. R.M. Ferguson, A.S. Creba, A.J. Thompson, D. Kim, C.D. Simpson, C.W. LeBlanc, E.T. Krogh, and C.G. Gill. Membrane introduction tandem mass spectrometry (MIMS-MS/MS) as a direct, real-time monitor for trace atmospheric contaminants. Pacifichem 2005 Conference Proceedings. Honolulu, HI. (2005).
62. C.D. Simpson, R.L. Dills, M. Paulsen, L.J.S. Liu, and D.A. Kalman. Determination of methoxyphenols in ambient atmospheric particulate matter: tracers for wood combustion. *Environ. Sci Technol.* **39:** 631–37 (2005).
63. N. Re-Poppi and M.R. Santiago-Silva. Identification of polycyclic aromatic hydrocarbons and methoxylated phenols in wood smoke emitted during production of charcoal. *Chromatographia.* **55:** 475–81 (2002).
64. R. Flamini, A.D. Vedova, D. Cancian, A. Panighel, and M. De Rosso. GC/MS -positive ion chemical ionization and MS/MS study of volatile benzene compounds in five different woods used in barrel making. *J. Mass Spectrom.* **42:** 641–46 (2007).
65. A. Demirbas. The influence of temperature on the yields of compounds existing in bio-oils obtained from biomass samples via pyrolysis. *Fuel Process. Technol.* **88:** 591–97 (2007).
66. C. Schmidl, L.L. Marr, A. Caseiro, P. Kotianova, A. Berner, H. Bauer, A. Kasper-Giebl, and H. Puxbaum. Chemical characterisation of fine particle emissions from wood stove combustion of common woods growing in mid-european alpine regions. *Atmospheric Environ.* **42:** 126–41 (2008).
67. T.B. Jordan, A.J. Seen, and G.E. Jacobsen. Levoglucosan as an atmospheric tracer for woodsmoke. *Atmospheric Environ.* **40:** 5316–21 (2006).
68. L.P. Naeher, M. Brauer, M. Lipsett, J.T. Zelikoff, C.D. Simpson, J.Q. Koenig, and K.R. Smith. Woodsmoke health effects: A review. *Inhalation Toxicol.* **19:** 67–106 (2007).
69. L. Riter, Z. Takats, L. Charles, and R.G. Cooks. High surface area membrane introduction mass spectrometry for analysis of volatile and semi-volatile organic compounds in air. *Rapid Commun. Mass Spectrom.* **15:** 1520–24 (2001).
70. L.S. Riter, Z. Takats, and R.G. Cooks. Single-sided membrane introduction mass spectrometry for on-line determination of semi-volatile organic compounds in air. *Analyst.* **126:** 1980–84 (2001).
71. M.A. Mendes and M.N. Eberlin. Trace level analysis of VOCs and semi-VOCs in aqueous solution using a direct insertion membrane probe and trap and release membrane introduction mass spectrometry. *Analyst.* **125:** 21–24 (2000).
72. J.J. Rook. Formation of haloforms during chlorination of natural waters. *Water Treat. Exam.* **23:** 234–43 (1974).
73. S.W. Krasner, H.S. Weinberg, S.D. Richardson, S.J. Pastor, R. Chinn, and M.J. Sclimenti. The occurrence of a new generation of disinfection byproducts. *Env. Sci. Technol.* **40:** 7175–85 (2006).
74. E.T. Krogh and C.G. Gill, U.S. Patent. US-2007-0181799-A1 (2007).
75. L.S. de Bruin, P.D. Josephy, and J.B. Pawliszyn. Solid phase microextraction of monocyclic aromatic amines from biological fluids. *Anal. Chem.* **70:** 1986–92 (1998).
76. C.L. Arthur, L.M. Kilam, S. Motlagh, M. Lim, D.W. Potter, and J.B. Pawliszyn. Analysis of substituted benzene compounds in groundwater using solid phase microextraction. *Environ. Sci. Technol.* **26:** 979–83 (1992).
77. R.P. Schwarzenbach, P.M. Gschwend, and D.M. Imboden. *Environmental Organic Chemistry*, 2nd ed., John Wiley & Sons, Hoboken, NJ, Appendix C.

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