

# Proton Transfer Mass Spectrometry (PT-MS) with $H_3^+$ as reagent ions

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## Introduction

### Challenge:

- Establish a universally applicable protonation source with no significant electrical field gradients present in the ionization region
- Adaptation of such ion source to a commercially available mass spectrometer (MS)
- Possibility to switch cleanly between charge transfer (CT) and proton transfer (PT) ionization mode

### Implementation:

- Application of  $H_3^+$  as the main primary charge carrier → one of the strongest known gas phase acids
- The Helium metastable enriched effluent of a DC-micro plasma source (PS) is mixed with a low-volume Hydrogen gas flow
- In a multi-stage process  $H_3^+$  is formed, with primary ionization of  $H_2$  and subsequent reactions with neutral Hydrogen [1]
- Spatial separation of the primary proton carrier generation and analyte ionization region

## Methods

### Detection

#### Mass spectrometer [2]

- The PT stage is directly coupled to a ToFwerk CTOF mass analyzer equipped with a custom ion transfer stage
- Narrow mass range filtering of reagent and carrier gas ions or other dominating ionic species allows the efficient enhancement of the dynamic range of the TOF mass analyzer

### Ionization

#### Protonation stage

- As protonation stage ("ion source") the first intermediate pressure chamber between skimmer and sampler is used
- The analyte gas stream is sampled through an orifice with less than 1 mm diameter
- Orthogonal arrangement of analyte delivery, plasma source, and skimmer

#### Plasma source

- Micro plasma operated with Helium 5.0 (Messer Industriegase GmbH, Germany)
- Hydrogen is supplied through a custom 3-way chamber ("T-piece"), with  $H_2$  mixing ratios ranging from 15 ppmV up to 15 %V in the plasma effluent
- Expansion of the reagent gas mixture into the first pressure stage ("ionization region") held at approximately 2 mbar
- All gas flows are controlled by mass flow controllers (MKS Instruments Deutschland GmbH, Germany)

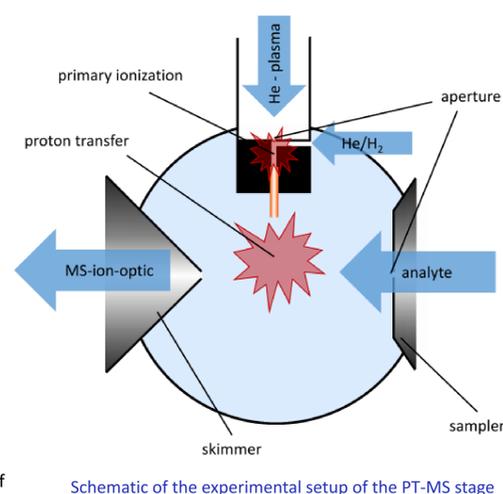
## Experimental Setup

### PT-MS stage:

- First pumping stage of a ToFwerk CTOF with custom designed ion transfer optics [2]
- Orthogonal arrangement of the plasma source with respect to the skimmer
- Windows allow visual inspection of the reaction region
- Bath gas pressure of approximately 2 mbar depending on flow rates

### Plasma source:

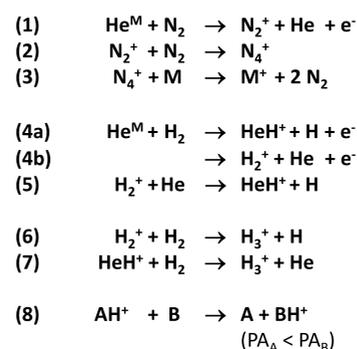
- DC-Plasma operating with Helium at reduced pressure
- Helium metastable enriched effluent is expanded in a gas flow of either pure Helium or a  $He/H_2$  mixture
- "T-piece" arrangement allows the spatial separation of reagent ion preparation and analyte ionization region
- For an enhanced separation of these two zones a piece of an uncoated quartz GC-capillary was tested



Schematic of the experimental setup of the PT-MS stage

## Primary Proton Carrier

- The formation of the primary charge carriers is driven in the reaction cascades 1-2 (CT) and 4-7 (PT)
- The plasma produces metastable Helium atoms ( $He^M$ ) which are expanded into a Helium gas flow containing approximately 750 ppmV  $H_2$
- Since plasma-generated cations cannot not leave the primary PS region, reagent ions are restricted to  $HeH^+$ ,  $H_2^+$  and  $H_3^+$
- The proton is then transferred collisionally controlled (in the ionization chamber held at about 2 mbar) via reaction 8 according to the proton affinities listed in Table 1
- As long as the measurement is taking place in  $N_2$  as bath gas, the main reagent species is restricted to  $N_2H^+$
- Therefore, with  $N_2$  as bath gas it is possible to observe  $XeH^+$  ( $PA_{N_2} < PA_{Xe}$ ) but not  $KrH^+$  ( $PA_{N_2} > PA_{Kr}$ )
- In the absence of  $N_2$  and He as carrier gas  $KrH^+$  is observed as well (see Figure 1)



Reaction system for CT mode (1 - 3) and PT-MS mode (3-8)

Analyte	Proton affinity [kJ/mol]
Helium	177.8
Neon	198.8
Argon	369.2
Oxygen	421.0
Hydrogen	422.3
Krypton	424.6
Nitrogen	493.8
Xenon	499.6
Water	691.0
Toluene	784.0

Table 1: Proton affinities of relevant matrix gases as well as Toluene as analyte for PT-MS [3]

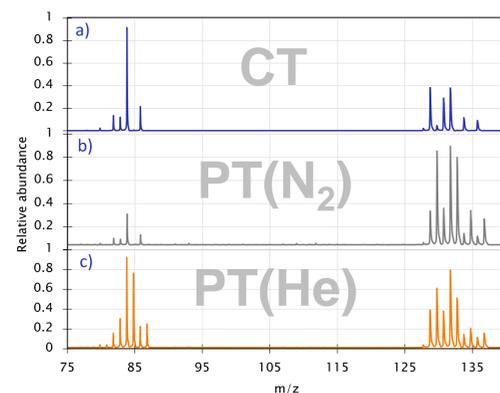


Figure 1: PT-MS mass spectra of Kr and Xe (10 ppmV each); a) charge transfer; b) proton transfer,  $N_2$  as carrier gas; c) proton transfer, He as carrier gas

## Proton Transfer vs. Charge Transfer

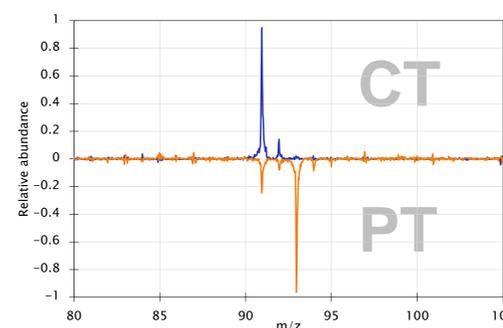


Figure 2: Mass spectra of Toluene in CT (top) and PT (bottom) mode; bath gas  $N_2$ ; 1 ppbV Toluene; 1 sec. acquisition time

- Switching between charge transfer and proton transfer mode simply by adding Hydrogen to the Helium gas flow
- The appearing analyte species is switching from  $M^+$  and/or fragments to mainly  $[M+H]^+$
- Clearly the protonating mode leads to less fragmentation (see also Figure 4)
- Depending on the detailed setup the analytical performance of the system is comparable in both modes
- By using the GC-capillary the degree of protonation ( $[M-H]^+/[M+H]^+$ ) is higher while the signal intensity decreases

Figure 3: Intensities of different Toluene ion signals depending on the Hydrogen mixing ratio; m/z 77 and 105 on secondary axis; 10 ppmV Toluene, setup without GC-capillary

- By changing the mixing ratio of  $H_2$  the degree of protonation is adjustable
- As demonstrated for Toluene (see Figure 3) with increasing  $H_2$  mixing ratio
  - The abundance of the fragment ion m/z 91 decreases
  - The product ion intensity (m/z 105) of the ion molecular reaction of m/z 91 and neutral Toluene decreases
  - The intensity of  $[M+H]^+$  (m/z 93) and the reaction product ion m/z 77 increases
- By further increasing  $H_2$  mixing ratio the intensities of all signals decrease

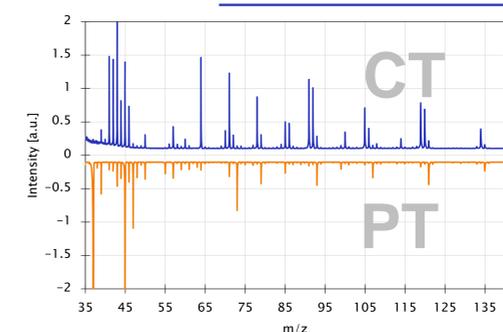
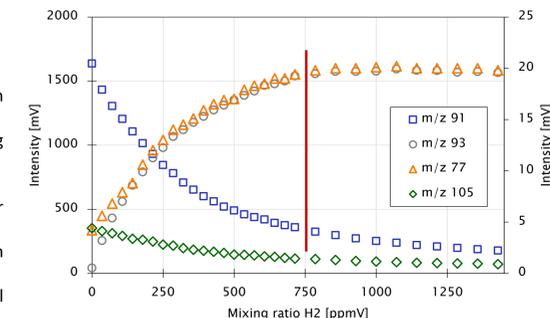


Figure 4: Mass spectra of a mixture of volatile organic compounds (VOCs) in synthetic air; top: ionized via charge transfer; bottom: with 750 ppmV  $H_2$  present; VOCs are present at ppbV mixing ratios

- In CT mode most of the VOCs show two or more ionic species around the radical cation (e.g.  $M^+$ ,  $[M-H]^+$ , ...)
- In PT mode the spectrum is far less congested
- Most species appear as  $[M+H]^+$
- In both modes all compounds present in the mixture are identified

## Proton Capacity

- For analytical applications it is necessary to ensure a large proton capacity which allows to quantify
  - multiple compounds at the same time
  - trace compounds in the presence of large excess amounts of other analytes
- To determine the proton capacity the extent of protonation of Xenon is measured while increasing the mixing ratio of Toluene
  - 10 ppmV Xenon/Krypton in  $N_2$
  - 10 ppbV to 400 ppmV Toluene
- Over the entire range the ratios  $Xe/XeH^+$  and  $[M-H]^+/[M+H]^+$  of Toluene are virtually constant
- Above 400 ppmV Toluene it appears as if the Xenon signal decreases slightly
- The  $[M+H]^+$  signal of Toluene exhibits a linear response over the full range spanning 5 orders of magnitude

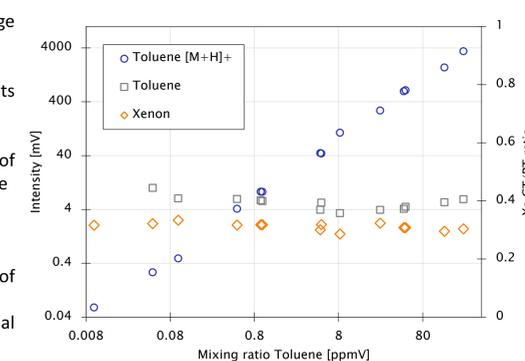


Figure 6: CT/PT ratio of Xenon at increasing mixing ratios of Toluene

## Conclusions

### Instrumentation:

- New powerful ionization source fully compatible for operation with a ToFwerk CTOF for PT-MS measurements
- "T-piece" geometry allows the separation of primary plasma, reagent ion formation and analyte ionization region, respectively
- Implementation of a GC-capillary leads to better protonation degrees but decreased sensitivity
- The protonation capacity of the source allows to fully protonate more than 400 ppmV analyte without observing competitive reactions

### Mechanism:

- With Kr/Xe in He as analytes it is unequivocally demonstrated that the primary proton carrier must be either  $H_3^+$ ,  $HeH^+$ , or  $H_2^+$ 
  - It is speculated that  $HeH^+$  and  $H_2^+$  are short-lived intermediates and do not leave the "T-piece" chamber
- Ionization in PT mode leads to less fragmentation as compared to CT mode

### Outlook:

- To minimize the Helium consumption,  $N_2$  as bath gas is currently investigated (formation of  $N_2H^+$  as highly acidic reagent ions)
- Further improvements of the geometry with focus on replacing the GC-capillary
- Investigations on the proton capacity at analyte mixing ratios exceeding 400 ppmV
- Measurements of atmospheric degradation reactions in the gas phase
- Investigations at strongly elevated water mixing ratios since water clusters represent a sink of protons

## Literature

- A.J. Dempster, L.II. The ionization and dissociation of hydrogen molecules and the formation of  $H_3^+$  (late 1852), *Philosophical Magazine Series 6*, 1916, 185, 438
- Brachthaeuser, Y.; Mueller, D.; Kersten, H.; Brockmann, K.; Benter, T., Development of a compact multiple-ionization-stage TOF mass analyzer system for trace component monitoring within chemically challenging process gas matrices, *62nd ASMS Conference on Mass Spectrometry and Allied Topics*, Baltimore, MD, USA (2014).
- E.P. Hunter and S.G. Lias, "Proton Affinity Evaluation" in *NIST Chemistry WebBook, NIST Standard Reference Database Number 69*, Eds. P.J. Linstrom and W.G. Mallard, National Institute of Standards and Technology, Gaithersburg MD, 20899, <http://webbook.nist.gov>, (retrieved May 11, 2015).

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