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Membrane inlet proton transfer reaction mass spectrometry (MI-PTRMS) for direct measurements of VOCs in water

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Abstract

The use of a membrane inlet proton transfer reaction mass spectrometry (MI-PTRMS) system was investigated for the quantitative analysis of VOCs directly from water. Compounds playing an important role in environmental, biological and health issues such as methanol, acetonitrile, acetone, dimethylsulfide (DMS), isoprene, benzene, and toluene have been analyzed both in fresh and salty water. The system shows very good sensitivity, reproducibility, and a linear response of up to five orders of magnitude. The detection limit for DMS is about 100 ppt and for methanol is about 10 ppb both in fresh and salty water. The response time of the various compounds across the membrane is on the order of a few minutes. This fast response and the fact that the PTRMS can perform absolute measurements without the necessity of calibration make the system suitable for on-line and -site measurements of VOCs directly from water.

Keywords: VOCs; MI-PTRMS; Water; Quantitative analysis

1. Introduction

The analyses of trace contents of volatile organic compounds (VOCs) in water, from anthropogenic or biogenic sources, are important environmental, biological, and health issues. Monitoring of such compounds gives a measure of marine, lake, and river water quality [1] of drinking water quality or of contamination of ground water.

Of all the VOCs present in seawater, dimethylsulfide (DMS) is the most abundant form of volatile sulfur and it is present in the oceans at concentrations up to 300 nM corresponding to 25 ppb in water (with average concentration of 1–10 nM) as a product of the enzymatic cleavage of dimethylsulfoniopropionate. Due to its emission into the atmosphere, DMS is well recognized as the main natural source of reduced sulfur in the global troposphere [2]. Benzene, toluene, isoprene, acetonitrile, acetone, and methanol are other VOCs that play a central role in the chemistry of the atmosphere, and they may be present in seawater (oceanic uptake) or as contaminant in ground water. These compounds are produced from car exhaust (benzene, toluene) [3] from biomass burning (acetonitrile, acetone, and methanol) [4], or via vegetation emission (isoprene) [5]. Methanol either exists naturally in volcanic gases, from vegetation, microbes, and insects, or is produced by industrial or biological processes such as decomposition of waste, sewage, and sludge [6]. Since all these compounds can lead to potentially harmful human health effects, and influence the chemistry of the atmosphere, it is quite important to monitor them not only in the air but also in water.

These VOCs are usually present at low concentration (ppb_w levels) in natural reservoirs of fresh water and seawater, and may thus require a preconcentration step before identification and quantification by conventional techniques, such as gas chromatography/mass spectrometry. Common methods of preconcentration include static or dynamic headspace techniques or liquid–liquid extraction [1]. Although preconcentration can extend absolute and relative detection limits,

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it requires extended analysis time and carries the risk of contamination or artifacts. An alternative technique, which does not require preconcentration, is membrane introduction mass spectrometry (MIMS). This is a technique by which sample components are introduced directly into the mass spectrometer by means of a membrane [7,8]. In the late 1970s the work of Westover et al. indicated that silicone–rubber membranes are very attractive for monitoring organic compounds in water because the membrane is impermeable to water [9] but permeable to VOCs. Compared with other sampling and concentration techniques, MIMS shows great potential for on-line, on-site, and continuous monitoring of drinking water resources, wastewater outlets, analysis of dissolved gases in rivers, lakes, oceans (ocean uptake of chemical species) [1]. MIMS has already been widely and successfully employed for trace gas analysis in water, coupled with different mass analyzer such as quadrupole, ion trap and time-of-flight (TOF) mass spectrometers, and recent reviews of the technique summarize most of the corresponding results [10,11]. Recently MIMS has been combined with a proton transfer reaction-mass spectrometer (PTRMS) [12] and the resulting MI-PTRMS system turned out to be a useful tool for the characterization of membrane materials [13] and for measurements of high moisturized gases/vapors [12].

PTR-MS is a sensitive method for on-line measurements of trace gases, and has so far been applied to various fields ranging from atmospheric chemistry, to food flavor and medical diagnostics [14]. The details of the PTRMS instrument are described elsewhere [15–17]. Briefly, the method is based on the reactions of H_3O^+ ions, which perform non-dissociative proton transfer to most of the common volatile organic compounds (VOCs), but do not react with any of the major components present in clean air (i.e., O_2, N_2). The generation of the primary H_3O^+ ion and the chemical ionization of the VOCs are individually controlled and temporally separated processes. Thus, online measurements with detection limits as low as 10 ppt_v are possible. Another important advantage is that absolute concentrations can be calculated without calibration or use of standards. This characteristic could make the PTRMS attractive for analysis of trace compounds in water. The PTRMS is an instrument designed for gas analysis and with the existing set-up it is not suitable for direct liquid sample analysis. Measurements of VOCs in water can be made only indirectly by measuring the headspace over the sample solution with a dynamic method and then calculating the concentration in the liquid using the air/water partition coefficients [18]. This method was used to measure methanol, acetone, and acetonitrile beneath the sea surface [4] but it necessitated sample collection and preconcentration thus not allowing online and onsite measurements. An alternative way to take advantage of the capability of the PTRMS to perform sensitive quantitative measurements for online analysis of VOCs dissolved in water is to combine the PTRMS with a membrane inlet [12].

We will show how a combination of a membrane inlet and PTRMS, recently developed in our labs for gas analysis and membrane characterization [12] can be used for measuring VOCs directly from water. It is demonstrated that this system can perform quantitative measurements with good reproducibility and sensitivity, detecting multiple species of VOCs at the same time over a large linear dynamic range. Solutions of methanol, acetonitrile, acetone, dimethylsulfide, isoprene, benzene, and toluene prepared using both fresh and salty water are used to investigate the properties of the MI-PTRMS system employed here.

2. Experimental

PTRMS instrument (prototype from Ionenphysik Institüt Innsbruck and a commercial one, Ionicon, Innsbruck) operated at standard conditions (drift tube voltage 600 V; drift tube pressure: 2.0 mbar). A schematic diagram of the setup is shown in Fig. 1. Silastic™ (Dow Corning) tubing with dimensions of i.d. 0.30 mm, o.d. 0.64 mm, and a length of 8.2 cm was used as interface between the aqueous sample and the drift tube of the PTRMS with a similar setup as used in a previous study [12]. During operation of the system a water stream is continuously supplied to the membrane inlet via a peristaltic pump (Gilson, Minipuls™ 3) resulting in a continuous flow around the membrane at atmospheric pressure with a flow rate of 10 ml/min. Sample injection was performed manually and consisted of moving the sampling tube (connected to the peristaltic pump) from a flask containing the mobile phase (distilled water) to a flask containing the solution to be introduced. The analytes will start to permeate through the membrane and their concentration in the carrier gas will increase until equilibrium is reached. This method (continuous flow method) was shown to give better quantification performances than the flow injection analysis (FIA) [19]. The sample transfer line consisted of Teflon tubing (1/16 in.) connected to short segments of Viton tubing (ANACHEM, Luton, UK; Tube Isoversic Collard) used for the peristaltic pump. The inner side of the membrane is directly connected to the drift tube of the PTRMS and held at a pressure of approximately 2 mbar. A carrier gas (zero

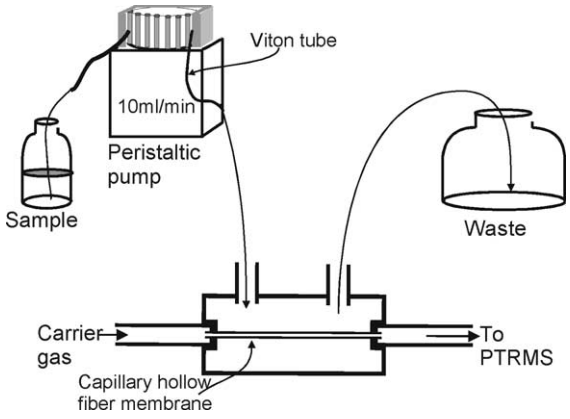

Fig. 1. Scheme of MI-PTRMS and sampling setup.

air) sweeps the inner walls of the membrane at 10 ml/min, transporting the analytes permeating through the membrane to the mass spectrometer. The membrane assembly and the sample are kept at room temperature, only the transfer line connecting the inner side of the membrane to the drift region is heated up to 60 °C.

In the work presented here, methanol, acetonitrile, acetone, dimethylsulfide (DMS), isoprene, benzene, and toluene (Sigma–Aldrich) were detected simultaneously both in fresh and salty water at various concentrations ranging from 100 ppt_w (part per trillion in water) to 1 ppm_w (part per million in water). Water solutions were prepared by serial dilution of an initial 100 ppm_w stock solution diluted in water (distilled water) and seawater. The seawater was prepared using a sea salt (Instant Ocean, 10 ml in 1 l distilled water) commercially available.

All the experiments were performed using selected-ion-mode (SIM) operation of the PTR-MS.

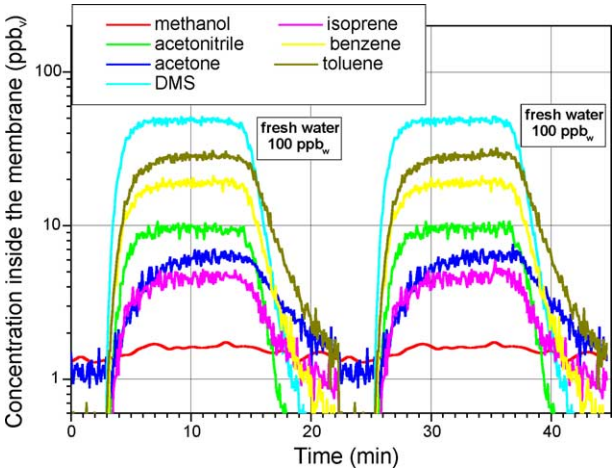

Fig. 3. Multiple species, including both polar and non-polar compounds are detected at the same time. Repeated measurements of a 100 ppb_w sample shows good reproducibility.

3. Results and discussion

The operating conditions for the membrane inlet PTRMS system (MI-PTRMS) were initially optimized in order to obtain reproducible and sensitive measurements. Particularly care had to be taken in assembling the line connecting the sample and the membrane inlet in order to avoid air bubbles in the sample. In fact when air bubbles are present in the sample the signal may show discontinuities of momentarily higher concentrations (see Fig. 2) instead of a continuous trend as expected. This effect is more pronounced for those compounds having lower solubility in water, i.e. hydrocarbons, because of a higher air/water partition coefficient thus showing higher concentration in air (bubbles of air) than in water. Repeated measurements of solutions of the seven compounds analyzed (see the experimental part) with the same concentration showed a good reproducibility of the system (see Fig. 3).

The seawater matrix contains dissolved electrolytes of very high ionic strengths [1] and an important step in developing a methodology for analyzing VOCs both in fresh and salty water samples by MI-PTRMS is to determine matrix effects. In a membrane inlet system, the salt and ionic compounds do not pass through the membrane; nevertheless deterioration of the membrane might be expected after prolonged operation. However, the same membrane and setup was used through all the experiments with both fresh and salty water samples for 7–8 h of continuous operation for several days, without encountering clogging problems due to the salt or memory effects due to the VOCs analyzed or deterioration of the membrane. This proves that a membrane inlet can operate for several days without problems in a saline environment.

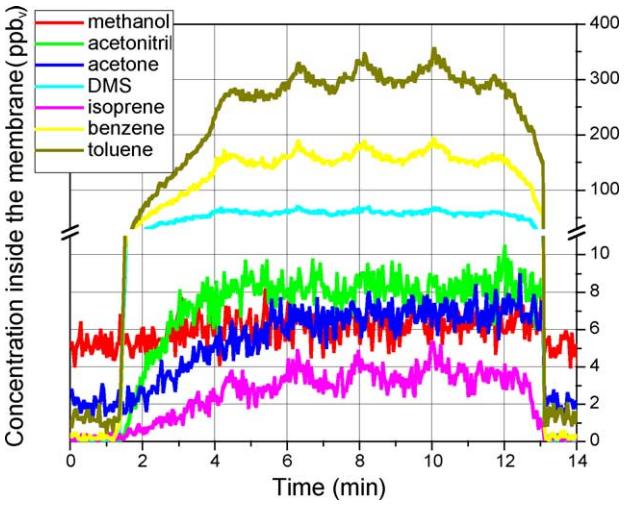

Fig. 2. When bubbles of air is present in the water samples, discontinuities may appear. This effect is bigger for hydrophobic compounds as toluene (no. 2), benzene (no. 3), and isoprene (no. 6).

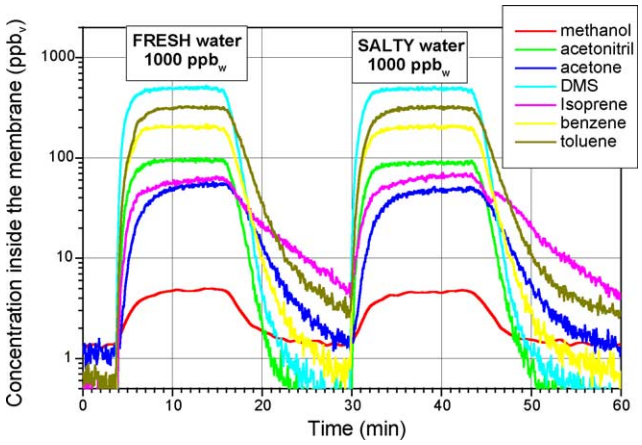

Fig. 4. Comparison of two 1 ppm_w solution in fresh and seawater shows no matrix effect due to the salt.

Table 1
Measured concentrations of seven VOCs in the MI-PTRMS (in ppb_v) versus concentration in fresh and salty water (ppb_w) at room temperature

Concentration in the MI-PTRMS [ppb_v]										
ppb_w	1000		100		10		1		0.125	0.1
Compounds	Fresh water	Salty water	Fresh water	Salty water	Fresh water	Salty water	Fresh water	Salty water	Fresh water	Salty water
Methanol	3.30	3.66	0.39	0.40	–	0.16	–	–	–	–
Acetonitrile	88.0	94.1	9.43	9.56	0.73	0.94	0.09	0.11	–	–
Acetone	47.0	53.4	5.00	5.21	0.45	0.56	–	–	–	–
DMS	488	499	51.3	48.0	4.77	4.83	0.47	0.50	0.07	0.06
Isoprene	61.2	60.7	5.80	4.65	0.53	0.52	–	0.07	–	–
Benzene	204	203	22.2	18.9	2.15	1.83	0.19	0.23	–	–
Toluene	303	314	30.1	28.7	2.61	2.99	0.28	0.30	–	–

Fig. 4 shows as an example the response of various compounds for a concentration of 1000 pbb_w both in fresh and salty water using a silicone membrane. This experiment did not show any matrix effect due to the salt in the seawater. The experiment was then repeated with the same mixture of compounds with different concentrations ranging from 0.1 to 1000 ppb_w, the results are shown in Table 1, and in all the cases no matrix effect was observed. Since water and seawater have different solubility for organic compounds, it would not be surprising for the nature of the mobile phase to have an effect. Previous studies have shown no effect due to seawater when using a FIA injection mode and very small effect on benzene response when using a continuous flow method [1,19]. Our results are thus in agreement with those reported in the literature.

As shown already in Figs. 3 and 4, methanol, acetonitrile, acetone, DMS, isoprene, benzene, and toluene could be detected simultaneously both in fresh and in salty water. Fig. 5 demonstrates the simultaneous detection of these compounds in salty water at concentrations ranging from 100 ppt_w to 1000 ppb_w.

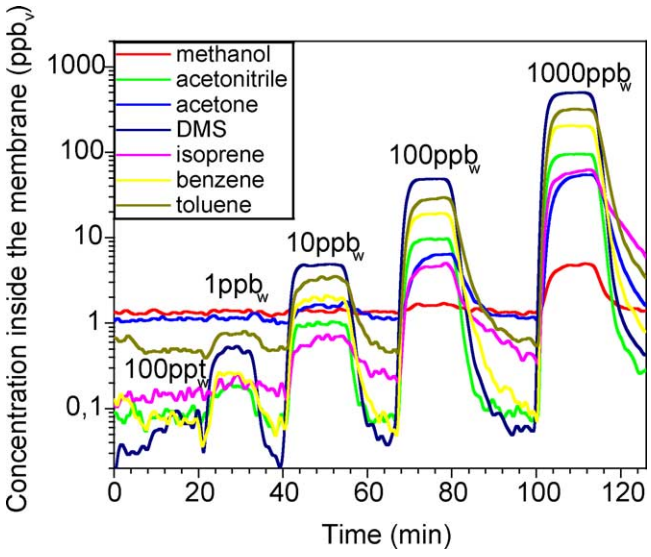

Fig. 5. Multiple species in salty water are detected simultaneously over a large concentration range, from 0.1 to 1000 ppb_w.

Due to the hydrophobic nature of the PDMS membrane employed, polar compounds showed longer rise time and smaller permeation through the membrane than non-polar compounds mostly due to polar-polar interactions. Rise time, calculated between the 10 and 90% of the steady state, ranged from 2.5 to 3 min for DMS, benzene, toluene, and acetonitrile to 4.5–5 min for methanol, acetone, isoprene (see Table 2). It is noteworthy that the rise time of acetonitrile is smaller than for isoprene although the former is a polar compound and the latter is a hydrocarbon not having polar groups. The most probable explanation is that in this case the interaction between the alkyl groups of isoprene with the methyl groups of the membrane is stronger than the polar-polar interaction between acetonitrile and the membrane [13]. These considerations are true for both fresh and salty water samples, and as shown in Table 2, no seawater matrix effect was observed on the rise time. From the values of the rise time we can evaluate that a steady state can be reached quite fast for all the compounds of the mixture, allowing eventual use of the MI-PTRMS system for online and onsite measurements. Faster steady state conditions can be achieved either by increasing the operating temperature of the membrane (the diffusion through the membrane becomes faster) or employing a thinner membrane as deducible from the expressions for the flow rate of a substance through the membrane [12,13,20,21].

$$F_{st} = \frac{2\pi LDKC_v}{\ln(r_0/r_1)} \quad (1)$$

where D is the diffusion coefficient, K the partition coefficient, L the length of the membrane, r_0 and r_1 the inner and

Table 2
Rise times in water and seawater (i.e. between the 10 and 90% of the steady state) for a 1000 ppb_w solution at room temperature

Compound	Rise time (min)	
	Fresh water	Salty water
Methanol	4.6	4.7
Acetonitrile	2.4	2.5
Acetone	4.8	4.9
DMS	2.4	2.7
Isoprene	5.4	4.6
Benzene	2.8	2.3
Toluene	3.3	3.0

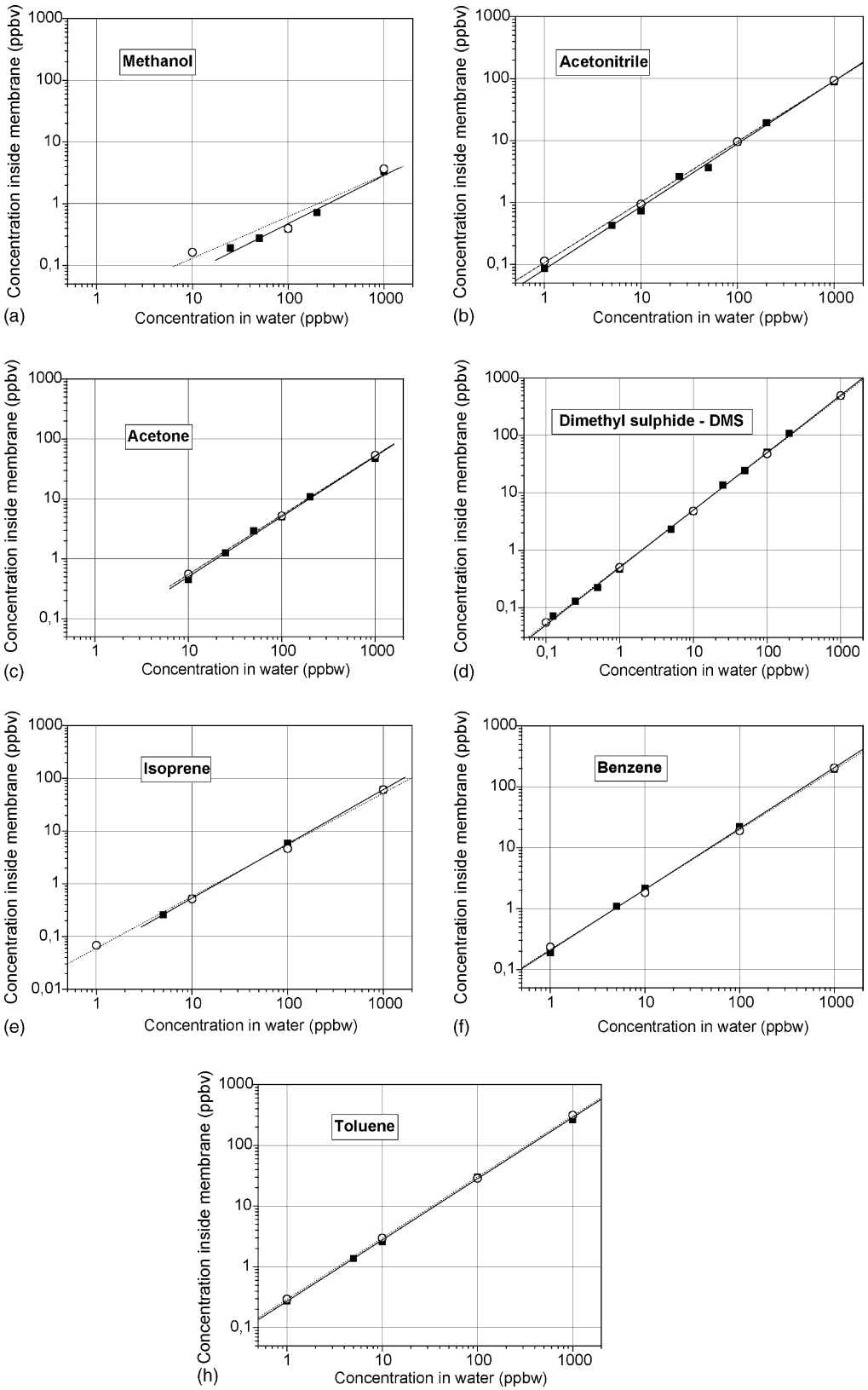

Fig. 6. (a–g) Log–log plot of concentration inside the membrane (response toward the membrane) vs. concentration for the seven compounds analyzed in water (■) and in seawater (◯). Linear fit in water (—) and seawater (···).

the outer membrane diameters, and C_v is the concentration of the analytes in the matrix.

As shown in Figs. 3–5, not all the compounds, although having the same concentration in water, permeate through the membrane to the same extent. Permeability depends on the interactions between membrane and specific compounds as does the rise time. The highest permeability is found for DMS which shows a response 1.6 times higher than toluene, 2.5 times higher than benzene, five times higher than acetonitrile, eight times higher than isoprene, 10 times higher than acetone, and about 140 times higher than methanol. The permeability through the membrane, beside the background/noise of the PTRMS, is the major limiting factor of the sensitivity of MI-PTRMS system toward specific compounds. Those compounds showing the highest permeability are detected at the lowest concentrations. This is the case of DMS whose detection limit (assuming a signal-to-noise ratio 3:1) is in the range of 100 ppt_w. This concentration is equal to approximately 1.2 nM, which is in the range of the lowest concentration of DMS found in natural seawater [2]. Isoprene, benzene, toluene, and acetonitrile, which permeate through the membrane at a lower extent than DMS, were detected down to about 1 ppb_w. Finally the most polar compounds, between those analyzed in this work, showed the highest detection limits: 10 ppb_w for acetone and 10–100 ppb_w for methanol.

Detection limits of MIMS systems reported in the literature, when employing the same kind of silicon membrane seem to be very much influenced by operating conditions, geometry and dimension of the membrane and by a jet separator between the membrane and the ion source of the mass spectrometer [11,21]. Detection limits ranging from 0.04 to 3 ppb_w have been reported for benzene in water [22] and from 0.4 to 5 ppb_w for toluene in water [1,7,11,19,20]. Higher detection limits than those observed with the MI-PTRMS system are reported in literature for DMS and methanol. The former have been detected in water at concentrations as low as 1 ppb_w [19] and the latter only down to 5 ppm_w [22] indeed one order and two orders of magnitude higher than with the MI-PTRMS. Better performances, higher permeability values thus lower detection limits, could be achieved with a longer membrane. In fact the flow rate of analyte molecules through the membrane is proportional to the surface area of the membrane exposed to the sample [12,20]. Temperature also influences the permeability, and referring to the work of La Pack et al. [20] at higher temperature organic permeabilities from water increases. Thus, the employment of a thinner membrane with a longer length and higher operating temperature could improve the performance of the system both increasing the speed of diffusion and the efficiency of transmission of the analytes through the membrane [21].

Besides good sensitivity toward VOCs directly from water, the MI-PTRMS also has a wide linear dynamic range for all the compounds analyzed in this work. Fig. 6a–g shows a linear response of up to five orders of magnitude for the present system, which will allow analysis of unknown samples with varying concentrations. Although the detection limit for each of the compounds analyzed was determined in this work, the upper concentration limit before the saturation of the system occurs has not been investigated. PTRMS can typically operate linearly up to concentrations in air of about 1 ppm_v. Depletion of the primary H_3O^+ may occur at higher concentrations of the analytes leading to unwanted secondary or switching reactions.*This upper range can be extended by operating at higher flow rates through the membrane as demonstrated previously* [12]. In this work, the water solutions were prepared always using the same concentration for each compound and the highest concentration analyzed was 1 ppm_w, in order to avoid the depletion of the primary ion signal. However, compounds as methanol, acetone, acetonitrile due to their volatility could be easily analyzed even at higher concentration in water, probably up to 100 ppm_w for methanol and 10 ppm_w for the latter ones. Further investigation on the upper limit of the system should be performed in future studies.

Due to the capability of the PTRMS to perform absolute measurements, no calibration of the system is necessary; therefore, once the response of the compounds of interest toward the membrane has been determined the system can be used without further calibration to quantify VOCs dissolved in water.

4. Conclusions

The MI-PTRMS has been proven to be a quite sensitive system for the direct and quantitative analysis of VOCs in water and seawater without necessitating of pre-sampling or pre-concentration procedures and calibration. Indeed DMS can be detected down to 100 ppt_w (∼1.2 nM) corresponding to the lowest concentration of DMS reported for seawater [2]. Due to these characteristics and the long stable operating time, this system is suitable for online and onsite measurements. Better performance may be achieved employing thinner membranes or utilizing higher operating temperatures, than used in the present investigation.

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