

Introduction

Challenge:

- Improvement of the previously introduced μpCI (µ-plasma) ionization source
- Characterization of different secondary reagent ions as proton sources
- Enhancement of the extent of kinetic control by decreasing the pressure in the analyte reaction chamber
- Increasing the analytical performance of the novel ion source - MS system focusing on the generation of protonated analyte ions

Implementation:

- Cascaded chamber system enabling the addition of different primary and secondary reagent gases
 - Thermodynamic control in the upstream reagent chambers (quantitative production of primary and secondary reagent ions)
 - Kinetic control in the protonation chamber
 - Thermal protonation is enabled
 - Setup readily adapted to individual needs
 - Different inner diameter of the protonation chamber allows reaction time adjustment
 - Variable number of attached chambers

Methods

Detection

• ABSciex API 3200 Triple Quadrupol MS

Ionization

Plasma source

- Micro DC-Plasma (Zeiss, Germany)
- Helium 5.0 (Messer Industriegase GmbH, Germany) purified with VLC Helium Purifier

Ionization stage

- Gas flows are controlled by mass flow controllers (MKS Instruments Deutschland GmbH, Germany)
 - Primary reagent gas hydrogen 5.0 (Messer Industriegase GmbH, Germany) purified with LN₂ cold trap
 - Secondary reagent gas mixtures (trifluoroethanol in $N_2 - 150$ ppmV, trifluoro-acetic acid in $N_2 - 13\%$, isobutane in He - 8.5% and methane in He – 200 ppmV)
 - Analyte gas mixtures (BTX in N₂ 10 ppmV, toluene in N₂ -10 ppmV)
- The original chambered structure^[1] (plasmareagent-, and protonation chamber) shown at ASMS last year is extended with an additional, reagent chamber for the controlled production of secondary reagent ions
- Pressure reduction allowing kinetic control

Improvement of µpCI for proton transfer reactions: a chambered ion source design for suppression of water-cluster

Operating pressure ranges

- Plasma source: 1550 1600 mbar
- Primary reagent chamber: 200 225 mbar
- Secondary reagent chamber: 120 125 mbar
- Analyte protonation chamber: 1.4 2.5 mbar

Primary ion (PI) production:

1)	$He^{M} + H_{2}$	→	HeH⁺ + H + e⁻	(a)
	-	→	H ₂ ⁺ + He + e ⁻	(b)
	-	→	H⁺ + He + H + e⁻	(c)
2)	H ₂ ⁺ + He	→	HeH⁺ + H	
3)	$H^{+} + H_{2}^{-}$	→	$H_3^+ + hv$	
4)	$H_2^+ + H_2^-$	→	H ₃ ⁺ + H	
5)	$HeH^+ + H_{a}$	→	$H_{a}^{+} + He + H$	

Secondary reagent ion production:

(6)
$$H_{3}^{+} + R \rightarrow RH^{+} + H_{2}$$

 Generation of secondary reagent ions as protonating agents envisioned to suppress proton loss in molecules with higher PA than the analyte, particularly H_2O

Analyte protonation with primary or secondary reagent ions $A + H_3^+ \rightarrow AH^+ + H_2$

	5		2
(0)		П

(8)

(depends on proton affinities (PA): $PA_{A} > PA_{PI}$)

 $\Delta G_{ges} = \Delta G_1 + \Delta G_2$



TFA and TFE

• Show extensive proton bound cluster formation Isobutane

- Protonated BTX analyte peaks observed
- Very promising initial results
- Reagent gas supply with higher purity required



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Experimental Setup



Figure 1:

Schematic of the experimental setup



Pumping port

Pressure variations

analyte

(9) $N_2H^+ + N_2 \rightleftharpoons N_4H^+$

- Standard conditions:

Secondary Ion Production

3.0E+06

2.5E+06

2.0E+06

1.5E+06

1.0E+06

5.0E+05



 ΔG_{geo}





2b: TFE - dimerization, trimerization, and proton bound clustering with water observed

Trifluoroacetic acid (TFA)

 $[TFA+H_2O+H]^+$

 \sim [TFA+2H₂O+H]⁺

 $[2TFA+H_2O+H]^+$

[2TFA+H]+

2c: Isobutane - two spectra showing the reference (background, N₂, blue) and the analyte (BTX, red) signals. No proton bound water-cluster visible. Poor quality of the isobutane used (impurities 1% VOCs) leads to congested spectra



Formation of proton bound water clusters (with $PA > PA_{analyte}$) leads to significant loss of primary and secondary reagent ions.

• With highly purified secondary reagent gases and even higher pressure in the secondary reagent chamber, cluster formation should be suppressed



Figure 5 a: methane as

analyte with

primary ion

0.0E+00

2.5E + 05

 H_3^+ as

5 b: methane as

with N₂

5 c: methane

He) as

secondary

toluene (10

analyte and

primary ion

ppmV) as

 H_3^+ as

ion with

primary ior

as analyte

(200 ppmV in

Reagent gas/Chamber-setup Dependence

Methane as analyte (protonation in the low pressure chamber)

- Measurements with increasing mixing ratio of CH₄ results in higher intensity and smaller ratio of primary ions ($N_{4}H^{+}$)
- Methane contains water (increasing signal of $[2H_2O+H]^+$)

Methane as primary ion (no H_2/H_3^+ present, He^{M} ionization)

Strongly congested spectra; high degree of He^M-induced fragmentation, purity of CH₄ too low

Methane as secondary ion $(H_2/H_3^+ \text{ present})$

Abundant generation of proton bound water clusters visible. This is again caused by the low purity of CH_{A}

Summary

- Recognizable differences between addition in variable chamber positions and hence pressure ranges
- Methane as analyte (protonation with H_{3}^{+}) shows fragments as described in literature^[3]
- Methane as secondary reagent gas (protonation with H_3^+) is a very promising approach
- Methane as primary reagent gas (ionization with He^M) shows numerous ionic species (due to fragmentation/ion chemistry)

Systematic Measurements

Pressure variation

- Increasing relative intensities of the analytes (BTX and water) with higher pressures
- Decreasing relative intensities of primary ions $(N_{4}H^{+}, N_{2}H^{+})$

Analyte flow

- Higher analyte flows results in higher pressures in the current setup
- Water and primary ion intensities are not noticeably effected



Figure 6:

Degree of protonation with different analyte flows and therefore pressure variations



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Figure 7 a: measurement with pressure variation b: measurement with analyte flow variation

Conclusions

Instrumentation:

- Improved ion source mounted on an ABSciex API 3200 Triple Quadrupol MS
- Three chamber setup
- The generation of secondary reagent ions leads to a reduction of the transferred energy to the analyte
- Suppression of the formation of proton bound water clusters is limited to the chambers within a pressure range above 1.5 mbar (higher degree of thermodynamic control)
- Two chamber setup
- Kinetic control is achieved at analyte protonation chamber pressures around 1 mbar

Ionization mechanism:

The reaction chains proceed via proton transfer from to the analyte with different possible intermediates

Outlook:

- Most importantly, purification of any reagent gases employed is mandatory; purities need to reach below ppmV levels
- Application of further reagent gases
- Without clustering characteristics to create stable PAs
- With higher PAs to further lower the transferred energy from reagent ion to analyte
- Measurements with low pressure range and high kinetic control
- VOCs as analytes
- Improving leak tightness of three chamber setup
- Kinetic modeling comparing theory and experiment
- Charge transfer may play a minor but distinct role in some reaction cascades

Literature

- Mueller. D.: Brachthaeuser, Y.; Hartmann, N.; Hillen R.; Erdogdu D. Brockmann. K.: Kersten, H.: Benter, T.; Aliman, M. Development of a novel ion source for μ -plasma induced proton transfer reaction mass spectrometry, 64rd ASMS Conference on Mass Spectrometry and Allied Topics, San Antonio, TX, USA (2016).
- E. P. L. Hunter and S. G. Lias. Evaluated Gas Phase Basicities and Proton affinities: An Update, J. Phys. Chem. Ref. Data, 1998, 27, 413.
- Munson, M. S. B.; Field, F. H., Chemical Ionization Mass Spectrometry. I. General Introduction, J. Am. Chem. Soc., 88 (12);

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