O_2^+ as reagent ion in the PTR-MS instrument: Detection of gas-phase ammonia

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Abstract

Oxygen was used as a source gas in a conventional Innsbruck PTR-MS instrument to produce O_2^+ ions as chemical ionization (CI) reagents instead of H_3O^+ ions. The use of O_2^+ ions as CI reagents allows for fast, highly sensitive and specific measurements of gas-phase ammonia (NH_3) via the electron transfer reaction $O_2^+ + NH_3 \rightarrow NH_3^+ + O_2$. The instrument was tested to be linear in the 2–2000 ppbv range. Instrument sensitivity was observed to be humidity-independent and amounted to ∼40 cps/ppbv. The instrumental background was determined by sampling NH_3-free air from a heated platinum/palladium catalyst. A humidity-dependent increase of the instrumental background from 70 pptv at dry conditions to 470 pptv at humid conditions was observed. The corresponding 2σ-detection limits at 1 s signal integration time were 90 pptv for dry conditions and 230 pptv for humid conditions, respectively. The observed background may be intrinsically formed in the instrument's ion source but it may also be the result of incomplete NH_3 oxidation in the catalyst used for zeroing. The reported background levels and detection limits are thus to be considered as upper limits. The 1/e response time of the instrument was in the range of 3–5 s. The PTR-MS instrument was successfully deployed in the field to monitor changes in gas-phase NH_3 concentrations in the few seconds to tens of seconds time range. Laboratory intercomparison measurements between the PTR-MS instrument and a commercial NH_3 analyzer (AiRRmonia) were in good agreement. The use of O_2^+ ions as CI reagents will significantly improve the analytical capabilities of the Innsbruck PTR-MS instrument.
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1. Introduction

Ammonia (NH_3) is the most abundant alkaline gas in the atmosphere. It plays an important role in neutralizing acidic gases and aerosol particles and it influences the composition of aerosol particles [1]. It is also suggested that NH_3 takes part in new particle formation in the atmosphere [2] and might therefore be of importance for the atmosphere climate regulation. Anthropogenic sources like livestock waste, application of fertilizers and biomass burning are estimated to be larger than the natural sources mainly from soils and oceans [3]. It is anticipated that the increased use of three way catalysts in automobiles will lead to increased NH_3 emissions in urban areas [4,5]. NH_3 is emitted and taken up by plants. It was found to have a positive effect on plants at moderate concentrations while it is harmful at high concentrations [6]. NH_3 will thus have an impact on the regional air quality as well as on plant biology. There are, however, still large uncertainties in the atmospheric NH_3 cycling mainly due to the lack of highly sensitive, accurate and fast NH_3 sensors with low detection limits.

Until the last decade most atmospheric NH_3 measurements were based on liquid chemistry with low time resolution [7,8 and references therein]. Chemical ionization mass spectrometry (CIMS) has the potential for fast and highly sensitive NH_3 measurements. Selected-ion flow tube mass spectrometry (SIFT-MS) based on proton transfer reactions from H_3O^+ ions (producing NH_4^+ ions) and electron transfer reactions to O_2^+ ions (producing NH_3^+ ions) has been used by Spanel and Smith [9] for on-line NH_3 detection. The SIFT-MS technique is limited in detection limit and has mainly been used for NH_3 analysis in breath [10,11], urine headspace [12] or vehicle exhaust [11] where mixing ratios usually exceed 1 ppmv. Milligan et al. [13] used SIFT-MS to measure NH_3 emissions from fertilized grassland but also then the detection limit was only 50 ppbv.

More sensitive CIMS techniques have been used by two groups in the USA for atmospheric NH_3 measurements. The NOAA-CDS atmospheric pressure ionization instrument [14] and the Georgia Tech low pressure flow tube reactor [15] both use protonated ethanol clusters or protonated acetone clusters as precursor ions to monitor NH_3. An improved airborne version of these CIMS instruments has been recently presented by Nowak et al. [16].

Proton-transfer-reaction mass spectrometry (PTR-MS) is a state-of-the-art CIMS technique for highly sensitive on-line measurements of volatile organic compounds (VOC). The detection limits are in the 10–100 pptv range for typical signal integration times of 1–10 s. PTR-MS is applicable to gas-phase analytes that have proton affinity higher than water (165 kcal mol^{-1} [17]). This applies mostly to organic species but also a few inorganic compounds including NH_3 (204.0 kcal mol^{-1} [17]). PTR-MS can therefore be used for NH_3 monitoring based on proton transfer reaction to form NH_4^+ ions at $m/z = 18$. The PTR-MS instrument suffers, however, from a high instrumental background at $m/z = 18$ due to intrinsic formation of NH_3 in the plasma ion source.

In this paper we propose to use oxygen (O_2) instead of water (H_2O) as source gas for the PTR-MS instrument. In this way the intrinsic formation of NH_3 is greatly reduced and the resulting O_2^+ reagent ions can be used for highly sensitive and specific detection of NH_3 via electron transfer reactions.

2. Experimental

2.1. The PTR-MS instrument

The instrument used here was a standard PTR-MS instrument built at the University of Innsbruck. The PTR-MS instrument is described in great detail elsewhere [18,19]. Only the essentials and the modifications made for NH_3 measurements are outlined here. A hollow cathode discharge and a source drift region act as source for chemical ionization (CI) reagent ions. In PTR-MS routine operation, H_3O^+ ions are generated in the hollow cathode ion source from pure H_2O vapor. The primary ions are injected into a flow drift tube, which is continuously flushed with analyte air at a pressure of approximately 2 mbar. In the flow drift tube, the primary ions undergo reactive collisions with trace analytes following simple pseudo-first order kinetics. Primary and product ions are separated by a quadrupole mass spectrometer and detected using a secondary electron multiplier pulse counting system.

In principle, H_3O^+ ions can be used as CI reagents for NH_3 detection via exothermic proton transfer reactions to produce NH_4^+ ions, in analogy to routine VOC detection by PTR-MS. If supplied with pure H_2O vapor, the PTR-MS hollow cathode ion source, however, produces large amounts (typically several 10^4 cps) of NH_4^+ ions. We presume that NH_3 is generated in the plasma ion source from H_2O and N_2 (leaking from the drift tube into the ion source) as observed in N_2/H_2 microwave discharge plasmas [20] and that NH_4^+ ions are thus formed in the ion source. Several attempts to reduce the NH_4^+ background failed and the lowest achievable background was equivalent to

an ambient NH_3 mixing ratio of ~100 ppbv. This large instrumental background significantly deteriorates the detection limit for NH_3 if the PTR-MS is routinely operated with H_2O as the source gas.

In an alternative approach we used pure oxygen (O_2, purity grade 5.2, Messer Austria, Gumpolskirchen, Austria) as a source gas. O_2 was supplied to the ion source at a flow rate of ~3 STP cm^3 min^{-1}. Extraction voltages into the drift tube were set to 170 and 50 V.

In standard PTR-MS instruments analyte air is supplied to the drift tube at a flow rate of ~30 STP cm^3 min^{-1} via a temperature and pressure controlled 50–100 cm long Silcosteel^{TM} (Restek Inc., Bellefonte, PA, USA) capillary. For this study we reduced the length of the inlet to ~15 cm to minimize potential surface wall interactions, which are critical for NH_3 [21]. The capillary was temperature controlled to 40 °C as well as pressure controlled.

The drift tube voltage was reduced from typical levels of 560 V to a value of 450 V (for details see Section 3.2) corresponding to an E/N ratio (E is the electric field across the drift tube and N is the gas number density) of 108 Td (1 Td = 10^{-17} V cm^2). The drift tube temperature was controlled at 60 °C and the drift tube pressure was kept at 2.0 mbar.

2.2. Generation of NH_3-free air

Two methods for generating NH_3-free air were used. The first method is based on the use of a mixed platinum/palladium (Pt/Pd) catalyst operated at 350 °C to oxidize NH_3 [22]. Removal efficiency was found to be ≥99% when the catalyst was supplied with 75 ppbv of NH_3. A water bubbler and a dew point generator (operating range: 0–25 °C dew point temperature, T_{DP}) were connected upstream the catalyst to produce NH_3-free air at different humidity levels. The catalyst was used for flows of up to 3 STP L min^{-1}.

The second method to produce NH_3-free air was the use of filters coated with oxalic acid [23]. Whatman 41 filters (47 mm) were soaked in 0.01 M oxalic acid in a 16/84 glycerol/methanol solution. The filters were placed in filter holders and dried with synthetic air. The NH_3 collection efficiency of two scrubber filters placed in series has been reported to be 98% for air with a relative humidity of 75%, but decreased with decreasing relative humidity [23]. The scrubber filters could be used with an air flow of up to 15 STP L min^{-1}.

2.3. NH_3 source

A standard for gas phase calibration of NH_3 was prepared using a permeation device containing anhydrous NH_3 (Real Sensors Inc., Hayward, CA, USA). The permeation tube was kept in a temperature controlled oven at 30 °C and was continuously flushed with 40 STP cm^3 min^{-1} of NH_3-free air. The permeation rate given by the supplier was 21 ng min^{-1} ± 50% at 30 °C (gravimetric calibration). Due to the large error given we calibrated the permeation rate using two methods: (1) NH_3 collection with an impinger filled with demineralized water followed by analysis with an AiRRmonia^{TM} instrument (Mecha-

tronics BV, Hoorn, The Netherlands) which itself was calibrated against a liquid standard and (2) NH_3 denuder sampling and analysis as described by Sutton et al. [24]. Both methods consistently yielded a permeation rate in the range of 51–55 ng min^{-1} at 30 °C which is outside the margin of error reported by the supplier.

Using one or two stage dilution with NH_3-free air from the Pt/Pd catalyst and/or the oxalic acid NH_3 scrubber, NH_3 mixing ratios in the range between 2 and 2000 ppbv could be generated.

3. Results

3.1. Reagent ions

In the standard mode of operation the PTR-MS hollow cathode ion source is supplied with 6–12 STP cm^3 min^{-1} of pure H_2O vapor. The resulting primary ion signal spectrum is dominated by $H_3O^+ \cdot H_2O_{n=0,1}$ ions which are typically present with a relative abundance of >99%, with O_2^+ and NO^+ ions being present as minor traces. The primary ion distribution obtained when the PTR-MS hollow cathode ion source is supplied with 3 STP cm^3 min^{-1} of pure O_2 is listed in Table 1. O_2^+ ions dominate the mass spectrum with H_3O^+, $H_3O^+ \cdot H_2O$, NO^+ and NO_2^+ ions being present as traces at the percent level. The relative abundances of H_3O^+ and $H_3O^+ \cdot H_2O$ ions increase with the humidity of the analyte air. Under dry conditions ($T_{DP} = 0$ °C) none of the trace ion signals exceeds 2.2% of the O_2^+ signal and even at humid conditions ($T_{DP} = 25$ °C) the H_3O^+ signal fraction is <10%. We believe that the relative abundances of H_3O^+ and $H_3O^+ \cdot H_2O$ ions could be even further reduced by optimizing the ion source geometry, ion source pressure and the electro-optic configuration. However, for NH_3 detection the presence of minor impurity ions is not critical (see Section 3.3).

We conclude that the PTR-MS hollow cathode ion source delivers a "clean" O_2^+ signal if operated with pure oxygen as a source gas.

3.2. CI detection scheme for NH_3

The recombination energy of O_2^+ is 12.07 eV [25] and the electron transfer reaction is exothermic for analytes having an ionization energy (IE) below that value. IE(NH_3) is 10.07 eV [25] and O_2^+ reacts with NH_3 by electron transfer:

$$O_2^+ + NH_3 \rightarrow NH_3^+ + O_2 \tag{1}$$

Table 1
Relative abundances of major ion signals observed when dry and humid air was supplied to the PTR-MS instrument operated with O_2 as source gas

	m/z				
	19	30	32	37	46
Ion	H_3O^+	NO^+	O_2^+	$H_3O^+ \cdot H_2O$	NO_2^+
Dry air ($T_{DP} = 0$ °C) (%)	0.8	1.3	100	0.1	2.2
Humid air ($T_{DP} = 25$ °C) (%)	9.6	1.5	100	3.6	2.6

Only ion signals with a relative abundance >1% for either of the conditions are listed.

This reaction scheme has been proposed earlier for the detection of NH_3 via SIFT-MS [9]. NH_3^+ detected at *m/z* 17 is the only product ion observed from NH_3 even if humid air ($T_{DP} = 25$ °C) is supplied to the PTR-MS instrument. The application of a drift field effectively prevents the formation of $NH_3^+ \cdot (H_2O)_n$ ($n = 1, 2$) cluster ions which are typically observed in SIFT-MS experiments [26]. Experimentally derived reaction rate coefficients for reaction (1) range from 1.0×10^{-9} to 2.4×10^{-9} cm^3 s^{-1} [27–29]. While the reported accuracy of these rate coefficients is rather low ($\pm 50\%$) these measurements suggest that reaction (1) occurs at or close to (>50%) the collision rate. The calculated collision rate [30] for the used mean relative collision energy in the center-of-mass-system of 0.084 eV [31] is 1.8×10^{-9} cm^3 s^{-1} (calculations based on a dipole moment $\mu(NH_3) = 1.47$ D [32] and a molecular polarizability $\alpha(NH_3) = 2.1$ Å^3 [32]).

Due to the short reaction time window in the PTR-MS drift tube ($\sim$100–150 μs) rapid secondary reactions of NH_3^+ ions with other compounds present in the analyte air (e.g., CH_4, NO, or NH_3 self reaction [33]) have to be considered only if these compounds are present at levels >10 ppmv. N_2, O_2, and CO_2 do not react with NH_3^+ [33], which holds also for the rare gases present in air. However, H_2O may potentially be involved in NH_3^+ secondary ion chemistry as it is the case for other species detected using the PTR-MS technique [34,35]. As pointed out by Kemper at al. [36] the $NH_3^+ + H_2O$ reaction rate coefficient depends on the NH_3^+ internal energy. No H_2O-dependence was reported for SIFT-MS instruments using O_2^+ precursor ions to detect NH_3 which indicates that NH_3^+ and H_2O do not react at thermal conditions in a flow tube. We observed a 20% decrease in the NH_3^+-signal at standard PTR-MS operating conditions ($E/N = 130$ Td) when the dew point temperature of the calibration gas mixture was increased from 0 to 25 °C. No such H_2O-dependence was observed when the E/N ratio was lowered to 108 Td. We conclude that the $NH_3^+ + H_2O$ reaction becomes relevant only at higher E/N ratio ($E/N > 120$ Td). At the lower E/N value used in this study this humidity-dependent NH_3^+ loss channel is suppressed.

3.3. Specificity

A potential problem with the detection of NH_3 as NH_3^+ on *m/z* = 17 is the presence of the isobaric ions OH^+ and/or CH_5^+. We can, however, exclude the presence of both ions with high confidence. OH^+ would rapidly react with both N_2 and O_2, if it was formed anywhere in the ion source, the drift tube or the ion extraction region. CH_5^+ could, in principle, be formed via proton transfer reactions to atmospheric CH_4—in analogy to the formation of CO_2H^+ from the reaction of H_3O^+ with atmospheric CO_2 [37]. This seems unlikely on at least two counts. First, we use O_2^+ ions as main CI reagents which cannot act as proton donors and H_3O^+ ions are present only at minor levels (typically < 10^6 cps). And second, atmospheric CH_4 levels are more than two orders of magnitude lower than atmospheric CO_2 levels.

Any interference may thus only arise from a compound that produces NH_3^+ when reacting with O_2^+ (or H_3O^+, $H_3O^+ \cdot H_2O$,
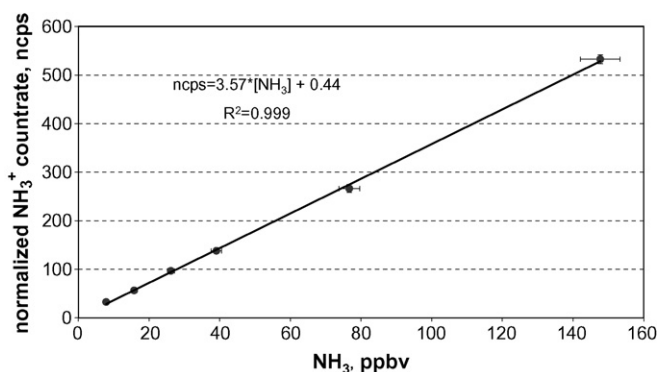
Fig. 1. Calibration curve of the PTR-MS instrument for NH_3 using O_2^+ as reagent ion. The signal is normalized to 1×10^6 cps of O_2^+ resulting in a sensitivity of 3.6 ncps/ppbv. The vertical bars represent the observed variability ($\pm\sigma$) of the signal at each mixing ratio and the horizontal bars represent the uncertainty in the permeation rate of the NH_3 source (53 ± 2 ng min^{-1} at 30 °C).

NO^+, NO_2^+). To the best of our present knowledge, there are no such interferences and we conclude that detection at $m/z = 17$ is specific for NH_3.

3.4. Sensitivity

The instrument was observed to have a linear response to NH_3 in the 2–2000 ppbv range with a sensitivity of $\sim$40 cps/ppbv NH_3 (3.6 ncps/ppbv; normalized to 1×10^6 cps O_2^+ ions, $E/N = 108$ Td) and an $r^2 > 0.999$. The sensitivity increased by a factor of two when the E/N ratio was lowered from 130 to 108 Td. An exemplary calibration curve is shown in Fig. 1. No change ($< \pm 5\%$) in sensitivity was observed when the dew point temperature of the calibration gas mixture was varied between 0 and 25 °C. The sensitivity of the PTR-MS was also calculated following a procedure outlined by Sprung et al. [38]. The following parameters were used for the sensitivity calculation based on simple pseudo first order kinetics: O_2^+ reaction time t, 155 ± 10 μs (Wisthaler, unpublished experimental results), reaction rate coefficient $k = 1.8$ $(+0.3, -0.8) \times 10^{-9}$ cm^3 s^{-1} (see Section 3.2), mass discrimination $NH_3^+/O_2^+ = 0.35 \pm 0.1$ (experimentally determined as outlined in [39]). The calculated sensitivity is 4.25 ncps/ppbv NH_3 which is in reasonable agreement with the measured sensitivity. It should, however, be pointed out that the calculated value is affected by large uncertainties in the input parameters.

The relatively low sensitivity may be explained by the fact that ion extraction from the drift tube and ion injection into the quadrupole MS were not optimized for ions with low m/z values.

3.5. Instrumental background and detection limit

The instrumental background was determined by monitoring the $m/z = 17$ signal when the instrument sampled NH_3-free air. Using dry air ($T_{DP} = 0$ °C) and two Pt/Pd catalysts in series to generate NH_3-free air we observed a minimum background signal equivalent to an NH_3 mixing ratio of 70 pptv. A 1 s signal integration time resulted in a 2σ-detection limit of 90 pptv. A linear increase of the background signal by $\sim$400 pptv was

observed when the dew point temperature of the NH_3-free air was increased from 0 to 25 °C. The detection limit at $T_{DP} = 25$ °C was 230 pptv (2σ, 1 s integration time). The observed background increase may be caused by the intrinsic formation of NH_3 in the ion source from traces of N_2 and H_2O. However, it may also be explained by the fact that the Pt/Pd catalysts do not reduce NH_3 levels below the observed levels and that their efficiency decreases with increasing humidity. The presence of water usually decreases the activity of catalysts for NH_3 oxidation [22, and references therein]. The reported background levels and detection limits have thus to be taken as upper limits. For typical humidity conditions encountered during a 3-week summer field intensive (see Section 3.8) this results in a background variation from 200 to 400 pptv on timescales of hours to days. The corresponding 2σ-detection limits (1 s integration time) are in the 150–210 pptv range. A 10 s signal integration time results in a typical 2σ-detection limit of $\sim$60 pptv.

According to these results further studies on the instrumental background need to be conducted if NH_3 is to be accurately measured at sub-ppbv levels.

3.6. Response time

Performance tests using different inlet materials (Teflon^{TM} PFA, Silcosteel^{TM}, parts of stainless steel) and different inlet temperatures (25–60 °C) showed only minor effects on the instrumental time response. We believe that the interaction of NH_3 with the inner walls of the PTR-MS drift tube (stainless steel rings and Teflon^{TM} PTFE spacers) limits the time response. Desorption of NH_3 from the drift tube walls was observed when the temperature was increased from 40 to 60 °C, and a slightly faster time response was obtained at higher drift tube temperatures. No changes in the time response were observed for different humidity levels of the analyte. Fig. 2 shows exemplary data of the NH_3^+ ion signal decay after removal of a NH_3 gas standard containing 125 ppbv and 1.2 ppmv of NH_3, respectively, from the PTR-MS inlet. Typically observed $1/e^2$ decay times varied between 15 and 30 s, while the $1/e$ decay times were in the 3–5 s regime. Rise times and decay times were similar. The observed variability in the time response of the instrument remains unexplained. The measured response time is longer than time response ($1/e$ decay time <2 s) reported for the new airborne CIMS instrument [16]. We believe that this can be attributed
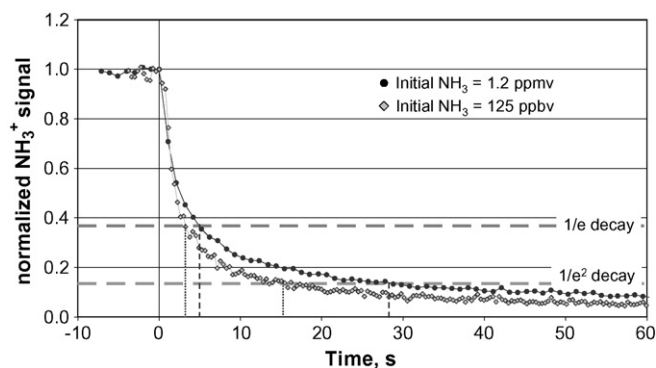

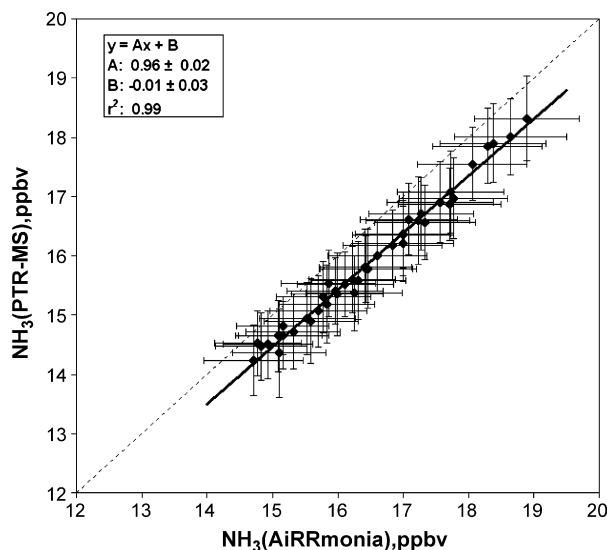Fig. 2. Instrumental NH_3 decay time.

Fig. 3. Comparison between PTR-MS and AiRRmonia data obtained when indoor air was sampled overnight after occupants had left the laboratory. Data points are 10 min means and the error bars represent the observed variability ($\pm\sigma$; see text). The dashed line gives the 1:1 relationship and the solid line gives the result of the reduced mean square regression.

to the fact that the flow through the PTR-MS drift tube is only $\sim$30 STP cm^3 min^{-1} while it is on the order of 2–4 STP L min^{-1} in the CIMS flow tube.

3.7. Laboratory intercomparison measurements

A brief laboratory intercomparison exercise between the PTR-MS instrument and a commercial AiRRmonia instrument for NH$_3$ detection was performed. The working principle and performance characteristics of the AiRRmonia analyzer are described in detail by Erisman et al. [7]. The AiRRmonia was calibrated using aqueous NH$_4^+$ standard solutions. Both instru-

ments monitored the overnight decay of NH$_3$ in indoor air after the occupants had left the laboratory. The PTR-MS sampling integration time on m/z = 17 was 0.5 s, the AiRRmonia analyzer produced one data point every minute. Ten minutes averages were calculated for both datasets and subjected to reduced major axis regression analysis. Ten minutes standard deviation values reflect the instrumental precision and the NH$_3$ decay within the averaging period ($\sim$10–20 pptv min^{-1}). The results are shown in Fig. 3. PTR-MS results were found to be in good agreement with the AiRRMonia data. A more detailed field intercomparison exercise was conducted within the frames of the NitroEurope project (see Section 3.8) in summer 2006. These results will be presented in a separate paper (Norman et al., manuscript in preparation).

3.8. Field measurements

The instrument was tested in the summer 2006 field campaign within the frames of the NitroEurope project (www.nitroeurope.eu) at the field site of Oensingen in Switzerland, described by Flechard et al. [40]. The PTR-MS instrument sampled air from a 17 m long 0.5 in. o.d. PFA tube flushed at 15 L min^{-1}. The inlet was placed 1.2 m above an intensely treated grass field. Fig. 4 shows data from 13 to 14 July including a fertilization period. The fertilization started at the far side of the field which caused a slight increase in the NH$_3$ mixing ratio from 7 ppbv up to several tens of ppbv. When the fertilization an hour later took place right in the vicinity of the measuring site a sharp increase in NH$_3$ levels from 15 ppbv up to 500 ppbv occurred. Also shown in Fig. 4 is a short period of fast (2 Hz) measurements about 3 h after fertilizer application. These results show that the PTR-MS instrument can be used to monitor changes in gas phase NH$_3$ concentrations in the few seconds to tens of seconds time range.
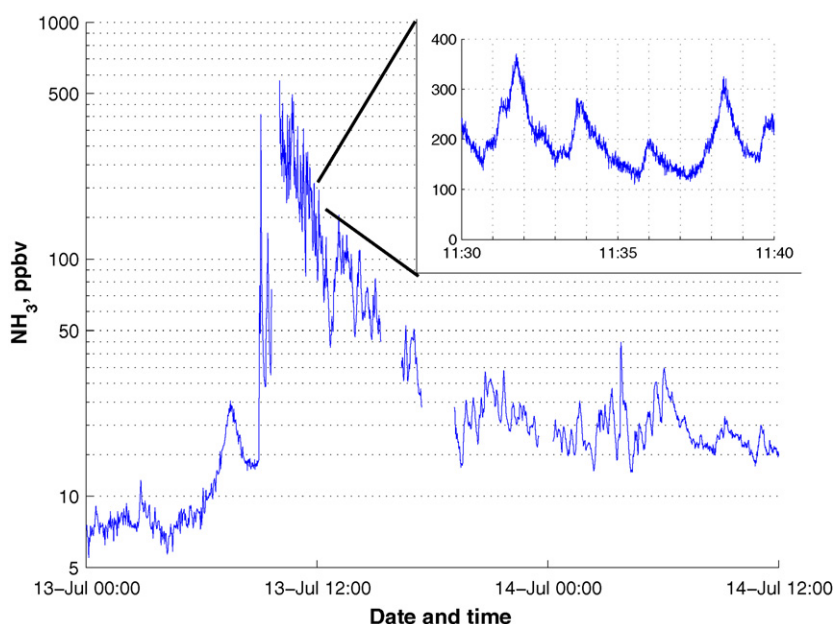

Fig. 4. NH$_3$ mixing ratios observed 125 cm above an intensely managed grass field. Main figure: 1 min values during 13–14 July (shown on logarithmic scale). Inserted figure: 2 Hz data obtained 3 h after fertilizer application (shown on linear scale). Fertilizer application took place between 09:00 and 11:00 on 13th July.

4. Conclusion

We have shown that a conventional Innsbruck PTR-MS instrument can be easily adapted to produce O_2^+ ions as CI reagents. Electron transfer reactions from NH_3 produce a specific ion at $m/z = 17$ (NH_3^+) allowing for fast, sensitive and highly selective measurements of atmospheric NH_3. The instrument response for NH_3 was tested to be linear in the 2–2000 ppbv range. The instrument sensitivity was humidity-independent and amounted to 40 cps/ppbv. When sampling NH_3-free air the instrumental background was found to increase from 70 pptv at dry conditions ($T_{DP} = 0\,^\circ C$) to 470 pptv at humid conditions ($T_{DP} = 25\,^\circ C$). The corresponding detection limits (2σ, 1 s integration time) were 90 pptv for dry conditions and 230 pptv for humid conditions, respectively. The observed background increase could not be unambiguously related to instrument intrinsic processes (e.g., the formation of NH_3 from N_2 and H_2O in the ion source) or a humidity bias in the generation of NH_3-free air (i.e., a humidity-dependent decrease in catalyst activity for NH_3 oxidation). The reported background levels and detection limits have thus to be taken as upper limits. The $1/e$ decay time was in the range of 3–5 s. Field test confirmed the capability to monitor NH_3 variations in the few seconds to tens of seconds time range.

PTR-MS measurements using O_2^+ ions as CI reagents are not only limited to NH_3 detection. Other compounds with ionization energy smaller than the recombination energy of O_2^+ (12.07 eV) are, in principle, detectable [41]. Simultaneously to NH_3 we detected benzene and toluene which in some instances might be useful markers to differentiate between urban and rural air masses.

Acknowledgments

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