On the development of a new prototype PTR-ToF-MS instrument and its application to the detection of atmospheric amines

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Abstract. We herein report on the development of a new prototype PTR-ToF-MS (proton-transfer-reaction time-of-flight mass spectrometry) instrument that combines a hollow cathode glow discharge (HCGD) ion source with a focusing ion–molecule reactor (FIMR), which consists of a resistive glass drift tube surrounded by quadrupole rods. The new instrument configuration hybridizes the two main current commercial PTR-ToF-MS instrument designs. We provide a detailed technical description of the new analyzer and its optimized operational settings for detecting volatile amines via proton transfer reactions from hydronium (H_3O^+) or ammonium (NH_4^+) ions. We show that the new prototype PTR-ToF-MS instrument is capable of monitoring rapid changes of sticky amines on the timescale of a few seconds and detects atmospheric variations of amines down to single-digit parts per trillion by volume (pptv) levels. Application examples given include the real-time monitoring of (i) methylamine emitted from a *Chenopodium vulvaria* L. plant, (ii) small alkylamines in ambient air on site of an agricultural research center (Senter for husdyrforsøk, Ås, Norway), and (iii) an industrial amine (2-amino-2-methylpropan-1-ol, AMP) on site and downwind of a carbon dioxide (CO_2) capture test center (Technology Centre Mongstad – TCM, Mongstad, Norway).

1 Introduction

Proton-transfer-reaction mass spectrometry (PTR-MS) is widely used in atmospheric sciences for the detection of non-methane organic gases (NMOGs; de Gouw and Warneke, 2007; Hansel et al., 1995; Yuan et al., 2017). PTR-MS is a direct-injection chemical ionization mass spectrometry (CIMS) technique. Direct injection means that the sample is directly introduced into the analyzer without any pre-collection or pretreatment. The measurements are thus conducted in real time, with a frequency of up to 10 Hz. In its original and still most widely used configuration, PTR-MS uses gas-phase hydronium ions (H_3O^+) as chemical ionization (CI) reagent ions. H_3O^+ ions react with most NMOGs in non-dissociative proton transfer reactions (Hunt and Ryan, 1972; Lindinger et al., 1998). PTR-MS distinguishes itself from other CIMS techniques in the way that the ionization is effected in a small flow tube reactor, at reduced pressure (1–4 mbar) and under the action of an electrostatic field (40–70 V cm^{-1}). The collisional drift of the ions at high velocities prevents them from getting hydrated and limits their residence time in the flow tube. Because of the presence of an electrostatic field, the flow tube reactor is commonly referred to as the drift tube (DT). While the original PTR-MS instrument was equipped with a quadrupole mass spectrometer (QMS), state-of-the-art analyzers include a time-of-flight mass spectrometer (ToF-MS).

Currently, atmospheric composition researchers mainly use two types of PTR-ToF-MS instruments, which are manufactured by two different producers. The instrument produced by Ionicon Analytik (Innsbruck, Austria) uses a hollow cathode glow discharge (HCGD) for producing H_3O^+ ions (Hansel et al., 1995; Müller et al., 2020). More details about this ion source are provided in the "Instrument description" section. In the conventional and widely used Ionicon instruments, the DT is composed of a stack of stainless steel (SS) rings, which are separated by insulating Teflon spacers. In the instrument produced by Tofwerk (Thun, Switzerland), also known as the VOCUS PTR-TOF or simply as

"the VOCUS", H_3O^+ ions are formed in a water plasma burning between two conical electrodes (Krechmer et al., 2018). In the VOCUS analyzer, the DT consists of a resistive glass tube surrounded by cylindrical quadrupole rods. The latter generate a focusing quadrupole field within the DT, which is thus commonly referred to as a focusing ion–molecule reactor (FIMR).

Herein, we report on the development and application of a new prototype PTR-ToF-MS instrument that hybridizes the two commercial PTR-ToF-MS designs, combining an FIMR with an HCGD ion source. In a conventional stacked-ring DT, the ion swarm broadens as it drifts through the reactor, and only a fraction of the ions are sampled through the exit aperture towards the mass analyzer. This loss in sensitivity can partly be compensated for by placing an ion funnel at the end of the DT (Barber et al., 2012). Such an ion funnel is routinely installed nowadays in most Ionicon analyzers (Pugliese et al., 2020). In the FIMR, a focusing quadrupole field acts over the entire drift region, which minimizes ion losses and boosts the instrument sensitivity ($10^3 - 10^4$ cps ppbv^{-1}; Krechmer et al., 2018). We thus decided to build an instrument based on the FIMR design proposed by Krechmer et al. (2018). Since the VOCUS ion source was not yet commercially available when we conceived the new instrument, we opted to couple the FIMR with the existing HCGD ion source.

We will describe the new prototype PTR-ToF-MS instrument in the "Instrument description" section of this paper. In the "Results and discussion" section, we will describe its performance for the detection of volatile amines and show laboratory and field data. Amines were chosen as target analytes because of the increasing interest of the atmospheric chemistry community in this class of compounds (Ge et al., 2011). This interest is mainly driven by the important role that amines play in new particle formation (e.g., Almeida et al., 2013). Amines are also being emitted to the atmosphere from carbon dioxide (CO_2) capture plants. Since the slip of amines from CO_2 capture plants may result in the atmospheric formation of harmful substances (e.g., nitrosamines and nitramines; Nielsen et al., 2012), amines are receiving increased interest from the air quality and health community. Atmospheric amines are however particularly challenging to measure. This is on the one hand caused by the fact that atmospheric levels are usually extremely low, requiring analyzers to be able to detect single-digit parts per trillion by volume (pptv) levels. On the other hand, amines are also known to be "sticky", meaning that they easily adsorb onto surfaces in the analyzer and in the inlet lines. Direct-injection CIMS is thus the method of choice for measuring pptv levels amines in the atmosphere in real time, and a series of instruments have recently been developed for detecting amines (Hanson et al., 2011; Lee, 2022; Pfeifer et al., 2020; Sellegri et al., 2005; Wang et al., 2020; Yao et al., 2016; You et al., 2014; Yu and Lee, 2012; Zheng et al., 2015). We will herein show that our new PTR-ToF-MS analyzer is also capable of detect-
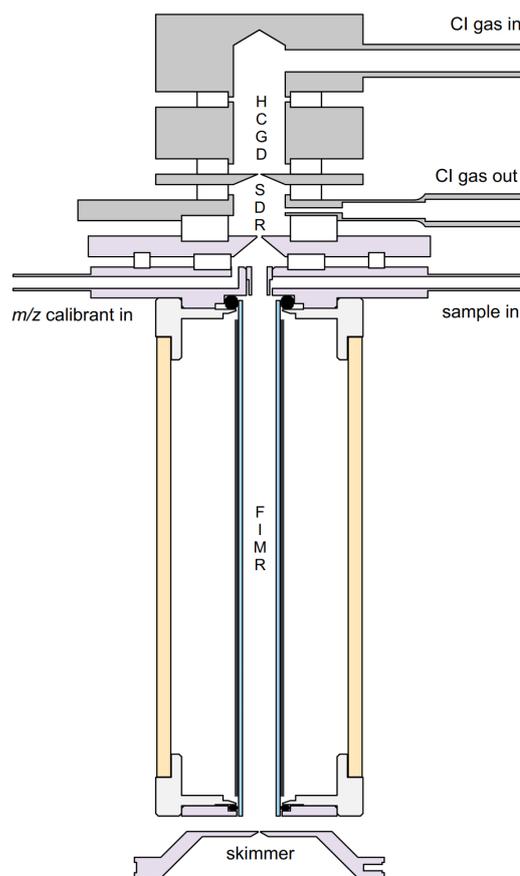
Figure 1. Schematic drawing of the new prototype PTR-ToF-MS analyzer. The instrument consists of a hollow cathode glow discharge (HCGD) ion source, a source drift region (SDR) and a focusing ion–molecule reactor (FIMR), which is a resistive glass drift tube surrounded by cylindrical quadrupole rods.

ing atmospheric amines down to single-digit pptv levels. We will furthermore demonstrate that our new instrument only has minor memory effects and is thus capable of monitoring changes of amines in the air on the timescale of a few seconds.

2 Experiment

2.1 Instrument description

The new prototype PTR-ToF-MS analyzer that combines a conventional HCGD ion source with the more recently developed FIMR is shown in Fig. 1.

The HCGD ion source and the processes occurring therein have been described in detail in the original PTR-MS publication (Hansel et al., 1995). Only minor modifications have been implemented since then, and the current configuration has been described by Müller et al. (2020). Only the essentials are thus outlined here (Fig. 1). A DC water plasma is generated inside a plasma source consisting of a hollow

cylinder anode, a hollow cylinder cathode and an anode lens with an exit orifice. The entire effluent from this plasma source, which includes ions, electrons, radicals and mostly neutral H_2O molecules, is introduced into a hollow cylinder electrode, which is commonly referred to as the "source drift region" or "source drift ring" (SDR). The SDR is a key component of the ion source setup because it is mostly here that O^+, H^+, H_2^+, OH^+ and H_2O^+ cations react with H_2O molecules to form H_3O^+ ions. Only ions ($\geq 98\%$ H_3O^+, with O_2^+ and NO^+ making up for the rest) are extracted via the SDR exit lens and injected into the drift region. It is also in the SDR that free electrons recombine with cations and that $OH^\bullet$ and other radical species are destroyed on SS surfaces. Importantly, the water vapor and other neutral plasma effluents are pumped off from the SDR and thus not brought into contact with the sample gas that is introduced into the instrument further downstream. This is a key design feature, which distinguishes the HCGD ion source from the commercial VOCUS ion source, in which the entire plasma effluent is introduced into the FIMR. From the available literature on the VOCUS ion source, it is not clear if the conversion to H_3O^+ ions is complete and if all radicals are quenched when the sample gas first interacts with the outflow from the ion source. We think that this should be investigated further, as non-protonated analyte molecules may be formed, and highly reactive NMOGs may be oxidized in the FIMR. The latter would result in important positive measurement artifacts for oxidized and highly oxidized compounds, even if only a very small and unnoticeable fraction ($\leq 0.1\%$) of highly reactive NMOGs were oxidized in the FIMR.

The entire HCGD ion source setup can be heated. Five parameters can be set in the HCGD ion source: (i) the source gas flow (Φ_{source}), (ii) the source temperature (T_{source}), (iii) the plasma current (I_{plasma}), (iv) the voltage between the anode lens and the SDR ($U_{SDR,in}$) and (v) the voltage between the SDR and the SDR exit lens ($U_{SDR,out}$). The specific settings used for the measurements reported herein will be reported below. The HCGD ion source has also been used for generating other types of CI reagent ions such as O_2^+ or NO^+ (Jordan et al., 2009) and NH_4^+ (Müller et al., 2020; Zhu et al., 2018). We only operated the new instrument in the H_3O^+ mode and in the NH_4^+ mode, since both of these CI reagent ions can be used for detecting amines via non-dissociative proton transfer reactions (Zhu et al., 2018).

The FIMR has been described in detail by Krechmer et al. (2018). We also use a 10 cm long resistive glass tube but with a slightly smaller diameter (8 mm o.d., 6 mm i.d.). Four operational parameters can be set in the FIMR: the frequency (f_{FIMR}) and peak-to-peak amplitude voltage ($V_{pp,FIMR}$) of the radio frequency (RF) applied on the quadrupole rods, the DC voltage applied across the ends of the glass tube (U_{drift}) and the pressure (p_{drift}) in the vacuum chamber in which the resistive glass tube is placed. The sample gas is introduced into the FIMR via a custom-made passivated (Sulfinert®, Restek, Bellefonte, PA, USA) gas inlet lens (GIL). The GIL

is placed between the SDR exit lens and the FIMR. Two additional voltages can be set relative to the GIL: (i) the voltage between the SDR exit lens and the GIL ($U_{GIL,in}$) and (ii) the voltage between the GIL and the upper end of the FIMR ($U_{GIL,out}$). The GIL is connected to a 15 cm long 1/16 in. o.d. Teflon PFA tube, which includes a T piece to branch off part of the inlet flow into a digital pressure controller (Bronkhorst High-Tech B.V., Ruurlo, the Netherlands). This device keeps the pressure in the Teflon inlet tube (p_{inlet}) (and thereby also p_{drift}) constant. The inlet line and gas inlet lens can be heated (T_{inlet}), which indirectly heats the FIMR. The GIL has a second port that is connected to a capillary leak through which a mass axis calibration gas (1,4-diiodobenzene; Sigma-Aldrich, Oslo, Norway) diffuses into the FIMR. The sample gas is pumped off through a 1 mm gap between the lower end of the FIMR and the skimmer lens at the entrance of the mass spectrometer. The skimmer is grounded, and the voltage between the lower end of the FIMR and the skimmer ($U_{FIMR,out}$) can be set. All specific settings used for the measurements reported herein will be reported below.

Our key strategy for reducing the instrumental time response was to maximize the flow through the low-pressure flow reactor. A dry multi-stage Roots pump (ACP40; Pfeiffer Vacuum, Asslar, Germany) pumps up to 0.80 standard liters per minute (slpm; "standard" herein means referenced to a temperature of 273.15 K and a pressure of 101 325 Pa) through the FIMR. For the measurements presented herein, we set the flow rate to 0.55 slpm, which is a factor of 5 higher than in commercial VOCUS instruments (Krechmer et al., 2018; Wang et al., 2020). We observed that increasing the reactor flow from 0.05 to 0.50 slpm reduced the $1/e^2$ decay time of a 20 pptv trimethylamine (TMA) signal from ~ 60 to ~ 5 s.

The mass analyzer used in our instrument is a quadrupole ion guide orthogonal acceleration reflectron ToF-MS (model HTOF; Tofwerk, Thun, Switzerland). The quadrupole ion guide (commonly referred to as the big segmented quadrupole, BSQ) was operated at an RF of 4.4 MHz and an RF amplitude between 300 and 320 V. It is important to note that we operate the BSQ at relatively high RFs to avoid strong mass discrimination effects in the m/z 30 to 60 region, which is typically observed for commercial VOCUS analyzers (Krechmer et al., 2018; Wang et al., 2020).

2.2 Laboratory test

The first application test was carried out in the laboratory. We cultivated a stinking goosefoot (*Chenopodium vulvaria* L.) plant, which is a weed covered by minuscule bladder hairs. Upon mechanical stress, these bladder hairs release TMA. The plant was placed in our laboratory next to the analyzer and mechanically stressed. The evolving TMA puff was monitored in real time by our new prototype PTR-ToF-MS instrument.

2.3 Field tests

A first field test was carried out on campus of a research center for animal husbandry (Senter for husdyrforsøk – Livestock Production Research Centre, Norwegian University of Life Sciences, Ås, Norway). The prototype PTR-ToF-MS analyzer was installed in a temperature-controlled enclosed car trailer. The trailer was placed close to large manure tanks where the animal excrement from the entire site is collected. The aim was to monitor atmospheric amines, with a focus on methylamine (MMA), dimethylamine (DMA) and TMA. Air was sampled through a hole in the lateral wall of the trailer, using a 130 cm long, heated (100 °C), Sulfinert®-passivated, 1/4 in. o.d. SS tube pumped at a flow rate of 25 slpm. The instrument subsampled from this main inlet flow. A flow of 2.5 standard cubic centimeters per minute (sccm) of 1 % ammonia (NH_3) in nitrogen (BOC Ltd., UK) was continuously added at the tip of the main inlet for chemically passivating all wetted surfaces in the inlet and in the instrument itself (Roscioli et al., 2015; Zhu et al., 2017). Excess ammonia is known to displace amines adsorbed onto surface sites (Ongwandee et al., 2005). The instrumental background was measured every 12 h for 25 min by overflowing the instrument subsampling flow with ambient air that had passed through a heated (350 °C) Pt–Pd catalyst. We have shown in previous work that MMA, DMA and TMA are efficiently detected in their protonated form if NH_4^+ ions are used as CI reagent ions in PTR-MS instruments (Zhu et al., 2018). In this first field study, we thus operated the HCGD ion source in the NH_4^+ mode with the following settings: $\Phi_{source} = 6$ sccm (1 %–3 % NH_3 in N_2, Nippon Gases Norge AS, Oslo, Norway) and $I_{source} = 4$ mA; $T_{source} = 100$ °C. Ions with a relative abundance $> 1 \%$ of NH_4^+ were H_3O^+ ($\sim 5 \%$), NO^+ ($\sim 3 \%$), O_2^+ ($\sim 3 \%$) and $NH_4^+(NH_3)$ ($\sim 1 \%$; Fig. S1 in the Supplement). For quantification, we estimated that NH_4^+ and H_3O^+ have a 50 % lower detection efficiency than the other three ion species (due to increased mass discrimination of ions with $m/z < 20$). The operational parameters of the instrument were as follows: $T_{inlet} = 100$ °C, $U_{SDR,in} = 234$ V, $U_{SDR,out} = 200$ V, $U_{GIL,in} = 78$ V, $U_{GIL,out} = 50$ V, $U_{drift} = 450$ V, $U_{FIMR,out} = 40$ V, $p_{drift} = 1.95$ mbar, $f_{FIMR} = 5.5$ MHz and $V_{pp,FIMR} = 350$ V. The FIMR was operated at relatively high RFs to avoid strong mass discrimination effects in the m/z 30 to 60 region. Calibrations were performed in the field using a liquid calibration unit (LCU) (LCU-a, Ionimed Analytik GmbH, Innsbruck; Fischer et al., 2013). An aqueous standard solution of MMA, DMA and TMA was prepared by diluting known volumes of commercial solutions of MMA ($40 \pm 3 \%$ wt. in H_2O), DMA ($40 \pm 2 \%$ wt. in H_2O) and TMA ($45 \pm 3.5 \%$ wt. in H_2O) with Type 1 Milli-Q® water. In the LCU, the standard solution was nebulized/evaporated at a known liquid flow rate (2–10 μL min^{-1}) into a known flow (typically 1 slpm) of NMOG-free air. The accuracy of

the MMA, DMA and TMA calibration is conservatively estimated to be $\pm 15 \%$.

Two additional field tests were conducted at and near the Technology Centre Mongstad (TCM; Mongstad, Norway). TCM is one of the world's largest test centers for amine-based CO_2 capture (de Koeijer et al., 2011). The measurements were carried out during a test campaign with a solvent containing 2-amino-2-methylpropan-1-ol (AMP; Languille et al., 2021). The instrument was calibrated with the LCU using an aqueous solution of AMP, which was prepared by diluting a weighted amount of the pure compound ($\geq 99 \%$; Sigma-Aldrich, Oslo, Norway) in Type 1 Milli-Q® water. The accuracy of the AMP calibration is conservatively estimated to be $\pm 15 \%$. The first test was carried out on the premises of TCM to demonstrate that the new instrument is capable of detecting solvent leaks in real time. For this purpose, a gas mixture containing 25 ppmv of AMP was deliberately released into the air at approximately 1 m distance from the instrument inlet using a HovaCAL® (model digital 211-MF; IAS GmbH, Oberursel, Germany) gas generator. The second test was to demonstrate that the new and highly sensitive PTR-ToF-MS analyzer is capable of detecting single-digit pptv levels of amines in the downwind atmosphere of a CO_2 capture facility. For this purpose, the instrument trailer was placed ~ 4.4 km north of TCM during a 1-week period with predominantly southerly winds. The measurements took place when ~ 1 ppmv of AMP of TCM was steadily emitted from TCM. For these measurements, the prototype PTR-ToF-MS analyzer was operated in the conventional H_3O^+ mode. Some operational parameters were thus modified as compared to the first field campaign: $\Phi_{source} = 6$ sccm (H_2O), $I_{source} = 4.5$ mA, $U_{SDR,in} = 377$ V, $U_{SDR,out} = 202$ V; $U_{GIL,in} = 89$ V and $U_{drift} = 400$ V. The instrumental background was measured once a day for 20 min by overflowing the instrument subsampling flow with ambient air that had passed through a heated (350 °C) Pt–Pd catalyst. The data from the first 5 min of zeroing were discarded because of signal tailing.

3 Results and discussion

3.1 Laboratory testing: detection of biogenic amines

Figure 2 shows the time evolution of TMA in laboratory air when a *Chenopodium vulvaria* L. plant was mechanically stressed by tipping a leaf with a pen. The stress resulted in a burst of TMA, and the new prototype PTR-ToF-MS instrument detected a short-term spike in TMA with a peak width (full width half maximum, FWHM) of 16 s. This was our first experimental evidence that the new prototype instrument is capable of monitoring rapid changes of amine levels in the air on the timescale of a few seconds. The TMA volume mixing ratio did not drop to pre-spike levels because the amine was released into and sampled from laboratory air. We
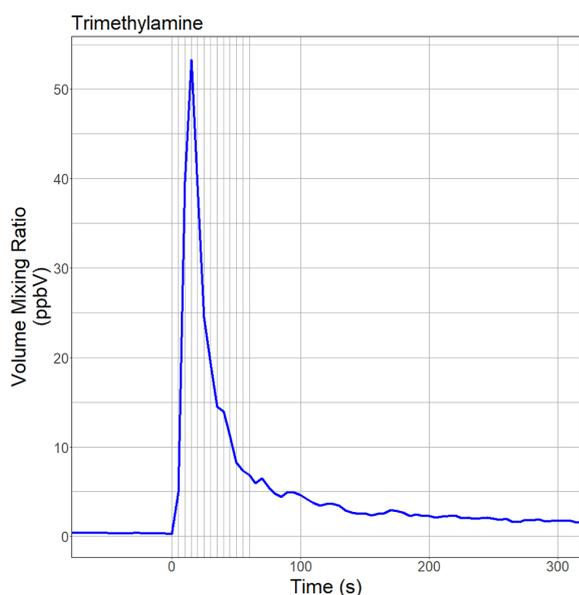
Figure 2. Time series of trimethylamine as measured in laboratory air when a *Chenopodium vulvaria* L. plant was mechanically stressed by tipping a leaf with a pen.

did not make any further attempts to quantify TMA emission rates.

3.2 Field testing: detection of agricultural amines

After the first successful laboratory tests, the instrument was taken to the field. The goal was to measure small alkylamines in ambient air on campus of an agricultural research center. As mentioned in the "Instrument description" section, the prototype PTR-ToF-MS instrument was operated in the NH_4^+ mode.

Figure 3 displays the calibration curves for MMA, DMA and TMA, as obtained from a calibration carried out in the field. The calibration curves show the normalized ion signal response (in normalized counts per second, ncps) as a function of amine volume mixing ratios in the 0 to 10 ppbv range. The signals were normalized to the average NH_4^+ signal (measured on the $^{15}NH_4^+$ isotope signal at m/z 19.031) observed over the course of the experiment. The three amines were detected in their protonated form at m/z 32.049, 46.065 and 60.081, respectively. The only additional signals observed were m/z 44.049 (2.5 %) and m/z 58.065 (4.0 %) for DMA and TMA, respectively. H_2 ejection is a frequently observed minor channel in the CI of amines (Harrison, 1992). No adduct ions were detected due to the high collisional energy of the ions in the FIMR. The protonated amines were detected at a mass-resolving power ($m/\Delta m$) of 3700, 4100 and 4250, respectively. The instrumental response factors (sensitivities) for MMA, DMA and TMA were 114, 156 and 126 ncps ppbv^{-1}, respectively. The instrumental response did not exhibit any humidity dependence (< 3 % analyte ion sig-

nal change over the range of typical ambient humidities). The relative precision (1σ) at the lowest calibration mixing ratio ($\sim$ 2 ppbv) was 4.3 %, 2.2 % and 4.3 % for MMA, DMA and TMA, respectively. The offset in the calibration curves mainly originated in a constant chemical background in the calibration device (LCU) from previous calibrations. The data shown in Fig. 3 were thus not used for deriving instrumental detection limits.

The instrumental response factors of the prototype PTR-ToF-MS analyzer are 1–2 orders of magnitude lower than those reported for commercial VOCUS analyzers (Krechmer et al., 2018; Wang et al., 2020). This is a result of a combination of various factors. First, we generally observe lower instrumental sensitivities when operating PTR-MS instruments in the NH_4^+ mode (Zhu et al., 2018). Second, we set the upper m/z limit in the TOF-MS to $\sim$ 500. Reducing the upper m/z limit to 100 would increase the sensitivity by a factor of 2.2 (higher duty cycle). Third and most importantly, our prototype instrument has a relatively large gap between the FIMR and the skimmer (to increase the flow through the reactor and thereby minimize memory effects), which results in increased ion losses at the end of the FIMR. Fourth, we apply a relatively low RF amplitude to the FIMR because at higher V_{pp}, O_2^+ ions efficiently formed within the FIMR. A high O_2^+ signal on m/z 31.989 severely compromises the detection of MMA at m/z 32.049. Fifth, we also apply a relatively low RF amplitude to the BSQ to avoid strong mass discrimination effects in the m/z 32 to 60 region. The small spread in the MMA, DMA and TMA sensitivity values confirms that no significant mass discrimination occurred in the m/z range of interest.

Prior to starting the measurements, we carried out another field test. Indole was among the analytes of interest for this field study (even though it was later only sporadically detected at very low levels), and laboratory tests had revealed that this amine is particularly sticky. The headspace from a vial containing indole was thus shortly blown towards the instrument inlet, and the protonated indole signal at m/z 118.065 was monitored at 1 s time resolution. Figure 4 shows the time series of indole as observed during this experiment. The initial volume mixing ratio on the order of 100 ppbv decreased by 2 orders of magnitude within 4 s, and background levels were reached within $\sim$ 40 s. We are fully aware that this instrument test deviates from the formal experimental procedure for determining an instrumental response time. However, these data do show the performance of the analyzer under field conditions and allow us to conclude that the new prototype instrument is indeed capable of monitoring rapid changes of sticky amines on the timescale of a few seconds.

Figure 5 shows the time series (5 min averages) of DMA and TMA as measured in ambient air on site at the agricultural research center over a period of 3 d. The instrumental background was stable for both DMA and TMA (see Fig. S2), which resulted in a detection limit (3σ, 5 min sig-

Field Calibration at SHF

(a) Methylamine

$y = 114x + 469, \ r^2 = 0.99$

(b) Dimethylamine

$y = 156x + 176, \ r^2 = 0.99$

(c) Trimethylamine

$y = 126x + 114, \ r^2 = 0.99$

Normalized Ion Count Rate (ncps)

Volume Mixing Ratio (ppbV)
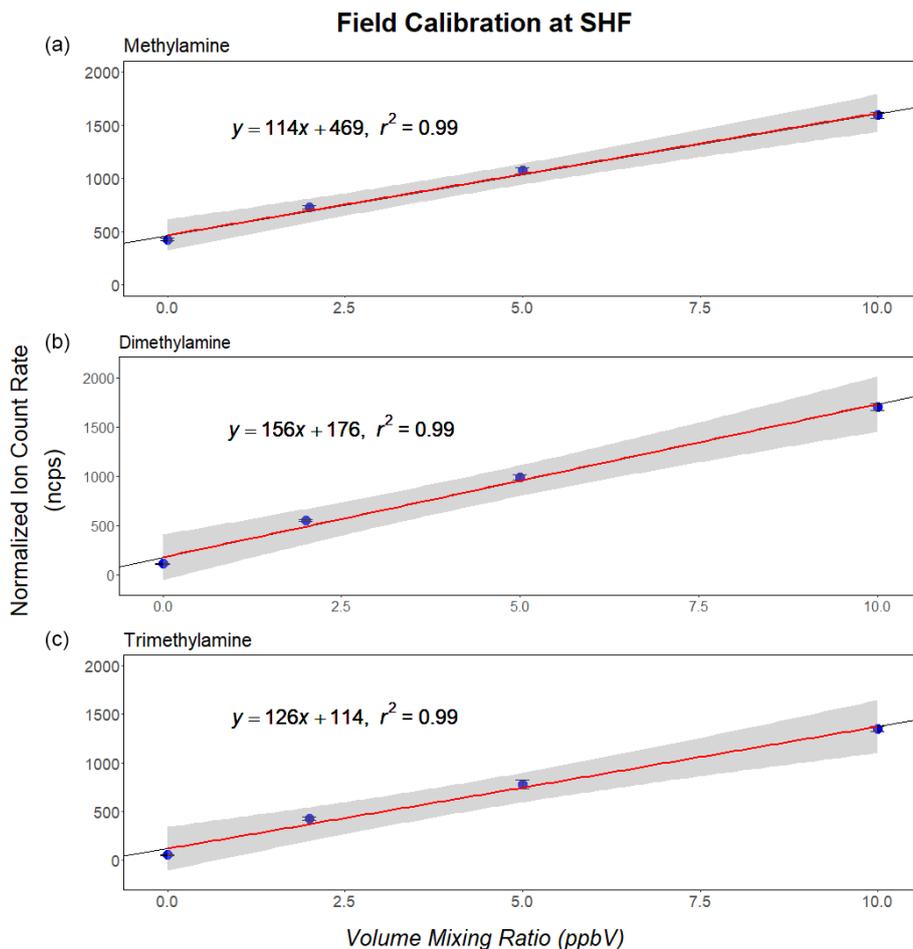
Figure 3. Calibration curves for methylamine **(a)**, dimethylamine **(b)** and trimethylamine **(c)**. The PTR-ToF-MS instrument was operated in the NH_4^+ mode (see text).

Indole

Volume Mixing Ratio (ppbV)
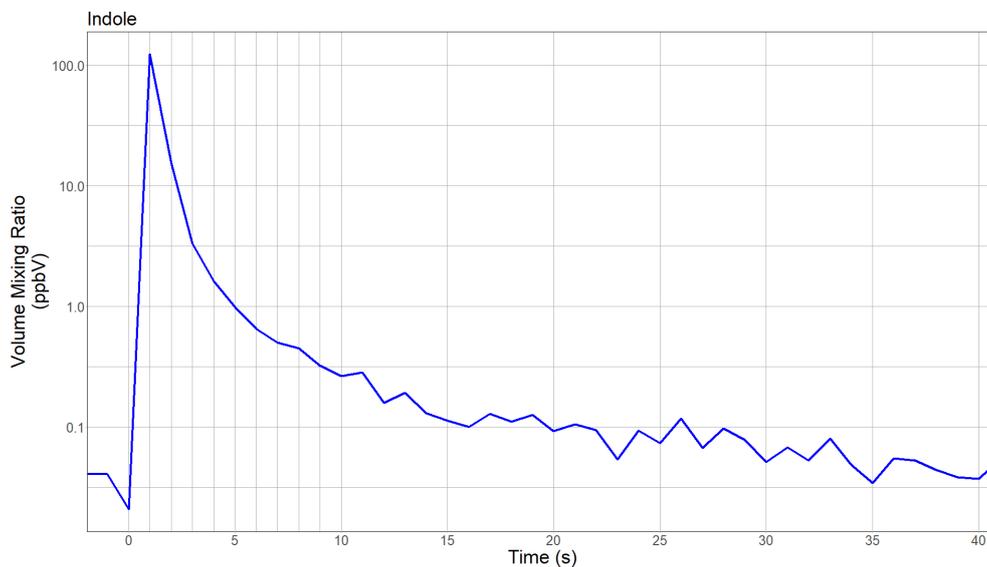
Time (s)

Figure 4. Time evolution of the observed indole volume mixing ratio (VMR) when the headspace from a vial containing indole was shortly blown towards the PTR-ToF-MS instrument in its field configuration.
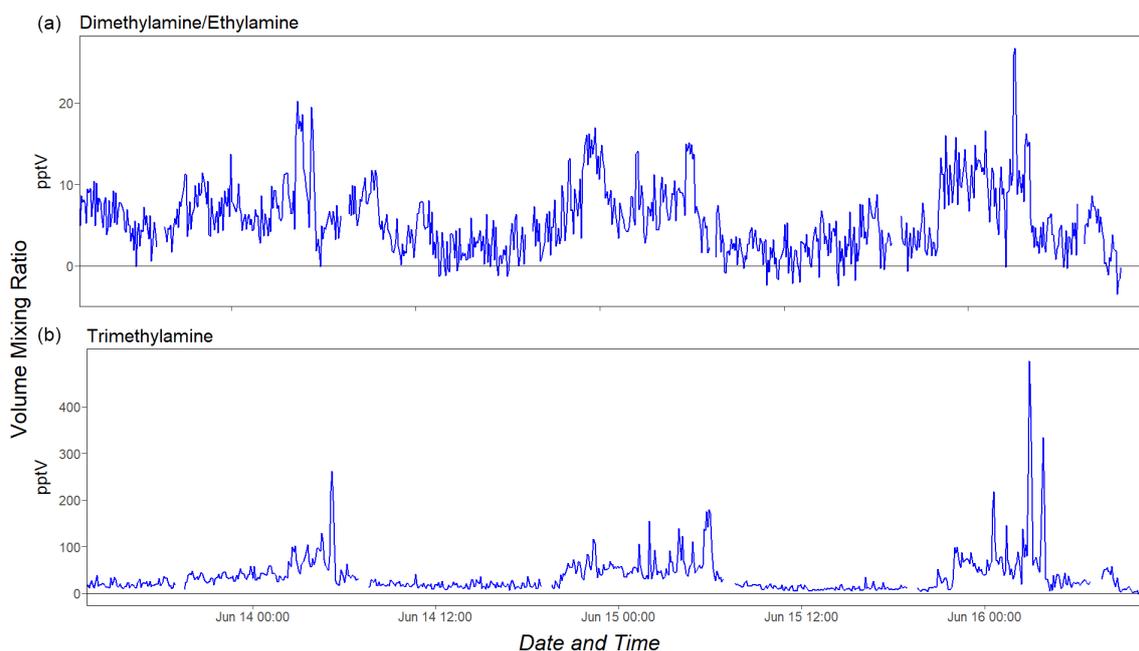
Figure 5. Time series (5 min averages) of dimethylamine/ethylamine **(a)** and trimethylamine **(b)** as observed in ambient air on site of an agricultural research center.
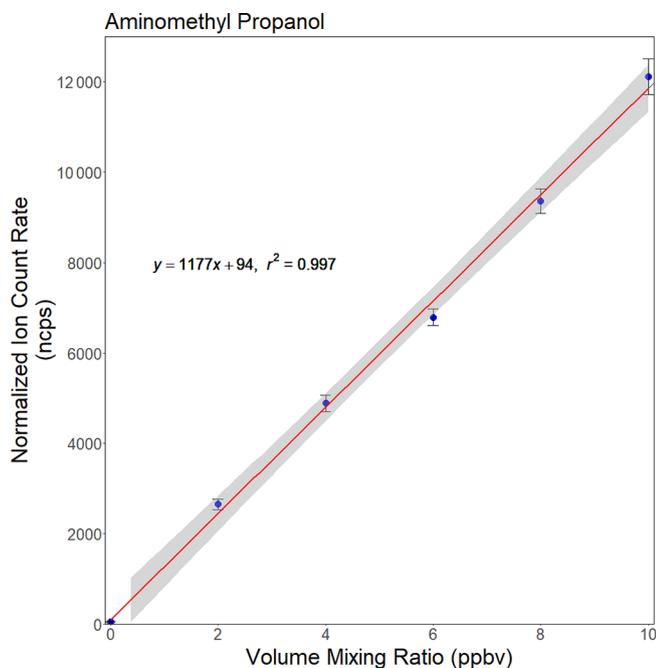
Figure 6. Calibration curve for 2-amino-2-methylpropan-1-ol (AMP). The PTR-ToF-MS instrument was operated in the H_3O^+ mode (see text).

nal integration) of ~ 5 pptv for these two amines. It was not possible to detect protonated MMA (m/z 32.049) because of the strong mass spectral interference from the adjacent O_2^+ peak (m/z 31.989). We subtracted the O_2^+ contribution, but the resulting detection limit (3σ, 5 min signal integration) was ~ 170 pptv. It is important to note that direct-injection CIMS methods do not resolve isomeric species. DMA only has one additional isomer (ethylamine, EA), while TMA has three isomers (ethylmethylamine, propylamine and isopropylamine). Previous work (Schade and Crutzen, 1995, and references therein) found trace levels of both EA and DMA in husbandry emissions, which is why we assign the m/z 46.065 ion signal to both of these compounds. The same literature reports that TMA is the dominant C_3 isomer, which is why we assign the m/z 60.081 signal to TMA only. We observed a clear diurnal pattern in the time profile of both species, with maxima occurring during nighttime when the planetary boundary layer is low.

3.3 Field testing: detection of an industrial amine

The field tests at and near the CO_2 capture plant were carried out with the instrument being operated in the conventional H_3O^+ mode. The calibration curve (Fig. 6) shows the m/z 90.091 normalized ion signal response (in ncps, normalized to the average $H_3O^+ + H_3O^+(H_2O)$ signal observed over the course of the calibration experiment) as a function of the AMP volume mixing ratio. The mass-resolving power ($m/\Delta m$) for this ion signal was 3700.
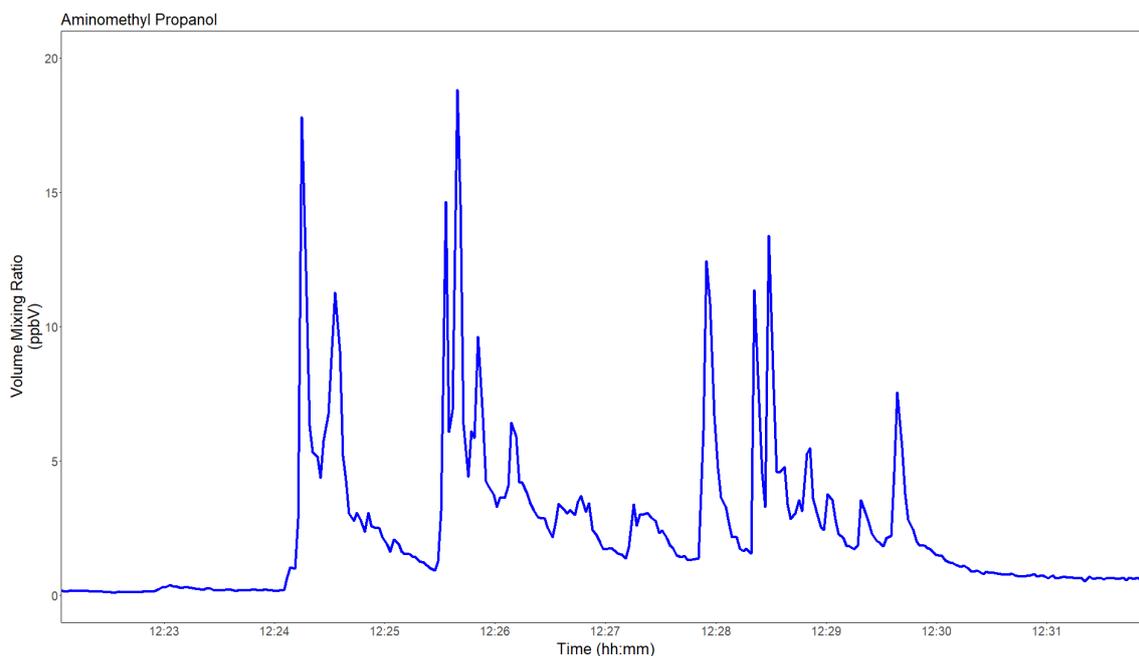
Figure 7. Time series (1 Hz) of 2-amino-2-methylpropan-1-ol (AMP) as measured when ~ 25 ppmv of this industrial amine was deliberately released into the air at approximately 1 m distance from the instrument inlet.
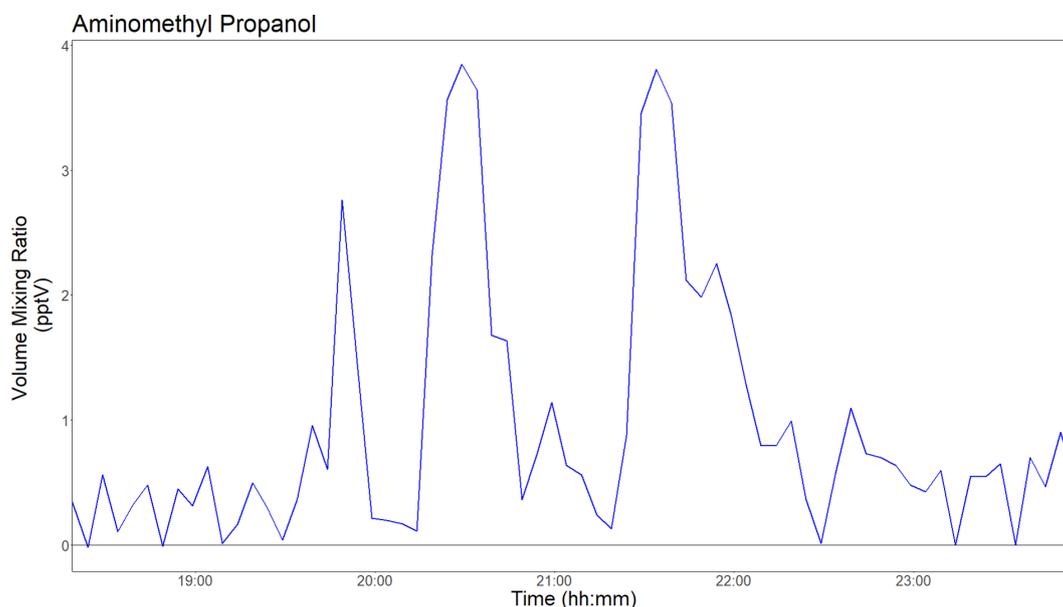
Figure 8. Time series (5 min averages) of 2-amino-2-methylpropan-1-ol (AMP) as measured at Sande, 4.4 km downwind of the TCM CO_2 capture plant. A steady level of ~ 1 ppmv of AMP was released from the stack during the measurement period, which resulted in single-digit pptv enhancements of AMP at the downwind site.

The calibration data show that the prototype PTR-ToF-MS instrument generated a signal response $> 10^3$ ncps ppbv^{-1}. This is still on the lower end of what has been reported for commercial VOCUS analyzers. As mentioned above, this is mainly due to ion losses in the relatively large gap between the FIMR and the skimmer, which is needed for increasing the FIMR flow. The relative precision (1σ) at the lowest calibration mixing ratio (~ 2 ppbv) was $\pm 4.2\%$ for AMP. The offset in the calibration curve was again caused by a constant chemical background in the LCU calibration device and not in the instrument itself. The data shown in Fig. 6 were

thus not used for deriving the instrumental detection limit for AMP.

The first test carried out at TCM was to demonstrate that the new instrument is capable of detecting amine solvent leaks in real time. A gas mixture containing ~ 25 ppmv AMP was deliberately released into the air at approximately 1 m distance from the instrument inlet. The test was carried out during strong and turbulent wind conditions, which are typical for the Norwegian west coast. As seen in Fig. 7, single- to double-digit parts per billion per volume (ppbv) levels of AMP were observed in real time (1 Hz). Notably, the instrument response was immediate, and the signal quickly returned to baseline levels once the artificial leak was closed.

The second test was to demonstrate that the new PTR-ToF-MS analyzer is capable of detecting ultra-trace levels of industrial amines in the atmosphere. During the measurement period, a steady level of ~ 1 ppmv AMP was released to the atmosphere from TCM, while the PTR-ToF-MS instrument sampled atmospheric air ~ 4.4 km downwind. Figure 8 shows 5 min average AMP data collected when the TCM plume crossed the measurement site. The instrumental background was low and stable (0.6 ± 0.2 pptv) throughout the measurement period (see Fig. S3), which resulted in a detection limit (3σ, 5 min signal integration) of ~ 0.5 pptv for AMP. As seen in Fig. 8, at 5 min signal integration variations < 1 pptv can be observed.

4 Conclusions

The PTR-MS technique was developed in the mid-1990ies at the University of Innsbruck. Initial method improvements focused on using different mass analyzers (e.g., Blake et al., 2004; Prazeller et al., 2003). The ion source and drift tube only underwent minor geometrical changes over a period of 2 decades. The past 5 years have, however, seen major developments in the drift tube and ion source design (e.g., Breitenlechner et al., 2017; Krechmer et al., 2018). We have herein presented one additional instrument variation, in which the well-characterized and "clean" HCGD ion source originally described by Hansel et al. (1995) is combined with the recently developed and highly sensitive FIMR design by Krechmer et al. (2018). We have shown data that demonstrate the capabilities of this new instrument in monitoring atmospheric amines at single-digit pptv levels. We have also shown that the new instrument only has minor memory effects for sticky amines, making it capable of monitoring rapid changes of amine levels in the air on the timescale of a few seconds. Further work is however required for achieving a time response of 1 s or less. This could be achieved by further optimizing the gas inlet or by heating the FIMR to $\geq 100\,^\circ$C. We have also made an argument that maximizing the instrument sensitivity should not be the only focus of PTR-MS instrument development and optimization. Minimizing potential neutral and ionic side reactions in the DT, reducing

sample memory effects and eliminating mass discrimination effects over the m/z range of interest are important for generating easily interpretable and quantifiable mass spectra. This is particularly important for the nonexpert user. The PTR-MS method is being rapidly developed in various directions, and different types of PTR-MS instruments and operation modes are being used nowadays for different types of applications. The PTR-ToF-MS presented herein has been optimized for the detection of atmospheric amines, which are currently in the research focus of our group. In future work, we will show how we have used the new prototype PTR-ToF-MS instrument for quantifying amine emission rates from animal husbandry and for investigating the atmospheric impact of amine emissions from CO_2 capture.

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