Development of a novel ion source for μ -plasma induced proton transfer reaction mass spectrometry

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Introduction

Principal Design Concept:

- (1) Helium operated μ -plasma for the initial formation of high energy carrying species.
- (2) Subsequent quantitative transformation into H_{3}^{+} as the primary proton carrying species [1][2].
- (2) Protonation of a vast analyte range in the absence of significant electrical field gradients.
- (3) Maintaining the protonation process under kinetic control.
- (4) Interfacing with an ABSciex API 3200 Triple Quadrupole MS.

Implementation:

- A stacked chamber system allows for separation of the different ion transformation stages and their required conditions, such as:
- Maintaining the primary plasma under optimized conditions.
- Efficient transformation helium of metastables into proton carriers.
- Analyte ionization under kinetic control.
- Modification of the MS inlet ensures optimized pressure conditions in the protonation stage.

Methods

Detection

Mass spectrometer

- \succ The ion source is directly mounted on the orifice plate of an ABSciex API 3200 Triple Quadrupole MS
- Modification of the skimmer inlet to increase the total gas flow into the MS

Ionization

Plasma source

Micro DC-plasma operated with helium 5.0 (Messer Industriegase GmbH, Germany)

lon source

- Hydrogen 5.0 (Messer Industriegase GmbH, Germany) is supplied in a separate chamber
- \succ Expansion of the reagent gas mixture into the "protonation chamber" maintained approximately 12 mbar
- > All gas flows are controlled by mass flow controllers (MKS Instruments Deutschland GmbH, Germany)
- \succ All gases are further purified either by cold traps with liquid nitrogen or by dry bed purifiers

Kinetic analysis

Cantera Software Version 2.2.1 [4]

Plasma source:

DC- plasma operated with helium at reduced pressure Helium metastable enriched effluent expands into a gas flow of hydrogen [2]

-	Conversion of helium metast			
	(1a)	$He^{M} + H_{2}$	\rightarrow	HeH⁺+
	(1b)		\rightarrow	$H_{2}^{+} + H_{2}^{+}$
	(2)	$H_2^+ + He$	\rightarrow	HeH⁺+
	(3)	$H_2^+ + H_2$	\rightarrow	${\rm H_{3}^{+} + H}$

- The stacked chamber system ensures spatial separation of primary proton carrier preparation and analyte protonation. This concept uncouples the individual required parameters.
- Conversion into protonated analyte molecules
- $AH^+ + B \rightarrow A + BH^+$ $(PA_{A} < PA_{B})$
- are N_2H^+ and N_4H^+

Analytical Performance – kinetics vs. thermodynamics

- Analytical performance like linear dynamic range and LODs were diluted in nitrogen.
- "Optimization").
- ppbV range with LODs between 100 700 pptV.
- signals decrease (figure 3 b)).



chamber), b) non linear curves of BTX in the ppmV range.

The impact of the protonation stage pressure on the transition from kinetic to thermodynamic control was experimentally investigated (figure 4).

- from kinetic to thermodynamic control sets in.
- affinities (Pa_{xylene} > Pa_{toluene} > PA_{benzene})

Experimental Setup - Chemistry

ables into proton carrier

• **H** + e⁻ le + e⁻

$HeH^+ + H_2 \rightarrow H_3^+ + He$

With nitrogen as bulk gas the main proton carrying species



Figure 1: Schematic view of the experimental setup.

measured with either toluene or BTX (benzene, toluene, xylene)

• For enhanced performance, the water mixing ratio in helium as well as in hydrogen must be minimized (see also

• As depicted in figure 2 the system shows linear response in the

• In the ppmV range only xylene shows reasonable linear response while the toluene and benzene corresponding

• For kinetic control of the protonation step the normalized signal is expected to be independent of the prevailing pressure. However, in case of analyte mixing ratios > 10 ppmV in combination with a pressure > 12 mbar a perceptible transition

• Steep increase of the [xylene+H]⁺ signal with increasing pressure at the cost of the [toluene+H]⁺ and [benzene+H]⁺ signals. The trends of the curves reflect the order of proton



Figure 2: Linear response of BTX signals in the ppbV range.

- Competitive reactions between protonated analytes are observed at protonation stage pressures of approx. 12 mbar and total neutral analyte mixing ratios exceeding 10 ppmV (figure 4).
- The total mixing ratio of proton carriers is approx. 30 ppmV.
 - A previous source version interfaced to a different setup had a proton capacity exceeding 100 ppmV [2].
 - > The cause of loss to the present version is still under investigation.
- Kinetic simulations resemble the experimental results (figure 3) Reducing the protonation stage pressure allows to shift the kinetic-thermodynamic transition area to higher mixing ratios. Requires increased pumping rate!



current, as function of the protonation stage pressure; pressure measured as shown in "Setup".





Figure 5: Protonation ratio of nitrogen and toluene dependent of : a: pressure in ionization chamber, b: H₂ flow, c: analyte flow, d: helium flow.

- Compared to PTR-MS, no significant electrical field gradients are present in the protonation chamber. Therefore, water cluster formation represents a thermodynamic sink for protons.
- In the protonation stage the presence of water is tolerable at low pressure conditions (figure 8), whereas water mixing ratios exceeding 1 ppmV in the reagent chamber lead to massive cluster formation (figure 7).
- Figure 6 displays the formation of the primary charge carrying species in dependence of the water mixing ratio in the reagent chamber. Below 100 ppmV of water, N₄H⁺ dominates, whereas at higher mixing ratios the less reactive species $[(H_2O)_3H]^+$ is the primary charge carrier.



Figure 7: Kinetic simulation of the ion distribution leaving the reagent chamber in dependence of the water mixing ratio.

protonation ratio is a main point of interest.

- A lower protonation ratio can indicate that helium metastables are not efficiently transformed to proton carriers and thus can leak into the ionization chamber.
- On the other hand, conditions like very low flow rates lead to low ion yields and a sub optimally driven plasma.
- Figure 5 summarizes the measurements: • The H₂ flow (b) shows a maximum at around 7 sccm, which should be the optimum between metastable conversion and diffusion of H_2 in the plasma region.
- The decreasing trend in (c) is most likely due to an increasing diffusion of N₂ into the reagent chamber and therefore an increasing formation of N_2^+ .
- The protonation ratio seems to be independent of the pressure in the ionization chamber as well as of the helium flow into the plasma source.



Figure 6: Relative signals of N_4H^+ and $[(H_2O)_3H]^+$ in dependence of the water mixing ratio in "reagent chamber", Blue curve: sum of the signals in cps.



Figure 8: Simulated water cluster distribution as a function of the protonation chamber pressure at 1‰ water mixing ratio

Chemical Blending – Stacked-Chamber-System

Analyte	Proton affinity [kJ/mol]			
Helium	177.8			
Hydrogen	422.3			
Nitrogen	493.8			
CH4	540.5			
Water	691.0			
Benzene	750.4			
Toluene	784.0			
p-Xylene	794.1			
Table 1. Droton affinition of				

lable 1: Proton affinities of relevant species [3].

Additional chambers allow to scale down the energy available for the analyte protonation.

- For example, $He \rightarrow H_2 \rightarrow CH_4 \rightarrow Analyte$ can be used as a "reagent cascade".
 - Since CH_{4} has a higher proton affinity (Table 1) N₂ would be "suppressed".
 - Exchange N_2H^+/N_4H^+ for CH_5^+ as main proton carrier.
 - Reagents with higher proton affinities than water shift the performance to greater tolerable water mixing ratios (e.g. for ambient air samples).

 Reagents can be protonated "softly" instead of being exposed to the plasma afterglow (figure 9).





1) Physical & Theoretical Chemistry

• Since the source is meant to protonate exclusively, the

• Protonation ratio is determined as: $PR = \frac{[M+H]^+}{[M]^+ + [M+H]^+}$



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Conclusions

Instrumentation:

- New ion source design compatible with an ABSciex API 3200 MS.
- Stacked reaction chamber system allows the separation of primary plasma, reagent ion generation and analyte protonation.
- No significant "backflush" of N_2 into the reagent chamber was observed.
- The required kinetic control was verified up to approx. 1 ppmV total analyte mixing ratio.

Mechanism:

- In the present configuration water is a thermodynamic sink with mixing ratios exceeding 1 ppmV in the *reagent chamber*.
- In the *protonation chamber* water is not a sink when the applied pressure is in the low mbar range or when this path is suppressed by appropriate scaled proton affinity of the primary proton carrier.

Outlook:

- Implementation of further reagent chambers should allow to scale down the energy available for the analyte protonation.
- Investigations on suitable reagent ions.
- Increase in sensitivity by chemical suppression of bulk gas ions (especially H_2O).
- Measurements of kinetic data as well as atmospheric degradation reactions.

Literature

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