H_2 plasma for the generation of protonation reagents with a standard APPI power supply

Tobias Kutsch, Kai Kroll, Kirsten Haberer, Thorsten Benter, Hendrik Kersten

Physical & Theoretical Chemistry
Wuppertal, Germany
Institute for Pure and Applied Mass Spectrometry

Introduction

In the long term we pursue the design of a plasma source for selective preparation of protonation reagents to be used with most standard mass spectrometers.

Choice of the power supply

APPI (VUV lamp) RF power supplies are readily available for a broad range of MS and fully integrated in the respective hard- and software. Moreover, they are known for their stability and robustness [1].

Discharge characteristics

The discharge is classified as a high density plasma in an electrodeless, helical resonator configuration [2]. Typical operation pressures range between 10^{-1} and 10^{1} mbar, which is compatible with the conditions in the first differentially pumped stages of most API instruments.

Choice of discharge gas

H_2 is cheap, readily available, and safely supplied using modern gas-generators. The discharge characteristics are closest to helium and with sufficient collisions abundant H_3^+ is selectively prepared as the initial single protonation reagent.

Question of concern in this contribution:

Can these power supplies sustain an open H_2-plasma for the preparation of sufficient amounts of cleanly prepared protonation reagents to achieve pptV level detection limits while maintaining kinetic control in the ion source?

Methods

MS	H-TOF with custom ion transfer optics (TOFWerk AG, Switzerland) Quad-MS HPR-60 (Hiden Analytical, UK)
RF power supplies	Syagen/Morpho APPI power supplies compatible with: (i) Thermo Fisher instruments (ii) Waters instruments
gases	H_2 and He (99.999 %; Messer Group GmbH, Germany) 1 ppmV benzene, toluene, xylene (BTX) in N_2 (custom)
current meter	610C (Keithley Instruments, USA)
glass tubes	12 mm o.d., 10.1 mm i.d. (#8252, Schott AG, Germany)
UV/VIS spectrometer	AvaSpec-3848 (Avantes BV, Eerbeek, The Netherlands

Experimental Setups

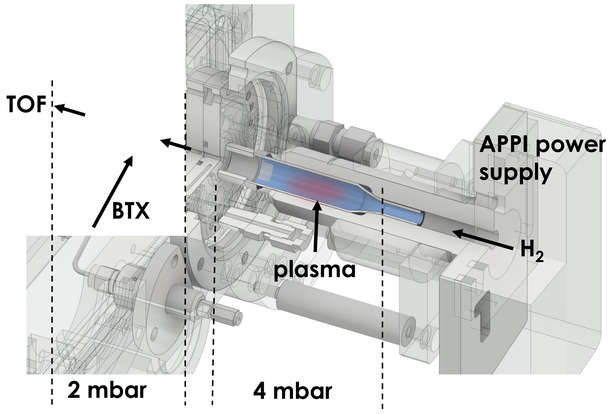

Fig. 2: Experimental setup with a custom RF discharge design and the integrated APPI power supply attached to a TOF MS.

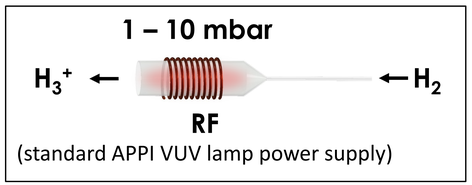

Fig. 2: Schematic of the general setup.

flow rates: 0 – 20 sccm

ignition pressure: H_2 (0.8 – 5 mbar)
He (0.6 – 25 mbar)

operating pressure: H_2 (0.8 – 10 mbar)
He (0.5 – 112 mbar)

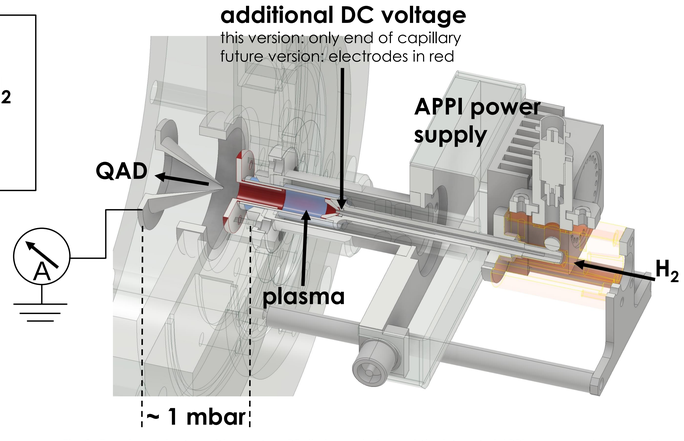

Fig. 3: Experimental setup with a custom RF discharge design and the integrated APPI power supply attached to a quadrupole MS. The current meter was connected to the first skimmer.

Experimental Results

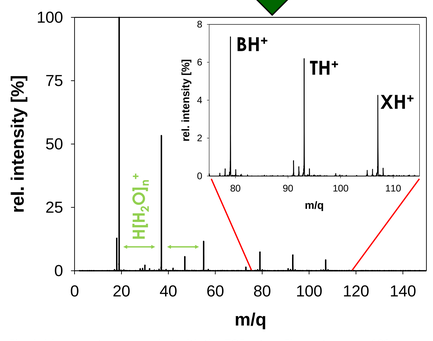

Fig. 4: Mass spectrum recorded with the TOF setup. Flow rates were 100 sccm BTX and 1 sccm H_2.

Significant proton bound water cluster formation!

(impure H_2 and long reaction times in the plasma region)

➧ ***needs to be reduced***

Lack of concentration overlap between analyte and protonation reagent.

➧ ***smarter design required***

pressure optimum

(quadrupole setup)

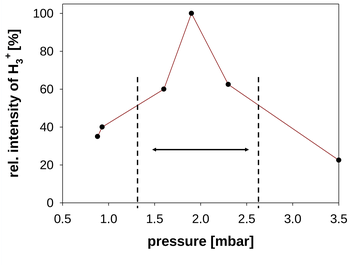

Fig. 7: H_3^+ intensity as a function of pressure in the first differentially pumped region of the quadrupole system.

Narrow pressure optimum.

Owing to the open geometry in the quad setup, any pressure changes significantly ***affect*** the ***plasma dynamics*** as well as the overall ***ion transfer*** and subsequent ***ion molecule reactions***.

➧ ***precise pressure control required***

Impact of an additional DC voltage?

(quadrupole setup)

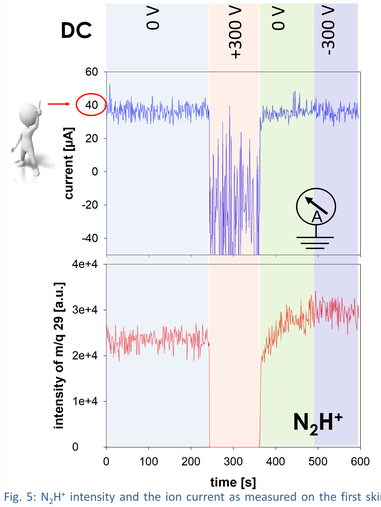

Fig. 5: N_2H^+ intensity and the ion current as measured on the first skimmer in the quadrupole setup. Both as a function of an applied DC voltage on the capillary end as shown in fig. 3. NOTE: *red electrodes are currently fabricated!*

Yes… however, not as expected.

The positive ion current measured on the first skimmer vanishes upon application of a positive voltage on the capillary end cap?

Under selected conditions initially formed H_3^+ is still present as the most abundant peak (not shown). As in fig. 4, the plasma gases need to be of higher purity.

➧ ***high purity H_2 needed***

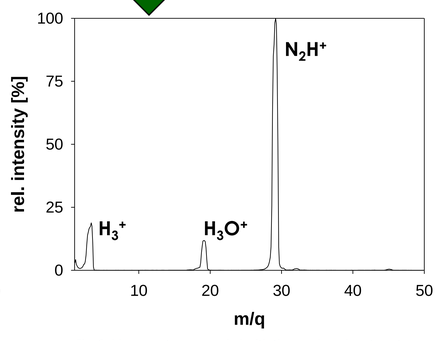

Fig. 6: Mass spectrum recorded with the quadrupole setup at a pressure of 1.5 mbar.

optical emission

(quadrupole setup)

Optical resolution currently insufficient to determine population changes of individual plasma species.

➧ ***higher resolution spectroscopy required***

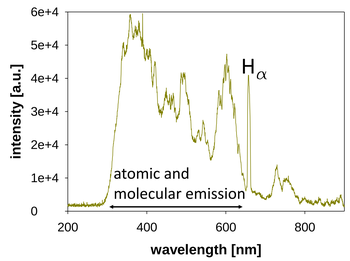

Fig. 8: Optical emission measured on the quadrupole setup at 1.5 mbar.

Conclusions & Outlook

- The standard APPI power supply generates a ***stable*** and ***reproducibly ignitable*** open H_2 plasma between 1 and 5 mbar.
- H_2 flow rates between 1 and 20 sccm
- Positive currents leaving the plasma zone are in the order of ***40 µA*** (corresponding to 10^{14} singly charged species per second) - sufficient for any MS application.
- Additional DC voltages reproducibly impact the RF plasma, however, not as expected.
- Mass spectra with abundant protonation reagents and efficient analyte protonation were recorded. However, a higher purity discharge gas and optimized reagent guidance are required.

next steps:

- Storing and pushing H_3^+ with additional high voltage DC pulses?
- Higher resolution spectroscopy to determine concentration changes in specific plasma species.
- Precise confinement and guidance of charged plasma species (varying electrode shapes inside the glass tube; red parts in fig 3)
- Fundamental investigation of the high voltage DC impact on the RF plasma.
- Gas supply from a hydrogen generator with higher purity (two orders of magnitude).

Literature

[1] Kersten, H., Kroll, K., Haberer, K., Brockmann, K.J., Benter, T., Peterson, A. : Design Study of an Atmospheric Pressure Photoionization Interface for GC-MS. Journal of the American Society for Mass Spectrometry. **27**, 607-614 (2016)

[2] Liebermann, M.A. and Lichtenberg A.J.: Principles of Plasma Discharges and Materials Processing. 2nd Edition, John Wiley & Sons Inc., Hoboken, NJ, USA (**2005**)

Acknowledgement

Equipment support of this work by the German Research Foundation (DFG) - project KE 1816/1-1 - and TOFWerk AG is gratefully acknowledged.