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## Membrane introduction mass spectrometry

# Simultaneous detection of volatile, semivolatile organic compounds, and organometallic compounds in both air and water matrices by using membrane introduction mass spectrometry

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### Abstract

We present results for the simultaneous detection of volatile organic compounds, semivolatile organic compounds, and organometallic compounds in air and water by using membrane introduction ion trap mass spectrometry. In these experiments, a membrane composed of a microporous polypropylene hollow support fiber coated with an ultrathin ( $\sim 0.5 \mu\text{m}$ ) polydimethylsiloxane layer serves as the interface between the sample and the vacuum of the mass spectrometer. Simultaneous detection of benzene, naphthalene, and ferrocene in aqueous solution is achieved by proton transfer chemical ionization using  $\text{H}_3\text{O}^+$  from membrane-diffused water. With the same membrane, we also demonstrate the simultaneous detection of methyl ethyl ketone, toluene, 1-methylnaphthalene, and ferrocene in air with chemical ionization employing membrane-diffused oxygen from air as the reagent gas. (Int J Mass Spectrom 212 (2001) 197–204) © 2001 Elsevier Science B.V.

**Keywords:** Membrane introduction mass spectrometry; MIMS; Simultaneous detection; Chemical ionization

### 1. Introduction

Improved characterization of complex mixtures continues to be a goal of environmental, pharmaceu-

tical, and biochemists. In the analysis of environmental samples, characterization often pertains to the ability to differentiate multiple components in a single chemical class [1–5]. Volatile and semivolatile organic compounds (VOCs and SVOCs) are often analyzed in the laboratory by using separate time-consuming extraction and preconcentration procedures, followed by analysis with gas chromatography/

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Dedicated to R. Graham Cooks on the occasion of his sixtieth birthday.

mass spectrometry (GC/MS) [2,3,6,7]. GC/MS is limited in that different columns are necessary to optimally analyze various classes of compounds (i.e. VOCs and SVOCs). Metal-containing compounds are frequently analyzed by ICP/MS, AAS, [8,9] or voltammetric methods [10]. A large fraction of mixed waste located at the U.S. Department of Energy's sites contains a wide variety of VOCs, SVOCs, heavy metals, radionuclides, and water, thus requiring the analysis of samples containing multiple components in multiple chemical classes [11]. The development of a single analytical method to simultaneously identify and quantify several classes (i.e. VOCs, SVOCs, and metals) of environmental pollutants in air, water, and/or soil samples in a continuous, real-time manner is appealing for the characterization and analysis of mixed wastes.

Current trends and applications of membrane introduction mass spectrometry (MIMS) were recently reviewed by Cooks et al. [12]. MIMS has been successfully applied in many areas of VOC and SVOC analysis and appears promising for characterizing complex, environmental samples.

We have developed MIMS for the analysis of several environmentally significant VOCs, SVOCs, and organometallic compounds in air and water using a polymeric silicone or an ultrathin polydimethylsiloxane membrane [13–18]. In a continuation of our effort to develop MIMS as a viable screening method for near real-time, on-line monitoring of a broad range of organic compounds (VOCs and SVOCs) and heavy metal contaminants in a variety of matrices and effluents, we now demonstrate the simultaneous detection of VOCs, SVOCs, and organometallic compounds by MIMS in both air and water samples. To our knowledge, this is the first time this has been accomplished.

## 2. Experimental

Caution: Many of the analytes and chemicals used in these experiments are known or suspect health hazards. Care should be exercised to minimize exposure during handling and use.

### 2.1 Apparatus and instrumentation

The membrane/jet separator assembly has been described in detail in previous work [14]. A composite hollow fiber membrane manufactured by NeoMecs Inc. (Eden Prairie, MN,) was used in the simultaneous detection experiments described here, and consists of a polypropylene microporous support fiber (240  $\mu\text{m}$  i.d.  $\times$  300  $\mu\text{m}$  o.d.) coated with an ultrathin ( $\sim$ 0.5  $\mu\text{m}$ ) highly crosslinked plasma polymerized polydimethylsiloxane (PDMS) layer [19]. Using epoxy (Varian Torr Seal<sup>TM</sup>), two parallel strands ( $\sim$ 10 cm each) of the membrane fiber were sealed within two Swagelok<sup>TM</sup> tees joined by a 5 cm piece of 1/4 in. o.d. Silcosteel tubing. Experimentally, we have found that two strands of the fiber provide an acceptable compromise between analyte signal and excessive matrix pervaporation. Excess water and air affect the tuning and the sensitivity of the ion trap mass spectrometer. Ultrapure helium, regulated by a variable leak valve (Granville-Phillips, Model 203, Boulder, CO), flows through the interior of the fibers and serves as both the sample transport gas and the ion trap buffer gas. Sample air or water flowing through the membrane assembly passes over the exterior of the fibers countercurrent to the helium flow [20]. Silcosteel tubing enclosing the membrane fibers is heated to 100  $^{\circ}\text{C}$ . The heated (100  $^{\circ}\text{C}$ ) metal jet separator is used for sample enrichment following membrane introduction [21].

Analytes of interest are detected by using chemical ionization (CI) from membrane-diffused oxygen and water, depending on the sample matrix, in a modified Finnigan Model 800 Ion Trap Detector (San Jose, CA). Previous work showed that chemical ionization leads to a more intense signal over electron ionization for a variety of sample types [13,16,18]. The CI ion yield ranges from 2 to 800 times better than electron ionization (EI) yield with single digit improvement for the majority of analytes. A supplemental waveform (nominally 530 kHz, 6 V peak-to-peak from a Hewlett-Packard 3312A function generator) was applied to one endcap electrode to implement resonant ejection. Ion trap manifold pressure was measured at  $2.6 \times 10^{-5}$  Torr.

During air or water sampling, membrane-diffused oxygen or water serves as a reagent gas for chemical ionization of the analytes. Two different mechanisms are responsible. Chemical ionization with  $O_2^+$  leads to an electron abstraction reaction that results in a charged molecular ion ( $[M]^+$ ), as opposed to a proton reaction leading to a protonated molecule ( $[M + H]^+$ ), as is the case for chemical ionization with  $H_3O^+$ . Oxygen, as an ionized species ( $O_2^+$ ), is a predominating species in the ion trap experiments with air samples, whereas water, in the form of  $H_3O^+$ , predominates in the ion trap experiments with water samples.

CI often yields more intense molecular ions than EI [18]. Both ionization modes lead to the formation of odd-electron molecular ions, but the internal energy deposited to the molecule is dependent on the mode of ionization. More energy is transferred to the analyte in the EI process, leading to more fragmentation of the analyte, than by chemical ionization with  $O_2^+$  or  $H_3O^+$ . Other reagent gases could be used but the availability of membrane-diffused water or oxygen as the chemical reagent ion serves to simplify the MIMS experiments. When mixtures of compounds are analyzed, quantification may be more easily accomplished with chemical ionization where only the

molecular and/or protonated ion is detected or fewer ions resulting from fragmentation are observed.

## 2.2. Sample preparation

The air sample mixture was prepared using a VICI Metronics Dynacalibrator (Model 340-24-Y, Santa Clara, CA). Room air, which was passed through an internal charcoal filter, was used to supply the Dynacalibrator. “Blank” air from the Dynacalibrator was used for establishing the background signal before and after the sampling period. Analyte concentrations in air were calculated based on chamber temperature (90 °C), dilution flow rate (200 mL/min) through the permeation chamber, and diffusion vial capillary length and opening. The transfer line from the Dynacalibrator to the membrane assembly was maintained at 100 °C to minimize the adherence of analytes (e.g. SVOCs and organometallics) to the metal surfaces of the tubing and fittings (see sec. 3). Air flow over the membrane matched the flow of the Dynacalibrator by means of a small diaphragm pump at the sample outlet of the membrane assembly. Separate diffusion vials contained methyl ethyl ketone (Aldrich), toluene (Aldrich), 1-methylnaphthalene (Aldrich), and ferrocene (provided by J.D. Williams at Purdue University).

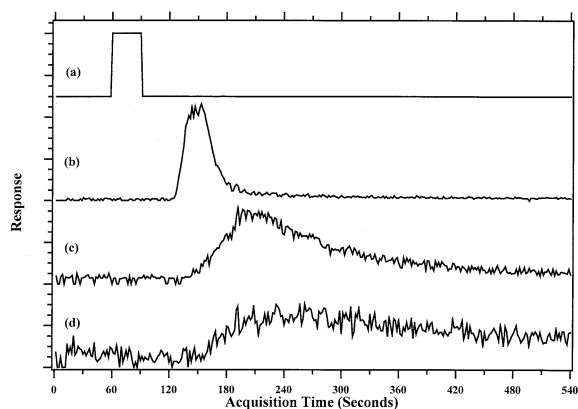


Fig. 1. (a) 30 s time period of membrane exposure to the aqueous mixture. Simultaneous detection of a single aqueous sample containing (b) 870 ppb benzene, VOC; (c) 150 ppb naphthalene ( $\times 2.5$ ), SVOC; and (d) 180 ppb ferrocene ( $\times 4$ ), organometallic using membrane introduction mass spectrometry.

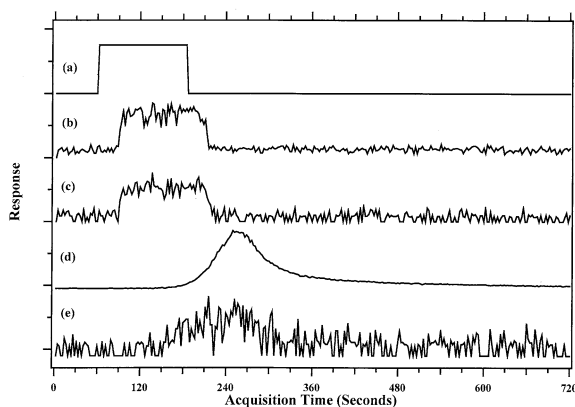


Fig. 2. (a) 2 min time period of membrane exposure to the air sample. Simultaneous detection of a single air sample containing (b) 660 ppb methyl ethyl ketone ( $\times 10$ ), VOC; (c) 7 ppb toluene ( $\times 25$ ), VOC; (d) 316 ppb 1-methylnaphthalene, SVOC; and (e) 700 ppb ferrocene ( $\times 60$ ), organometallic using membrane introduction mass spectrometry.

Table 1  
Individual compounds detected by MIMS in our laboratory<sup>a</sup>

	Compound detected by MIMS <sup>b</sup>	CAS no.	Air, water, or both	b.p. (°C)	Vapor pressure (Torr) <sup>c</sup>	Lowest concentration analyzed <sup>d</sup>	Nominal molecular weight	
VOCs	Acetaldehyde	75-07-0	A	21	750		44	
	Acetone	67-64-1	B	56	180	900 ppbv ( <i>a</i> )	58	
	Benzene	71-43-2	B	80	75	3 ppbv ( <i>a</i> )	78	
	Carbon tetrachloride	56-23-5	B	77	91.3	8 ppbv ( <i>a</i> )	154	
	Chlorobenzene	108-90-7	A	132	8.8	36 ppbv ( <i>a</i> )	113	
	Hydroxy acetone (2-propanone)	116-09-6	A	131	10 (39.7 °C)		74	
	1-Hydroxy-2-butanone <sup>e</sup>	5077-67-8	A	164	1 (25.5 °C)		88	
	Isopropyl alcohol	67-63-0	B	82	40	132 ppbv ( <i>a</i> )	60	
	Methyl alcohol	67-56-1	B	65	97.3	5 ppmw ( <i>w</i> )	32	
	Methylene chloride	75-09-2	B	40	400		85	
	Methyl ethyl ketone	78-93-3	B	80	100	7 ppbv ( <i>a</i> )	72	
	Methyl isobutyl ketone	108-10-1	A	117	16	23 ppbv ( <i>a</i> )	100	
	3-Pentanone	96-22-0	A	102	27		86	
	Propanal (propionaldehyde)	123-38-6	A	49	300	1.8 ppmv ( <i>a</i> )	58	
	Toluene	108-88-3	B	111	22	20 pptrv ( <i>a</i> )	92	
	Trichloroethane	71-55-6	A	74	100	7 ppbv ( <i>a</i> )	133	
	Trichloroethylene	79-01-6	B	87	61	50 pptrv ( <i>w</i> )	131	
	SVOCs	Acenaphthene	83-32-9	A	283	10 (131 °C)	1.3 ppmv ( <i>a</i> )	154
		Acetophenone	98-86-2	A	203	1 (15 °C)		120
Aniline		62-53-3	B	184	0.6	13 ppbv ( <i>a</i> )	93	
2-chlorophenol		95-57-8	B	175	1 (12.1 °C)	10 ppbv ( <i>a</i> )	129	
3-chlorophenol		108-43-0	A	214	1 (44.2 °C)	43 ppbv ( <i>a</i> )	129	
4-chlorophenol		106-48-9	A	217	1 (49.8 °C)	109 ppbv ( <i>a</i> )	129	
Cyclohexanol		108-93-0	W	161	1 (21 °C)	19 ppbv ( <i>a</i> )	100	
Cyclohexanone		108-94-1	W	156	2		98	
1,3-Dichlorobenzene		541-73-1	A	173	1.9 (25 °C)	24 ppbv ( <i>a</i> )	151	
1,4-Dichlorobenzene		106-46-7	A	174	0.6	574 ppbv ( <i>a</i> )	147	
2,4-dichlorophenol		120-83-2	A	210	1 (53 °C)	117 ppbv ( <i>a</i> )	163	
2-(diethylamino) ethanol		100-37-8	A	162	1		117	
Diethyl malonate <sup>e</sup>		105-53-3	A	199	1 (40 °C)		160	
Diisopropyl aminoethanol <sup>e</sup>		96-80-0	W	187	0.1	35 ppbv ( <i>a</i> )	145	
Dimethyl methyl-phosphonate <sup>e</sup>		756-79-6	A	181	<0.1 (10 °C)	430 ppbv ( <i>a</i> )	124	
2,4-Dimethylphenol		105-67-9	A	210	1 (51.8 °C)	31 ppbv ( <i>a</i> )	125	
Dimethyl sulfoxide		67-68-5	A	189	0.4	140 ppbv ( <i>a</i> )	78	
4-Hydroxy-4-methyl-2- pentanone		123-42-2	A	164	1.1		116	
Malathion		127-75-5	A	157	0.7 (157 °C)	82 pptrv ( <i>a</i> )	330	
Methyl salicylate		119-36-8	A	223	1 (54 °C)	3 ppbv ( <i>a</i> )	152	
1-Methyl-naphthalene		90-12-0	B	245	0.1 <sup>g</sup>	316 ppbv ( <i>a</i> )	142	
Naphthalene		91-20-3	B	218	0.5	16 ppbv ( <i>a</i> )	128	
Nitrobenzene		98-95-3	A	211	0.3	900 pptrv ( <i>a</i> )	123	
Phenol		108-95-2	A	40	0.4 (25 °C)	78 ppbv ( <i>a</i> )	94	
Pyruvic acid <sup>e</sup>		127-17-3	A	165 <sup>f</sup>	1 (21.4 °C)		88	
1,2,4-trichlorobenzene		120-82-1	A	214	1 (38.4 °C)		181	

(continued on next page)

Table 1 (continued)

	Compound detected by MIMS <sup>b</sup>	CAS no.	Air, water, or both	b.p. (°C)	Vapor pressure (Torr) <sup>c</sup>	Lowest concentration analyzed <sup>d</sup>	Nominal molecular weight
Organometals <sup>e</sup>	Ferrocene	102-54-5	B	249	2.6 (100 °C)	180 ppbw (w)	186
	Molybdenum hexacarbonyl	13939-06-5	A	156	0.1 (25 °C)		266
	Lead acetylacetonate	15282-88-9	A	NA <sup>g</sup>	NA		405
	Nickel acetylacetonate	3264-82-2	B	220 <sup>f</sup>	11 (220 °C)		257
	Triphenyl tin chloride	639-58-7	B	464	<1		385

<sup>a</sup>Chemical abstract service registry numbers (CAS no.), boiling points (b.p.), vapor pressure data, and molecular weights were acquired from Material Safety Data Sheets (MSDS).

<sup>b</sup>Compounds were analyzed using the two membrane configurations described. Although VOCs were primarily analyzed using the hollow fiber silicone membrane (see Sec. 3), they were also often analyzed with the ultrathin PDMS membrane assembly. SVOCs and Organometals were analyzed using the ultrathin PDMS membrane configuration.

<sup>c</sup>Vapor pressure data at sea level is reported at 20 °C, unless indicated otherwise.

<sup>d</sup>If available, the lowest concentration analyzed in our laboratory is shown. The lowest concentration analyzed is a function of methodology (i.e. the Dynacalibrator technology used to make the air samples) and does not indicate the instrument detection limit. Sample matrix is indicated by *a* (air) or *w* (water).

<sup>e</sup>Not listed as a hazardous compound in the chemical index at the Envirofacts Master Chemical Integrator website: [http://www.epa.gov/enviro/html/emci/emci\\_query.html](http://www.epa.gov/enviro/html/emci/emci_query.html)

<sup>f</sup>Decomposition temperature.

<sup>g</sup>NA: not available on MSDS form.

Excess sample flow from the Dynacalibrator and sample effluent was vented through charcoal filters.

The aqueous mixture sample was prepared from stock solutions of benzene (Aldrich), naphthalene (Aldrich), ferrocene (Aldrich), and HPLC grade water (Fisher). Samples were passed over the membrane at a flow rate of 16 mL/min using a peristaltic pump (Model 7524-10, Cole-Parmer Instrument Co., Niles, IL). HPLC grade water was used for establishing the background signal before and after each sampling period.

### 3. Results and discussion

In the present experiments, we investigated the capability of MIMS by using an ultrathin PDMS membrane for simultaneously detecting multiple analytes with known concentrations contained in aqueous and air samples. Each sample had at least one analyte from each of three chemical classes: VOC, SVOC, and organometallic. Simultaneous detection refers to the ability to qualitatively and quantitatively determine the presence of multiple chemical classes of analytes within a single experimental run. Each mem-

brane-diffused analyte was monitored continuously throughout an experiment by tracking the molecular ion,  $[M]^+$  for air samples, or the protonated molecular ion,  $[M + H]^+$  for water samples, produced during the ionization process.

Fig. 1 shows the simultaneous detection of (b) benzene (VOC), (c) naphthalene (SVOC), and (d) ferrocene (organometallic compound) in aqueous solution, and was obtained with chemical ionization by using  $H_3O^+$  as the reagent ion from membrane-diffused water. The membrane was exposed to an aqueous sample containing the mixture of analytes for a period of 30 s (starting at 60 s), shown as the plot in Fig. 1(a). This was sufficient to detect 870 ppb benzene, 150 ppb naphthalene, and 180 ppb ferrocene in water, as is illustrated by the response profiles (i.e. ion signals) obtained. The molecular and protonated molecular ion signals are summed in Fig. 1. The benzene signal shows a sharp rise beginning at 125 s followed by a sharp decrease from 155 to 180 s. The response time lag of more volatile compounds like benzene is expected to be about 60 s, and represents the minimum time necessary for highly volatile analytes to travel through the transfer lines from the

sample container to the membrane assembly, and finally to the ion trap mass spectrometer. Naphthalene ( $\times 2.5$ ) and ferrocene ( $\times 4$ ), on the other hand, show more gradual increases and decreases in ion signals, indicative of the longer diffusion times required for the less volatile compounds (than benzene) to pass through the membrane into the sample transport gas (i.e. helium). Permeation of the analyte through the membrane is governed directly by the diffusivity and solubility constants with diffusion being the rate-limiting step for species with similar solubility [12].

The same membrane assembly used for the aqueous mixture (Fig. 1) is also suitable for the detection of a mixture of two VOCs, one SVOC, and one organometallic compound in air (Fig. 2). Fig. 2 illustrates the simultaneous detection of (b) 660 ppb methyl ethyl ketone (VOC), (c) 7 ppb toluene (VOC), (d) 316 ppb 1-methylnaphthalene (SVOC), and (e) 700 ppb ferrocene (organometallic) in air, and was obtained with chemical ionization by using  $O_2^+$  as the reagent ion from membrane-diffused air. The 2 min sampling period begins at 60 s [Fig. 2(a)]. The response profile of the more volatile compounds, such as methyl ethyl ketone (MEK) and toluene, matches the sampling time period of 2 min. A time lag of about 30 s, corresponding to the time necessary for highly volatile analytes to travel through the transfer lines from the Dynacalibrator, the membrane assembly, and finally into the ion trap mass spectrometer, is observed for MEK and toluene. Analyte adsorption onto the surfaces of the transfer lines, membrane assembly, and jet separator is possible but was minimized by short, straight transfer lines and elevated temperatures of those surfaces (100 °C). The vapor pressure of 1-methylnaphthalene (MNAP) at 100 °C is 11.8 Torr and surface adsorption on transfer lines, the membrane assembly, or the jet separator should not present a problem. The response profiles of MEK ( $\times 10$ ) and toluene ( $\times 25$ ) show very sharp increases in the molecular ion signals ( $m/z$  72 and 92, respectively) followed by sharp decreases. Slower compound diffusivity is observed for the less volatile compounds of MNAP and ferrocene. The response time lag of the membrane to MNAP is 70 s after sample release from the Dynacalibrator. The total response profile of

MNAP ( $m/z$  142), illustrated in Fig. 2(d) by the gradual decrease in the molecular ion signal, extends beyond the 2 min sample exposure time by greater than one minute. The response profile of ferrocene ( $\times 60$ ,  $m/z$  186) in Fig. 2(e) shows a weaker response than MEK, toluene, and MNAP. The ferrocene response time lag is approximately 60 s.

Although the technique could be optimized in terms of sensitivity or limits of detection for any single analyte in a mixture, we are interested in MIMS as a broad-spectrum screening tool. Hence, our studies have used experimental conditions we believe provide the best possible performance for simultaneous detection. A limitation to the simultaneous detection method is that the sensitivity of MIMS to each compound is different. For example, the sensitivity of MIMS to individual compounds can be dependent on a number of factors including the volatility of the compound, the solubility and diffusivity of the compound through the membrane, the temperature of the transfer lines, membrane assembly, and jet separator, the sampling period and flow rate, the ionization mechanism, and finally, chemistry in the ion trap mass spectrometer. Having said all this, a few of the advantages of MIMS are speed, no sample preparation, and the analysis of multiple matrices with minimal instrumental modifications.

Assuming that the observed analyte response (i.e. ion signal) is in the linear portion of the calibration curve for each compound, the MIMS method, as expected, is most sensitive to the volatile organic compounds and least sensitive to the low volatility organometallic compound. Based on a signal-to-noise ratio of three, detection limits for the aqueous analytes (Fig. 1) can be estimated at  $\sim 41$  ppb for benzene,  $\sim 29$  ppb for naphthalene, and  $\sim 98$  ppb for ferrocene. Detection limits for the analytes in air (Fig. 2) can be estimated at  $\sim 311$  ppb for MEK,  $\sim 4$  ppb toluene,  $\sim 74$  ppb for 1-methylnaphthalene, and  $\sim 537$  ppb for ferrocene.

The detection of ferrocene in water with MIMS is considerably more sensitive than that of ferrocene in air. The total mass flow over the membrane is calculated as 1.44 and 417.2  $\mu\text{g}$  ferrocene in water and air, respectively. The lower sensitivity of the air sample

may have resulted from sample loss on the transfer line or jet separator surfaces, characteristics of the different ionization mechanisms ( $\text{H}_3\text{O}^+$  versus  $\text{O}_2^+$ ), sampling at a higher flow rate, and/or oxidation reactions during the ionization process.

The versatility of hollow fiber silicone membranes in the MIMS technique is demonstrated by the ability to detect several classes of compounds such as volatile, semivolatile, and organometallic compounds [12]. To date, we have used MIMS to detect 43 individual volatile and semivolatile organic compounds (see Table 1 for a list of the compounds detected in our laboratory) without preconcentration, primarily from an air matrix by using two experimental configurations. The two setups differ in the choice of membrane material used and in ionization method. In our early experimental MIMS work [15,18], a thicker hollow fiber silicone membrane (0.020 in. i.d.  $\times$  0.037 in. o.d.) was used for analyzing the VOCs. The sample flowed coaxially over the outside of the membrane and countercurrent to the helium flow. Of the two membrane types used—the single-stranded silicone or the ultrathin PDMS (in a multiple fiber configuration)—the ultrathin membrane provides a faster response, and reduces the effect of slow compound diffusivity [16]. SVOCs and organometallic compounds, as well as several of the VOCs, were analyzed using the ultrathin PDMS membrane configuration. Other groups have demonstrated the ability to detect multiple compounds in a single chemical class with MIMS [22–26].

The 43 volatile and semivolatile analytes range in boiling point from 21 to 283 °C and include chlorinated and oxygenated solvents, chlorophenols, polycyclic aromatic hydrocarbons, and substituted benzenes. Many of the compounds listed in Table 1 have been identified as hazardous environmental contaminants by one or more regulatory agencies [27].

#### 4. Conclusion

The data presented in Figs. 1 and 2 demonstrate that multiple classes (VOC, SVOC, and organometallic) of compounds in either an aqueous or air sample

can be detected simultaneously. The simultaneous diffusion of volatile, semivolatile, and organometallic compounds through the ultrathin polydimethylsiloxane membrane in MIMS is one of the method's strengths in that all of the analytical information is obtained in a relatively short time—on the order of seconds to minutes. Although the semipermeable membrane permits the influx of air or water matrix into the ion trap mass spectrometer, the method takes advantage of the presence of those components. No additional gases are needed for chemical ionization.

The relatively low vapor pressure of organometallic compounds, combined with differences in solubility and diffusivity in the membrane between organometallic compounds and VOCs and SVOCs, make the detection and analysis of organometallic compounds in air and water a challenging problem. Alternative membranes (other than polydimethylsiloxane) [14], which selectively bind and release analytes, may be more suitable for improving the sensitivity and selectivity of MIMS to VOCs, SVOCs, and organometallic compounds. Further development and application of the MIMS technique to the problem of real-time, on-line simultaneous monitoring of VOCs, SVOCs, and heavy metal compounds in the environment could lead to substantial savings in time and costs.

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