

Transfer of plasma-generated ions into a Fourier Transform Quadrupole Ion Trap (FT-QIT) with running RF trapping field



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Introduction

Commercially available scanning quadrupole ion traps (QIT) with external ionization and ion transfer stage are widely used in mass spectrometric applications.

Scanning QIT are usually operated at Helium buffer gas pressures up-to 10^{-3} mbar allowing collisional cooling of ions injected into the trap. Otherwise ions entering the trap volume will immediately exit on the opposite side or collide with electrodes due to their kinetic energies.

Fourier transform (FT) based quadrupole ion traps require low background trap pressure ($p < 10^{-7}$ mbar) to allow collision free oscillations of the ions in the trap, which are necessary for the detection of ion frequency dependent image currents on the endcap electrodes.

Thus, the requirement of a buffer gas for cooling of injected ions on the one hand and the necessity of low trap pressures on the other hand demonstrate the challenging task of introducing externally generated ions into an FT QIT.

At ASMS 2015 we presented a compromise to reach sufficient FT measurement conditions as well as cooled ion injection by introduction of plasma-generated ions via a quartz capillary into the ion trap.

This setup has been rebuilt for further and much more detailed investigations. First spectra to proof the operative readiness of the setup were carried out. In this contribution, we review the currently available data regarding cooled ion introduction, reduced ion load, and FT analysis in the context of the knowledge gained over the last years.

Methods

Mass analyzer:

Zeiss Fourier Transform Quadrupole Ion Trap (Prototype generation)

Ionization Method:

Custom DC micro-plasma source operated with Helium 5.0 (Messer Industriegase GmbH, Bad Söden, Germany)

Transfer:

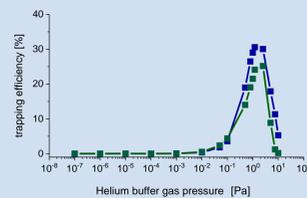
Quartz capillary (GC column, uncoated, ID 0.5 mm)

Gas mixtures:

Toluene in Nitrogen / Hydrogen

Scanning QIT vs. FT-QIT

Scanning QIT	Zeiss FT-QIT
<ul style="list-style-type: none"> Ion introduction through one of the endcap electrodes and ejection through the other electrode Electrode opposite to entrance may be used for deceleration of ions Helium buffer gas at approx. 10^{-3} mbar for collisional cooling of introduced ions Ion transfer and ion injection studies carried out experimentally and with simulation tools for Bruker Esquire 3000 <ul style="list-style-type: none"> Energy distribution of introduced ions: 2-5 eV [2] Example: Dependence of ion accumulation efficiency on Helium buffer gas pressure. Ion start position: 5 mm from ring electrode; kinetic energy: 4 eV; accumulation time: 100 μs; ion current: 150 ions/μs. 	<ul style="list-style-type: none"> Both endcap electrodes used for image current detection Ion introduction through ring electrode Trap kept at low pressure to enable FT-analysis <ul style="list-style-type: none"> Use of Helium buffer gas not favored <p>Possible simple ion transfer coupling approaches (simulation studies):</p> <ul style="list-style-type: none"> RF trapping field turned off for ion introduction <ul style="list-style-type: none"> Stretched ion packet through center axis Trapping efficiency: 40%. <ul style="list-style-type: none"> With deceleration potential on endcap electrodes: up-to 70% But: No accumulation via repeated ion packet injection possible RF trapping field kept on while ion introduction <ul style="list-style-type: none"> Thermal ions ($E_{kin} \approx 50$ meV) approaching the ion trap are rejected as they experience repulsive forces of several RF cycles ($f_{RF} = 1$ MHz) Ions with kinetic energies of several eV are not trapped as long as there is no collisional cooling gas

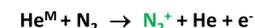


A Helium buffer gas pressure of at least 10^{-4} mbar is required for ion accumulation.

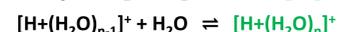
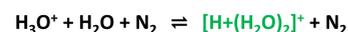
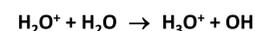
Ion Chemistry

Formation of reagent ions:

Penning ionization of initially plasma-generated helium meta-stables (He^M ; 19.8 eV) leads to the formation of N_2^+ and N_4^+ with N_2 as matrix gas:

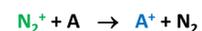


In the presence of water at elevated mixing ratios protonated water clusters form rapidly, with n depending on the water mixing ratio and temperature ($n = 3...6$)

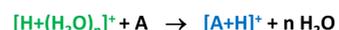


Formation of analyte ions:

Charge transfer reactions of N_2^+ and N_4^+ (when the ionization potential of the analyte < ionization potential of reagent gas)

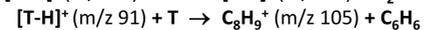
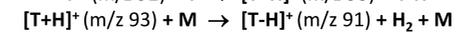
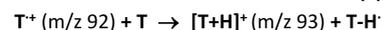


After activation of the protonated water clusters ($n \rightarrow 0, 1$) in the ion trap, protonation of the analyte molecules is observed



(strongly simplified reaction scheme)

Selected ion-molecule reactions of Toluene (T):



Experimental Setup

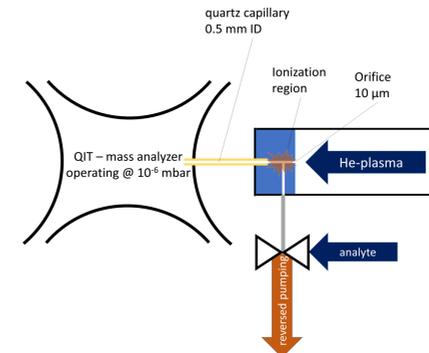


Fig. 1: Schematic of the plasma-source/FT-QIT setup.

- Plasma source connected to ring electrode by short GC column (length approx. 20 mm and ID 0.5 mm)
- Primary plasma region and ionization region separated by an orifice of 10μ m diameter
- Analyte introduction into ionization region and ion source pumping enabled by use of a three-channel valve
- By ion source pumping the time to reach suitable FT-pressures is strongly reduced
- Using sampling pressures of ≈ 100 mbar the pressure for ionization is favorable *and* the amount of gas entering the trap has an additional ion cooling effect

Results

Fig. 2 shows a mass spectrum recorded with 200 pptV Toluene in Nitrogen mixing ratio, sampled from a reservoir held at 100 mbar. Three Toluene dependent mass signals are recorded:

T^+ : Charge transfer from N_2^+ and N_4^+

$[T+H]^+$: Protonation by activated protonated water clusters

$[T-H]^+$: Collision induced dissociation of T^+ with release of H_2

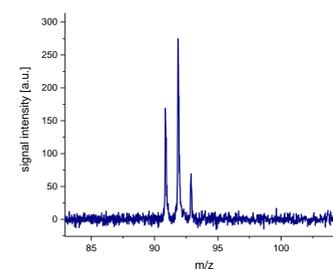


Fig. 2: Mass spectrum of 200 pptV Toluene in Nitrogen.

Operation of the ion trap in FT mode allows the repeated acquisition of mass spectra for the same ion population. As ions are not ejected from the trap, they can be excited multiple times.

Figure 4 shows the temporal evolution of ion signals recorded for Toluene diluted in Nitrogen according to the reaction scheme on the left hand side.

Analytes diluted in Hydrogen:

With Hydrogen as matrix gas, abundant protonating reactant ions, such as H_3^+ are generated, subsequently leading to protonated analyte ions.

Maintaining stable conditions of the plasma, however, is challenging with the addition of hydrogen, possibly due to diffusion of Hydrogen into the primary plasma region.

The lower mass cut-off (LMCO) is 30 Da, thus N_2^+ ions are not trapped.

The absence of N_2^+ in the trap is favorable to record well-resolved Toluene mass signals since the impact of space charge effects (mass shifts, peak fusion, signal suppression, ...) is strongly reduced.

Linear dependence of the recorded signal intensity on the mixing ratio was investigated in the range of 200 pptV to 1 ppbV (see Fig. 3).

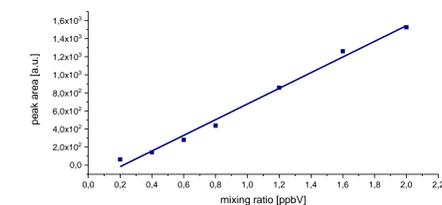


Fig. 3: Linearity from 200 pptV to 1 ppbV (m/z 92).

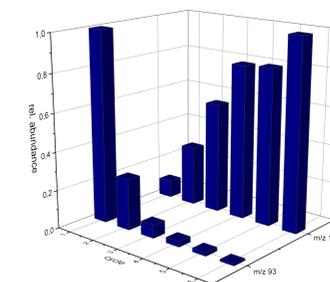


Fig. 4: Temporal signal evolution of Toluene from m/z 93 to m/z 105.

Conclusions

- The custom DC micro plasma source is successfully coupled to the Zeiss FT-QIT
- A quartz capillary (GC column, length: approx. 20 mm, ID 0.5 mm) is used for direct coupling
- The adjustable valve opening times allow adaptation to the sample pressure, tolerating pressures up-to several hundreds mbar
- Ion source pumping is pivotal for successful operation in FT mode
- Suitable trap pressures are currently only reached within seconds, limiting the measurement repetition rate
- Lower limit for the sample pressure depends on the reaction rates between analyte molecules and He^M and/or reactant ions

How do we explain the successful introduction of ions into the ion trap while the RF trapping field is on?

- Ions are gas-dynamically driven into the ion trap against the rejecting voltage of the RF trapping field.
- The Helium effluent of the plasma source flowing into the ion trap acts as in-situ cooling gas.
- Suitable FT pressure reached by ion source pumping of the gas load.

Outlook

As the setup is successfully rebuilt, we are currently investigating:

- The dependence of spectra quality on the helium base pressure
- The impact of the plasma current
- Helium pressure in plasma source
- Sample pressure
- Optimization of valve switching times for analyte introduction and ion source pumping

Literature

- Thinius, et. al.; Simulations of collisional interactions of background gas mixtures with trapped ions; 66th Conference on Mass Spectrometry and Allied Topics; San Diego, CA, USA (2018)
- Thinius, et. al.; Evaluation of kinetic energy distributions in API-MS ion transfer stages; 66th Conference on Mass Spectrometry and Allied Topics; San Diego, CA, USA (2018)
- Brachthäuser, Yessica; Development and characterization of a Fourier Transform based Quadrupole Ion Trap (FT-QIT) technique for process and residual gas analysis; Dissertation; Wuppertal, Germany (2017)

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