

Evaluation of a kinetically controlled chemical ionization setup

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Introduction

Ion transformation processes, in particular ion molecule reactions, as subsequent steps upon directing generated ions to the analyzer region may significantly change the outcome of a mass spectrum. Once the ionization process instantaneously transfers the neutral sample out of its equilibrated state the ion population relaxes into a new equilibrium. Usually the thermodynamically most favorable constitution that includes ions significantly differs from its neutral counterpart. The extent of mismatch increases with increasing complexity of the sample and increasing number of total collisions occurring after the ionization process. To keep the initial information, which does reflect the neutral sample composition the number of ion molecule collisions after initial ion formation needs to be minimized. This type of process control is termed "kinetic control" within the present framework.

Approach:

- Application of one of the strongest known gas phase acid, H_3^+ as the main primary charge carrier.
 - Generation of H_3^+ either by a high pressure DC plasma or a low pressure RF discharge
- Subsequent quantitative transformation of H_3^+ into reagent ions (N_2H^+ and N_4H^+) for less exothermic analyte protonation. Direct exposure of the analytes to the plasma afterglow is largely avoided.
- Maintaining the protonation reactions of the analyte under kinetic control

Methods

MS HTOF with custom ion transfer optics, TOFWERK AG, Thun, Switzerland
CTOF, TOFWERK AG, Thun, Switzerland

Ion Source Custom high pressure DC plasma source, custom low pressure RF discharge source

Gases Helium 5.0 and Nitrogen 5.0, Messer Group GmbH, Krefeld, Germany

Analytes Benzene, toluene, m-xylene in nitrogen (1 ppmV), CARBAGAS AG, Kümliigen, Switzerland
Custom gas mixtures: Benzene, toluene, o-xylene in nitrogen (10 ppmV, 1 ppmV, 10 ppbV)
All gases were used without further purification

Gas Flows All gas flows are controlled by mass flow controllers, MKS Instruments Deutschland GmbH, Berlin, Germany

Experimental setup

①–③ The gas phase sample is introduced into the transfer quadrupole at variable axial positions, determining the ionization time and the time for subsequent ion molecule reactions ("transformation processes") to occur.

④ A steady flow of primary reagent ions (H_3^+ or N_2H^+) expands coaxially into the quadrupole within the first differentially pumped pressure region.

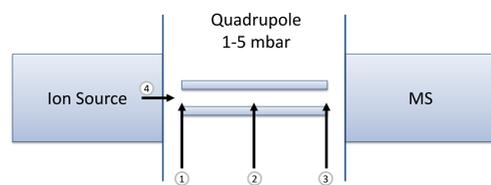


Figure 1: Schematic view of the experimental setup

Ion Sources

Two alternative ion sources are mounted on a custom Time-of-Flight mass spectrometer: A high pressure DC plasma (i) and a low pressure RF discharge (ii). A steady flow of primary reagent ions (H_3^+ or N_2H^+) expands coaxially into a quadrupole within the first differentially pumped pressure region (1 – 5 mbar), which corresponds to roughly a million collisions with background particles per second, estimated from simple gas kinetic theory. A sample introduction stage allows to add the neutral sample at precisely determined positions into the quadrupole, which in turn determines the total number of collisions. The extent of kinetic control with respect to the detection limits is assessed as a function of mixing ratios, amount of primary reagent ions and sample introduction position. Furthermore, the ability of the chemical system to dissipate excess energy from the protonation step is evaluated by the observed degree of fragmentation.

High pressure DC plasma (i)

The DC plasma is operated with helium at elevated pressure, which leads to the production of metastable helium atoms (He^M). In reaction cascade H_3^+ is formed by Penning ionization of H_2 and subsequent reaction steps with neutral hydrogen [1].

Low pressure RF discharge (ii)

The RF discharge source is operated directly with hydrogen at low pressure. The discharge source includes a helical coil resonator (HCR) providing sufficient RF energy to sustain the discharge. The RF plasma leads to the direct production of H_3^+ (For more details cf. Poster TP 422)

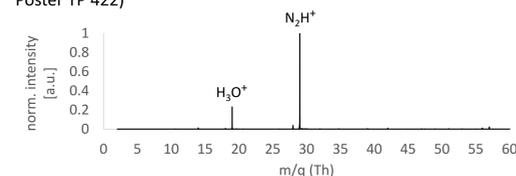


Figure 2: Mass spectrum with nitrogen as bulk gas obtained with the low pressure RF discharge ion source

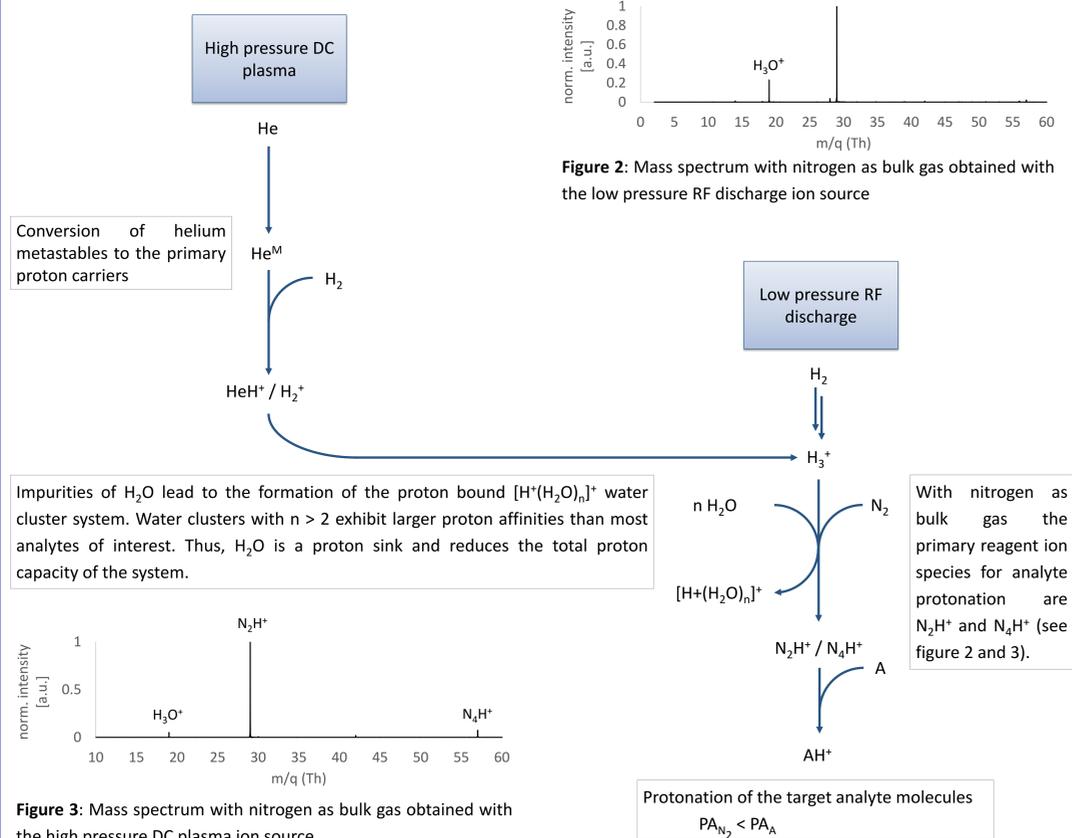
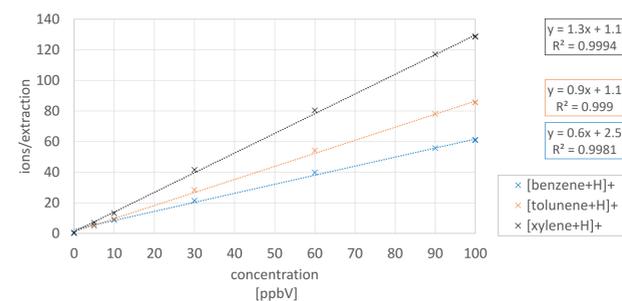


Figure 3: Mass spectrum with nitrogen as bulk gas obtained with the high pressure DC plasma ion source

Results

Analytical Performance



	Limit of Detection* [pptV]	Degree of Protonation**
Benzene	34	> 96
Toluene	10	> 95
Xylene	5	> 97

*estimate from S/N = 3. ** $[M+H]^+ / ([M]^+ + [M+H]^+)$

The high pressure DC plasma source shows a linear response for a benzene/toluene/m-xylene (BTX) mixture in a range of 5 – 100 ppbV (figure above). An approximate estimate of LODs values of the BTX mixture is obtained from the signal-to-noise ratio of the analyte measured with a blank. LOD values in the low pptV range are obtained and a high degree of protonation with up to 97 % is observed (cf. table above).

Kinetic vs. Thermodynamik Control

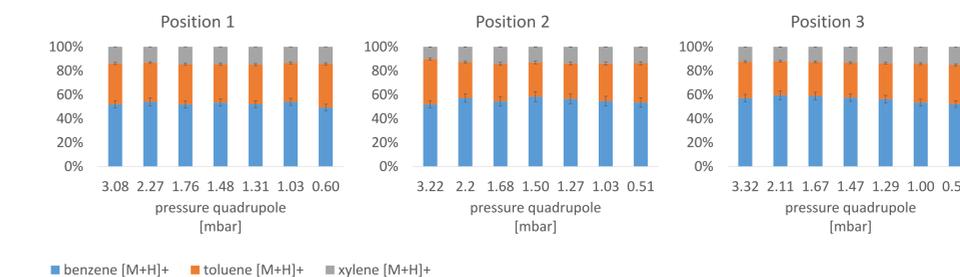
Kinetic control

The reaction system is *not* allowed to equilibrate before mass analysis. The ion population resembles closely the neutral analyte composition in the matrix.

Thermodynamic control

The reaction system has time to equilibrate, driven by the Gibbs energy. The resulting ion system *may* represent the neutral analyte composition, but this is rarely the case.

Constant analyte signal ratios with varying reaction times indicate the absence of competitive reactions between protonated analytes and thus strongly suggest a kinetically controlled ionization process.



The figure above displays the protonated BTX signal distribution for three different sample introduction positions in dependence of the transfer quadrupole background pressure for a 10 ppm BTX mixture.

→ The observed signal distributions are not sensitive to the quadrupole pressure and sample position.

The upper figure on the left shows the total signal intensities and the lower figure on the left the signal distributions for a BTX mixture introduced at three different positions into the quadrupole at the same pressure.

→ The analyte signal intensities increase with the distance of the sample introduction position to the quadrupole exit.

All these observations strongly suggest, that the analyte protonation step is under full kinetic control with regard to all three sample introduction positions.

Conclusions

- Both ion sources, the high pressure DC plasma and the low pressure RF discharge source lead to comparable mass spectra when employing nitrogen as bulk gas
- Subsequent quantitative transformation of H_3^+ into the reagent ions N_2H^+ and N_4H^+ for less exothermic protonation is demonstrated
 - degree of protonation for the used analytes is > 95 %
 - Exclusive formation of $[M+H]^+$ ions observed.
- Protonation of an BTX mixture under full kinetic control is demonstrated with LODs reaching low pptV levels.

Outlook

- Evaluation of a spark discharge plasma as a further alternative ion source for the formation of H_3^+ as primary charge carrier.
- A more detailed investigation of the extent of kinetic control with respect to detection limits, mixing ratios, amount of primary reagent ions and sample introduction positions.
- Comparison of the proton capacities of the different ion sources and determination of the total primary and analyte ion currents.
- Temporally resolved experiments with pulsed ion sources (laser ionization) to determine the absolute reaction times in the quadrupole.
 - Numerical simulations of reaction kinetics and ion trajectories in the quadrupole
- Search for suitable reagent ions for a "reagent cascade" to further lower the excess energy upon protonation

Literature

- [1] Mueller, D.; Brachhauser, Y.; Hartmann, N.; Hillen, R.; Erdogan, D.; Brockmann, K.; Kersten, H.; Benter, T.; Aliman, M. Development of a novel ion source for μ -plasma induced proton transfer reaction mass spectrometry, 64th ASMS Conference on Mass Spectrometry and Allied Topics, San Antonio, TX, USA (2016)
- [2] Kersten, H.; Kutsch, T.; Kroll, K.; Haberer, K.; Benter, T. H_2 -plasma for the generation of protonation reagents with a standard APPI power supply, 64th ASMS Conference on Mass Spectrometry and Allied Topics, Indianapolis, IN, USA (2017)

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