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Short communication

Direct aqueous injection analysis of trace compounds in water with proton-transfer-reaction mass spectrometry (PTR-MS)

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ABSTRACT

Here we present proof-of-principle investigations on a novel inlet system for proton-transfer-reaction mass spectrometry (PTR-MS) that allows for the analysis of trace compounds dissolved in water. The PTR-MS technique offers many advantages, such as real-time analysis, online quantification, no need for sample preparation, very low detection limits, etc.; however it requires gas phase samples and therefore liquid samples cannot be investigated directly. Attempts to measure trace compounds in water that have been made so far are mainly headspace analysis above the water surface and membrane inlet setups, which both are well suitable for certain applications, but also suffer from significant disadvantages.

The direct aqueous injection (DAI) technique which we will discuss here turns out to be an ideal solution for the analysis of liquid samples with PTR-MS. We show that we can detect trace compounds in water over several orders of magnitude down to a concentration level of about 100 pptw, while only consuming about 100 μl of the sample. The response time of the setup is about 20 s and can therefore definitely be called "online". Moreover the method is applicable to the analysis of all substances and not limited by the permeability of a membrane.

1. Introduction

Since the late 1990s proton-transfer-reaction mass spectrometry (PTR-MS) is a well established technique for online quantification of traces of volatile organic compounds in air. Already the first commercially available instruments showed great sensitivities and very low detection limits as well as response times in the seconds scale. During the years these parameters were all continuously improved and just recently [1] we reported about the latest achievements reaching the ppqv (parts-per-quadrillion) region in terms of detection limit and response times below 100 ms. Another big step in the success story of PTR-MS was the coupling of the PTR ionization technique with a high mass resolution time of flight analyzer (called PTR-TOFMS) [2], which makes it possible to separate isobaric compounds with a mass resolution of over 7000 m/Δm and therefore leads to a more unambiguous identification of the obtained mass spectra. The latest major improvement in commercially available PTR-MS instruments was the introduction of switchable reagent ions (SRI), which means the possibility to switch between the commonly used H_3O^+ primary ion and additionally NO^+ and O_2^+ ions [1] in less than 10 s.

All of the above-mentioned improvements and developments lead to the fact that nowadays PTR-MS is a technique for a rapidly growing field of applications, from atmospheric chemistry to the detection of illicit substances such as explosives or chemical warfare agents [3,4]. However, one drawback of PTR-MS is that it is only possible to measure compounds that are present in the gas phase. Trace compounds, e.g., dissolved in water can only be investigated via measurements of the headspace above the liquid surface. The Henry constant gives the relation between the concentration of a substance in the liquid to the concentration in the headspace, i.e., substances having a very high Henry constant are extremely difficult to detect in the headspace and must be present in very high liquid concentrations to be detectable in the gas phase [5,6]. Among the molecules having a high Henry constant are very important environmental toxins (see the extensive list of Henry constants in [5]), for which a very low detection limit would be highly desirable (e.g., 0.0001 mg/l for pesticides in drinking water according to the German ministry of justice [7]).

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To overcome this problem Boscaini, Alexander et al. developed a membrane inlet (MI) system for PTR-MS [8,9] and published extensive studies on volatile organic compounds (VOCs) in water using this membrane inlet mass spectrometry (MIMS) setup. However, using a membrane to introduce VOCs from liquids into PTR-MS has several considerable disadvantages, e.g., selectivity of the membrane, low sampling speed, cross-contaminations when changing the sample, etc. Therefore, in the present work we have explored a different approach, namely direct injection of water into an airstream, which has several advantages, i.e., (i) being very simple in handling (no pre-treatment of the sample or pre-concentration), (ii) minimized losses of volatile analytes, (iii) fast response times, etc.

Assuming that the injected liquid is evaporated completely in the carrier air flow and assuming that the gas volume per time unit originating from the evaporating water is negligible compared to the carrier airstream, we can write for the concentration C_{PTR} (volume concentration), which we measure with the PTR-MS instrument

$$C_{PTR} = \frac{C_w \cdot l}{f_{air} \cdot M_w} \cdot V_{mol}, \quad (1)$$

where C_w is the concentration of the dissolved compound in water (mass fraction) to be determined, l is the liquid flow rate ("injection rate"), f_{air} is the flow rate of the carrier airstream, M_w is the molecular weight of the dissolved compound and V_{mol} is the molar volume.

In this paper, we demonstrate proof-of-principle investigations of direct aqueous injection (DAI) coupled with PTR-MS and show first results obtained for methanol, acetonitrile, pyridine and cyclohexanol contained in water matrices.

2. Experimental

A schematic illustration of the present direct aqueous injection (DAI) inlet system is given in Fig. 1. The carrier airstream generated by a diaphragm pump (KNF Lab, N86KT.18) passes first through an activated charcoal filter (Supelco, 22445-U) and then a cooling trap to efficiently reduce and stabilize humidity prior to injection. The temperature of the cooling trap was kept at 0–4 °C using ice cubes, which ensures a constant relative humidity in the carrier gas of well below 3% in the injection region (at 70 °C). After that, a mass flow controller adjusts the exact amount of clean and dry air entering the injection region, which is heated to 70 °C in a thermostatic heating box to ensure that all parts (tubes, fittings, connectors, etc.) are at the same temperature, so that no condensation on cold spots can occur. The injection itself takes place in a T-piece which is mounted directly into the carrier gas line and has one of the three openings sealed with a standard septum. The needle of the syringe holding the water to be analyzed can then simply be pierced through this septum, and the injection speed is controlled by a high precision syringe pump (Nemesys, Cetoni). After this first T-piece there is a short transparent tube, which allows for checking if the injected liquid is completely vaporized, i.e., if there is any formation of droplets. Finally a second T-piece serves as connector to the PTR-MS instrument, as well as bypass for the excess airstream which is not introduced into PTR-MS (typical airstream in the DAI system: 1000–2000 sccm; typical amount of air sampled with PTR-MS: 100 sccm).

The PTR-MS instrument used for the present studies was a high sensitivity (HS) quadrupole based one (Ionicon Analytik), which has recently been proven to reach a detection limit below the pptv level [1]. Proton transfer ionization, the PTR-MS technique itself and the broad field of possible applications have already been described in great detail in various publications [10,11], reviews [12,13] and conference contributions [14,15].

Water solutions were prepared with 1–1000 ppbw (part per billion weight: μg/l) of methanol (Wako Chemical), acetonitrile (Sigma–Aldrich), pyridine (Sigma–Aldrich; additional mixtures down to 125 pptw were prepared) and cyclohexanol (Sigma–Aldrich). Since cyclohexanol is not well soluble in water (water solubility of cyclohexanol is 36 g/l at 20 °C [16]), 1 ml of cyclohexanol and 1 ml of water were mixed in a glass bottle and shaken for 1 h. Afterwards 300 μl were taken and diluted in 10 ml of water as a starting sample. For the other chemicals, which are well soluble in water, 1 g/l solutions were prepared first. Simple distilled water (Brenntag CEE) was used for dilution to prepare all samples.

The PTR-MS instrument was operated at standard conditions (reduced electric field strength approximately 130 Td). The temperatures in the PTR-MS were 70 °C for the inlet-tube and 80 °C for the drift-tube. In each experiment, background signals were measured in the first 100 cycles without any dosing from the syringe and afterwards subtracted from the obtained signals. Subsequently, sample gases were introduced and measured with a defined liquid flow for 20–30 min to check the stability and the absence of fluctuations.

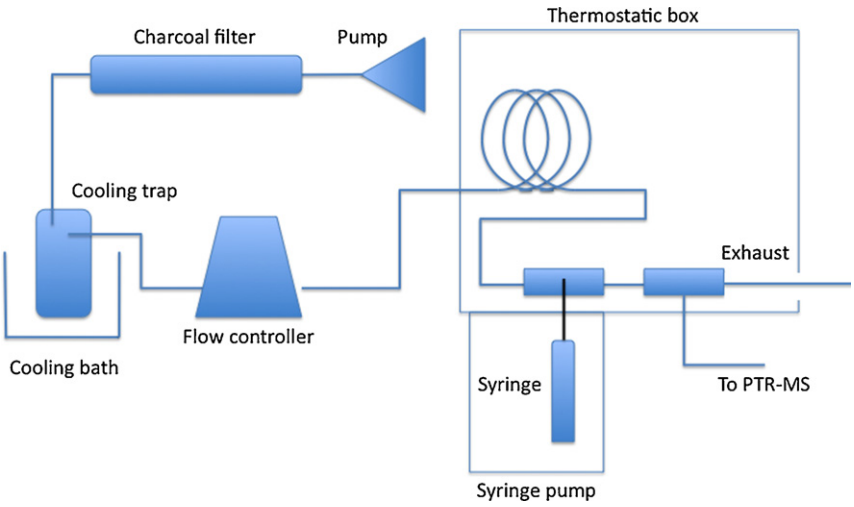

Fig. 1. Schematic drawing of the novel DAI inlet system.

3. Results and discussion

Perhaps the most crucial parameter for our new DAI inlet system is the ratio between the airstream (air flow in l/min) and the injection speed (liquid flow in μl/s). On the one hand it is obvious that the more liquid is injected per time unit, the lower the detection limit will be because of less dilution of the vapor by the airstream. On the other hand it is absolutely necessary that 100% of the injected liquid gets vaporized immediately, because otherwise droplets will form and cause falsification of the results.

To find out the best ratio between airstream flow and injection rate we prepared a mixture of 1 ppmw acetonitrile (protonated mass 42 m/z), 1 ppmw pyridine (protonated mass 80 m/z) and 100 ppmw methanol (protonated mass 33 m/z) in distilled water and injected it at a constant liquid flow rate of 0.1 μl/s while varying the airstream. Fig. 2a shows the concentrations in air we obtained by changing the air flow from 0.5 l/min up to 2.3 l/min. As this should give a $1/x$ dependence, we choose the inverse air flow as the scale of the x-axis (i.e., min/l). The measured concentrations from 2.3 l/min (corresponds to approximately 0.4 min/l; maximum of the pump) down to about 0.9 l/min (approx. 1.1 min/l) show a very good linearity, although below 1 l/min already some droplet formation between the injection region and the PTR-MS inlet could be observed (in the short transparent tube). The last measurement point for the three substances at 0.5 l/min (approx. 2 min/l) is already well below the expected value, which can be explained via strong formation of droplets, i.e., only a part of the injected liquid is vaporized.

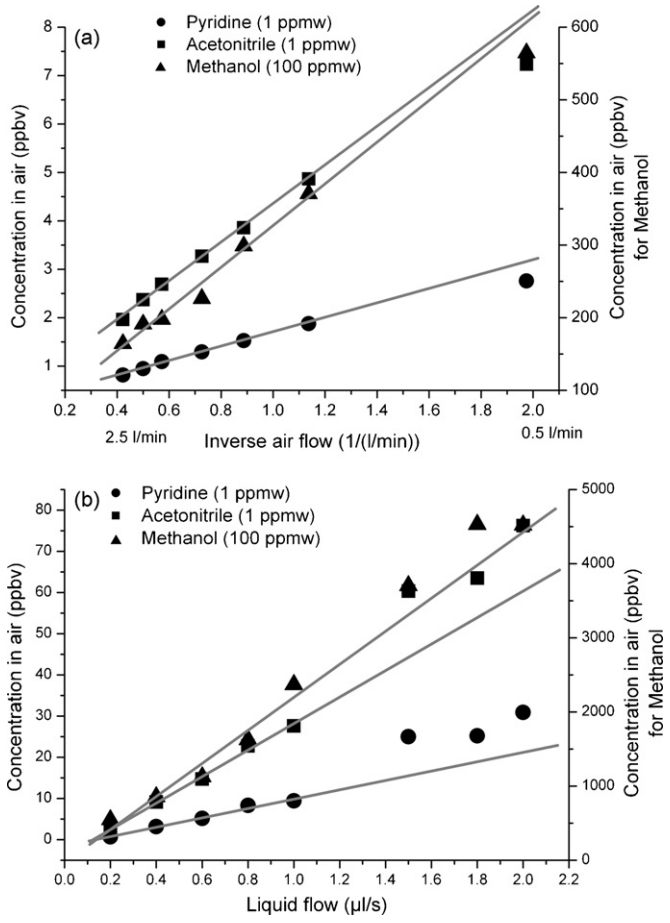

Fig. 2. (a) Measured concentrations in the gas phase for 1 ppmw acetonitrile, 1 ppmw pyridine and 100 ppmw methanol in water as a function of the inverse airstream flow. The injection rate was 0.1 μl/s. Droplet formation was spotted starting at about 1 l/min. (b) Measured concentrations in the gas phase for the same mixture but as a function of the injection rate (liquid flow) at a constant airstream flow of 1.75 l/min. Droplet formation was spotted starting at about 1 μl/s.

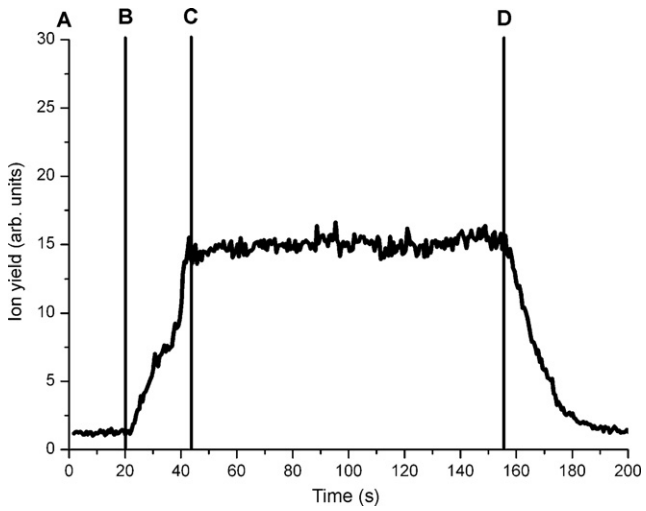

Fig. 3. Response of the PTR-MS instrument at (A) no injection, (B) injection starts, (C) reaching stable signal, and (D) injection of pyridine (protonated mass 80 m/z) stops. The time between start of the injection and reaching a stable signal can be estimated to be about 20 s.

To be on the safe side we decided to use an air flow from the center of the linear region, i.e., 1.75 l/min, for further investigations. Fig. 2b shows results obtained from the above-mentioned mixture at a constant air flow of 1.75 l/min while varying the injection rate from 0.2 to 2.0 μl/s. Again, as long as no droplets are formed (about up to 1 μl/s), the data show great linearity. Based on the measurements displayed in Fig. 2a and b, we conclude that the ideal injection parameters are 1.75 l/min for the airstream and 0.6 μl/s for the injection rate, thus being an ideal compromise between high signal intensity and avoiding the formation of droplets.

After finding the ideal injection conditions, we measured the response time of our DAI inlet system, i.e., the time needed between starting the injection and getting a stable PTR-MS signal. Fig. 3 shows a signal vs. time measurement for a 1 ppmw pyridine mixture. In region (A) no injection takes place, i.e., the background signal is displayed, at the beginning of (B) the injection starts and about 20 s later a stable signal status is reached (C). Finally the injection is stopped and the signal drops down to the background level again (D). The response time can therefore be estimated to be about 20 s, which is significantly faster than for PTR-MS coupled with MIMS [8,9]. Furthermore the response time is, in contrast to MIMS, virtually independent from the sample molecule under study, thus allowing for very fast results for all substances that can be ionized via proton transfer from hydronium or via charge transfer from NO^+ or O_2^+ when using a PTR-MS equipped with the SRI feature [1].

The most important proof-of-principle measurement is presented in Fig. 4. There we plot the measured concentrations in air for acetonitrile (at protonated mass 42 m/z), pyridine (protonated mass 80 m/z) and cyclohexanol (fragmenting mainly to 83 m/z) at different liquid concentrations. It can be seen immediately that the correlation is linear over several orders of magnitude for all three compounds. In order to explore the detection limit of our DAI inlet system, we extended the measurements in Fig. 4 to lower liquid concentrations of pyridine. It can be seen that the instrument's response stays linear down to a concentration of about 100 pptw and therefore we claim that the detection limit lies at least in the range of 100 pptw (for an integration time of about 5 min). It should be noted that this detection limit is dependent on the molecular mass of the sample compound (directly proportional, i.e., at lower

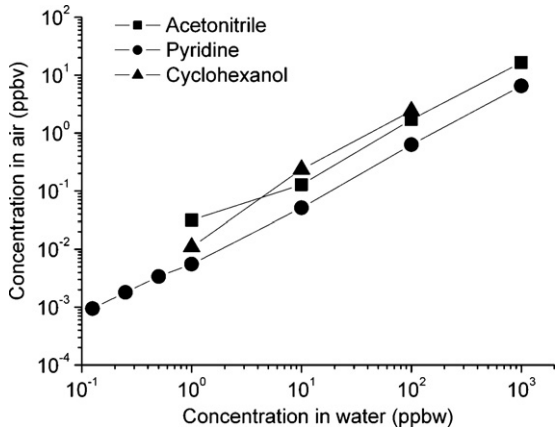

Fig. 4. Correlation between the measured concentration in the gas phase and the concentration in the water sample for acetonitrile (protonated mass 42 *m*/*z*), pyridine (protonated mass 80 *m*/*z*) and cyclohexanol (fragments to mass 83 *m*/*z*). On mass 80 *m*/*z* the background signal is low enough to explore the lowest possible detection limit, therefore for pyridine mixtures were prepared and measured down to 125 ppbw.

masses the detection limit gets better/lower; according to Eq. (1)). Compared to PTR-MS coupled with MIMS, where the detection limit is strongly dependent on the permeability through the membrane, i.e., 100 pptw can be reached only for a handful of highly permeable compounds (e.g., dimethyl sulfide in [9]) and 10 ppbw are the limit for common compounds like acetone, this means a far better sensitivity for investigating a wide range of substances dissolved in water.

4. Conclusions

We present proof-of-principle measurements for our newly developed direct aqueous injection (DAI) inlet system coupled with PTR-MS. It is found that the best injection conditions are 0.6 μl/s liquid flow into 1.75 l/min air flow (at 70 °C). With these parameters we achieve good linearity over several orders of magnitude between the concentration in the liquid and the measured concentration in air, a response time of about 20 s and a detection limit of about 100 pptw (for pyridine at protonated mass 80 *m*/*z* and about 5 min integration time).

The DAI PTR-MS method carries the advantages of the PTR-MS technology, i.e., (i) no sample preparation, (ii) fast response times, (iii) low detection limits, (iv) real-time quantification, etc. to the analysis of liquid samples and will therefore open completely new fields of application (e.g., detecting toxins in ground-water, monitoring pollutants in oceans, lakes and rivers, applications in food/beverage industry, medicine and many more).

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