

# A novel method for producing $\text{NH}_4^+$ reagent ions in the hollow cathode glow discharge ion source of PTR-MS instruments

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## ABSTRACT

Proton-transfer-reaction mass spectrometry (PTR-MS) is seeing an increased use of  $\text{NH}_4^+$  ions for the detection of amines and labile oxygenated organic compounds.  $\text{NH}_4^+$  ions are usually generated from ammonia or ammonium-containing chemicals. We herein present a simple method for generating  $\text{NH}_4^+$  reagent ions in the hollow cathode glow discharge ion source that nowadays most proton-transfer-reaction mass spectrometry (PTR-MS) instruments are equipped with. We show that  $\text{NH}_4^+$  ions can be generated in high purity and yield by simply introducing a mixture of water vapor and nitrogen in the ion source. We also show that rapid switching ( $\sim 10$  s loss of data) between the  $\text{H}_3\text{O}^+$  and  $\text{NH}_4^+$  operation modes is possible. Our new method can be easily implemented in most PTR-MS instruments that are currently in use, thus opening the possibility to easily operate the PTR-MS analyzer in the  $\text{NH}_4^+$  chemical ionization mode.

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## 1. Introduction

Proton-Transfer-Reaction Mass Spectrometry (PTR-MS) is nowadays widely used in environmental, food and medical sciences to monitor organic trace constituents in air [e.g., 1]. PTR-MS is an online chemical ionization (CI) technique; that is, air is directly introduced into the instrument and analyte ions are generated via gas-phase ion-molecule reactions with pre-generated reagent ions. In the standard PTR-MS operation mode,  $\text{H}_3\text{O}^+$  ions are used as protonating agents for organic analyte molecules [2]. Instruments from different manufacturers and self-built machines vary in their set-up, but the most widely used ion source is a hollow cathode glow discharge (HCGD). Pahl et al. [3] found that  $\text{H}_3\text{O}^+$  ions are formed in high abundance when argon containing trace impurities of water is introduced in a HCGD. A similar HCGD ion source operating on pure water vapor was then implemented in the first PTR-MS instrument [4]. For selected applications, the use of other reagent ions ( $\text{NO}^+$ ,  $\text{O}_2^+$ ,  $\text{Kr}^+$ ,  $\text{Xe}^+$ ) has been proposed [5,6].

$\text{NH}_4^+$  is widely-used as a CI reagent ion outside the PTR-MS community [7,8].  $\text{NH}_4^+$  acts as a specific protonating agent for organic nitrogen bases, and labile organic analytes are often detectable in their unfragmented form as ammonium adducts. In the early days of PTR-MS,  $\text{NH}_4^+$  has been proposed and even used as a reagent ion [9,10] but little follow-up work has been done for almost two decades [11,12]. In the past two years,  $\text{NH}_4^+$  and  $\text{NH}_4^+(\text{H}_2\text{O})$  reagent ions have received increased attention and successfully been used for the detection of amines [13], highly oxidized organic molecules [14], organic radicals [15], small oxygenates [16], ketones and monoterpenes [17], and a peroxide [18].

In all of the studies cited above,  $\text{NH}_4^+$  ions were formed from either gaseous ammonia (pure  $\text{NH}_3$  or  $\text{NH}_3$  diluted in  $\text{N}_2$ ) or from ammonium-containing liquids or solids. The handling of these chemicals constitutes a safety hazard, and the chemicals may not be available when operating in the remote field. In addition, impurities in these chemicals may increase the instrumental background. We will herein present a new method on how to easily produce  $\text{NH}_4^+$  ions in high yield in a HCGD ion source without using ammonia or ammonium-containing chemicals.

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## 2. Method

The data presented in this study were obtained with a PTR-TOF 6000X2 instrument (Ionicon Analytik GmbH, Innsbruck, Austria). All past and present PTR-MS instrument types commercialized by this manufacturer include the same or very similar HCGD ion source, meaning that the results can be extrapolated to >350 instruments.

Fig. 1 shows a sketch of the HCGD ion source. The source gas is introduced to the cylindrical hollow anode. We fed a mixture of water ( $\text{H}_2\text{O}$ ) vapor and ultrapure nitrogen ( $\text{N}_2$ , purity 6.0; Messer Austria GmbH, Gumpoldskirchen, Austria) to the ion source via two digital mass flow controllers (High-Tech B.V., Ruurlo, The Netherlands). PTR-MS instruments in the “switchable reagent ion” (SRI) configuration [5] are equipped with three mass flow controllers, meaning that no instrument modifications are required for reproducing our experimental set-up. The source gas flows through the hollow anode-cathode, passes through the exit lens orifice, and enters the so-called source drift region (SDR) from where it is pumped out. The pressure in the ion source is defined by the mass flow rates of  $\text{H}_2\text{O}$  ( $\Phi_{\text{H}_2\text{O}}$ ) and  $\text{N}_2$  ( $\Phi_{\text{N}_2}$ ) and the setting of the so-called source valve (SV), which is a digitally controllable proportional valve (Bürkert Fluid Control Systems, Ingelfingen, Germany). The SV is installed in all SRI-PTR-MS instruments to control and vary the flow resistance in the pump out line. The optimized flow and valve settings are a result of this work and thus presented in the Results section. Older PTR-MS instruments which do not include the SRI option need to be retrofitted with a second mass flow controller and the SV for reproducing the results presented herein.

Fig. 1 also shows the electrical configuration of the HCGD ion source. A high voltage is applied between the hollow anode and the

hollow cathode which results in the formation of a stable current-limited ( $I_{\text{hc}}$ ) plasma. A DC voltage ( $U_s$ ) is applied for extracting cations from the negative glow region (Fig. 1, in violet) into the SDR. A DC voltage ( $U_{\text{so}}$ ) is applied for extracting the reagent ions from the SDR into the drift tube, *i.e.* where the ion-molecule reactions between the reagent ions and the analyte molecules occur. The optimized settings for these voltages are again a result of this work and thus also presented in the Results section.

## 3. Results and discussion

When a PTR-MS instrument is operated in the  $\text{H}_3\text{O}^+$  mode,  $\text{NH}_4^+$  ions are usually formed in the HCGD ion source as a nuisance [19]. It is well-documented in the literature that  $\text{NH}_3$  efficiently forms in a low-pressure plasma via dissociation of  $\text{N}_2$  and  $\text{H}_2$  and the subsequent reaction of N and H radicals on the walls of the ion source [20,21]. The same process is believed to generate  $\text{NH}_3$  in the PTR-MS HCGD ion source when  $\text{N}_2$  efficiently diffuses back from the drift tube to the  $\text{H}_2\text{O}$  plasma region at low pressure.  $\text{NH}_3$  formed on the electrode walls desorbs, reacts with  $\text{H}_3\text{O}^+$  ions and generates  $\text{NH}_4^+$  ions (typically  $\leq 0.1\%$  of  $\text{H}_3\text{O}^+$ ). It is straightforward to exploit this mechanism for producing  $\text{NH}_4^+$  ions in high yield in the HCGD ion source of PTR-MS instruments. It is basically sufficient to feed the plasma with both  $\text{H}_2\text{O}$  and  $\text{N}_2$ , and to make minor adjustments to the pressure and the electric potentials applied to the ion source lenses. Table 1 summarizes the optimized settings we used for operating the HCGD ion source in the  $\text{NH}_4^+$  and  $\text{H}_3\text{O}^+$  mode, respectively. The reader should note that it is not essential to exactly reproduce the listed settings. For running the PTR-MS instrument in the  $\text{NH}_4^+$  mode, we recommend keeping the total flow ( $\Phi_{\text{H}_2\text{O}} + \Phi_{\text{N}_2}$ ) in the 5–7 sccm range and the  $\Phi_{\text{N}_2}/\Phi_{\text{H}_2\text{O}}$  ratio between 0.5 and 1.0. For generating  $\text{NH}_4^+$  ions in high purity, it is important to reduce the SV opening to 40–45%.

The ions generated in the HCGD ion source when operated in the  $\text{NH}_4^+$  mode are shown in Fig. 2.  $\text{NH}_4^+$  (100%) ions dominate the mass spectrum; impurity ions include  $\text{H}_3\text{O}^+$  (0.7%),  $\text{NO}^+$  (0.2%),  $\text{O}_2^+$  (0.1%),  $\text{NH}_4^+(\text{NH}_3)$  (0.6%), and  $\text{NH}_4^+(\text{H}_2\text{O})$  (0.7%) ions. The numbers in parentheses are relative abundances. Absolute  $\text{NH}_4^+$  signal count rates of a few times  $10^7$  counts per second (cps) can be easily obtained with a PTR-TOF 6000X2 instrument, which is comparable to the reagent ion count rate in the  $\text{H}_3\text{O}^+$  mode. Since the detector is in saturation at such high count rates, we used the  $^{15}\text{NH}_4^+$  isotopologue signal ( $m/z$  19.031) with a relative abundance 0.365% for determining the reagent ion count rate. Note that abundances of the  $\text{NH}_4^+(\text{NH}_3)$  and  $\text{NH}_4^+(\text{H}_2\text{O})$  cluster ions will depend upon the electric field strength, pressure and temperature in the drift tube and upon the ion extraction conditions.

For selected applications, it may be desirable to periodically switch between  $\text{H}_3\text{O}^+$  and  $\text{NH}_4^+$  reagent ions. Since PTR-MS is often used to monitor chemical variations in the seconds to minutes

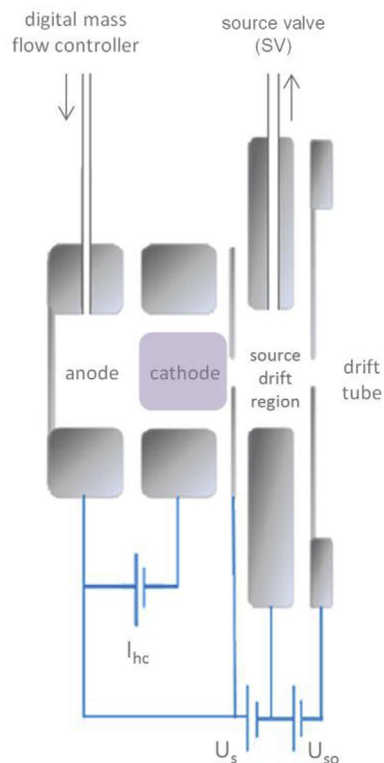


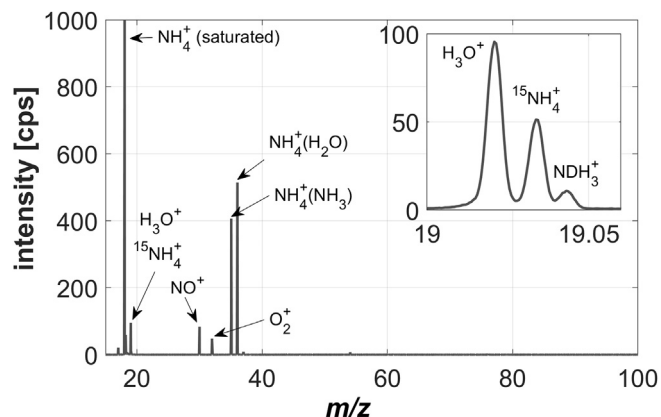
Fig. 1. Schematic drawing of the HCGD ion source that is implemented in most PTR-MS instruments currently in use.

Table 1

Typical ion source settings for operating the HCGD ion source in the  $\text{NH}_4^+$  and  $\text{H}_3\text{O}^+$  mode, respectively.

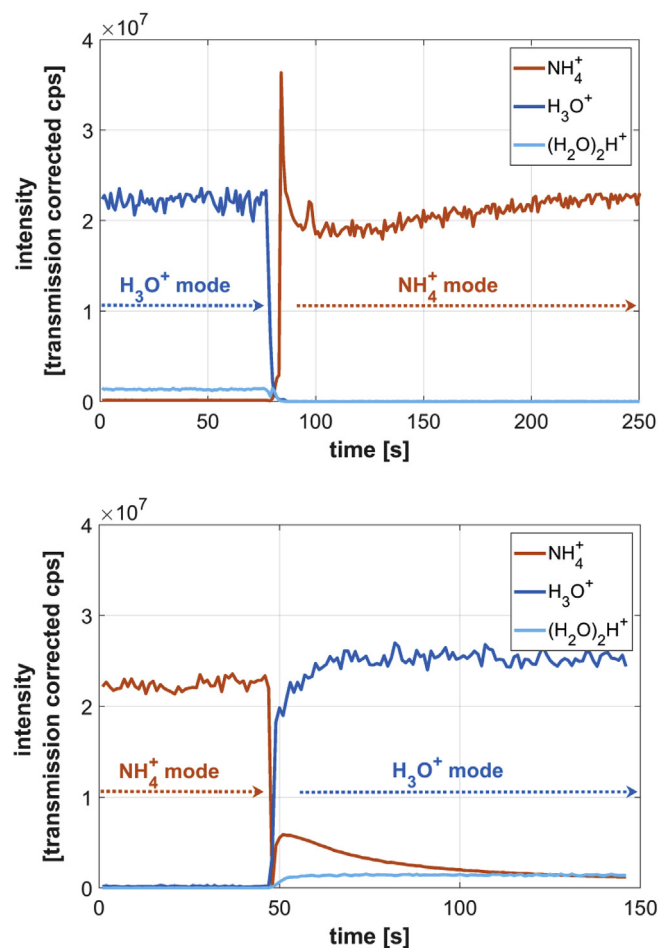
Parameter	$\text{NH}_4^+$	$\text{H}_3\text{O}^+$	Unit
SV	45	50	%
$U_s$	150	150	V
$U_{\text{so}}$	100	110	V
$I_{\text{hc}}$	4	4	mV
$\Phi_{\text{H}_2\text{O}}$	3	7	sccm
$\Phi_{\text{N}_2}$	2	0	sccm

Note that the MFC conversion factor was 1.00 for the measurement of both  $\Phi_{\text{H}_2\text{O}}$  and  $\Phi_{\text{N}_2}$ .



**Fig. 2.** Mass spectrum obtained when a mixture of  $N_2$  and  $H_2O$  was fed to the PTR-MS HCGD ion source. The insert shows the high resolution mass spectrum at  $m/z$  19, with the  $^{15}NH_4^+$  isotopologue signal being used for determining the reagent ion count rate.

regime, it is important to determine how quick the transition between different reagent ions can be effected. In our test, we switched between the two settings listed in Table 1. Fig. 3 (upper panel) shows that the transition from  $H_3O^+$  to  $NH_4^+$  reagent ions can be effected within 10 s, which is basically the time required to stabilize the plasma in the ion source and the pressure in the drift tube. The analysis of PTR-MS data routinely involves normalization



**Fig. 3.** Time series showing the fast switching from  $H_3O^+$  to  $NH_4^+$  mode (upper panel) and  $NH_4^+$  to  $H_3O^+$  (lower panel).

towards the reagent ion signal to account for variations in the HCGD ion source output. The small variations in the  $NH_4^+$  signal after the initial spike can thus be easily corrected for. Fig. 3 (lower panel) shows that the transition from the  $NH_4^+$  mode to the  $H_3O^+$  mode can be effected equally fast. After switching,  $NH_4^+$  ions do, however, remain present in high relative abundance for several minutes. This is caused by the stickiness of  $NH_3$ , slowly desorbing from the stainless steel surfaces in the ion source and SDR. It is worth noting that the presence of elevated levels of  $NH_4^+$  ions is not problematic for most measurements in the standard  $H_3O^+$  operation mode since  $NH_4^+$  ions only react with few selected analytes (e.g., amines).

#### 4. Conclusion

We have shown that  $NH_4^+$  ions are formed in high purity and yield in a HCGD ion source that is fed with water vapor and nitrogen. Our new method allows operating PTR-MS instruments in the  $NH_4^+$  mode without using ammonia or ammonium-containing chemicals. Rapid switching ( $\sim 10$  s loss of data) between the  $H_3O^+$  and  $NH_4^+$  operation modes is possible. Our new method can be easily implemented on all PTR-MS instruments including the SRI option. It opens the possibility to easily operate the PTR-MS analyzer in the  $NH_4^+$  chemical ionization mode which is increasingly being used for detecting amines and labile oxygenated organic compounds.

#### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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