

A FT 3D Ion Trap with in-trap electron ionization and pulsed gas inlet: transient pressure profile and space charge induced effects

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Introduction

State of the art:

A compact mass spectrometric setup is developed for process-, residual- and trace gas measurements within challenging gas matrices (e.g. H₂).

The compact design is realized by the application of Fourier Transform technique to a 3D ion trap with in-trap electron ionization and a pulsed sample gas inlet via a fast switching valve.

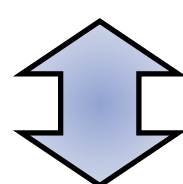
Initial results on the analytical performance have been presented at ASMS 2016.

In this contribution, we focus on investigations of the transient pressure profile and space charge induced effects.

Challenge:

- The compact design is the most challenging factor in the operation of the FT 3D ion trap.

- An efficient ionization with EI requires elevated numbers of neutral molecules.



- For favorable image current detection trap pressures < 10⁻⁶ mbar are required.

- High ion densities within the ion trap cause a number of space charge effects, such as ion signal suppression and mass shifts.

Goal:

- A characterization of the pressure profile inside the trap will help to adapt measurement parameters for optimum instrument performance.

- Space charge induced effects can be avoided by a careful adjustment of measurement parameters and the application of advanced excitation schemes, such as SWIFT (Stored Waveform Inverse Fourier Transform).

Methods

Mass Analyzer:

Zeiss Fourier Transform Quadrupole Ion Trap (based on iTrap® technology)

Ionization Method:

Filament driven electron ionization

Chemicals:

Custom gas mixture: 10 ppmV Toluene in N₂

Gases: N₂ (purity: 5.0); O₂ (purity: 5.0)

Further equipment:

Pulse Function Arbitrary Generator, Model 81150A, Keysight, Böblingen, Germany

Pirani/Cold Cathode vacuum gauge, Model PKR 261, Pfeiffer Vacuum, Asslar, Germany

Experimental Setup

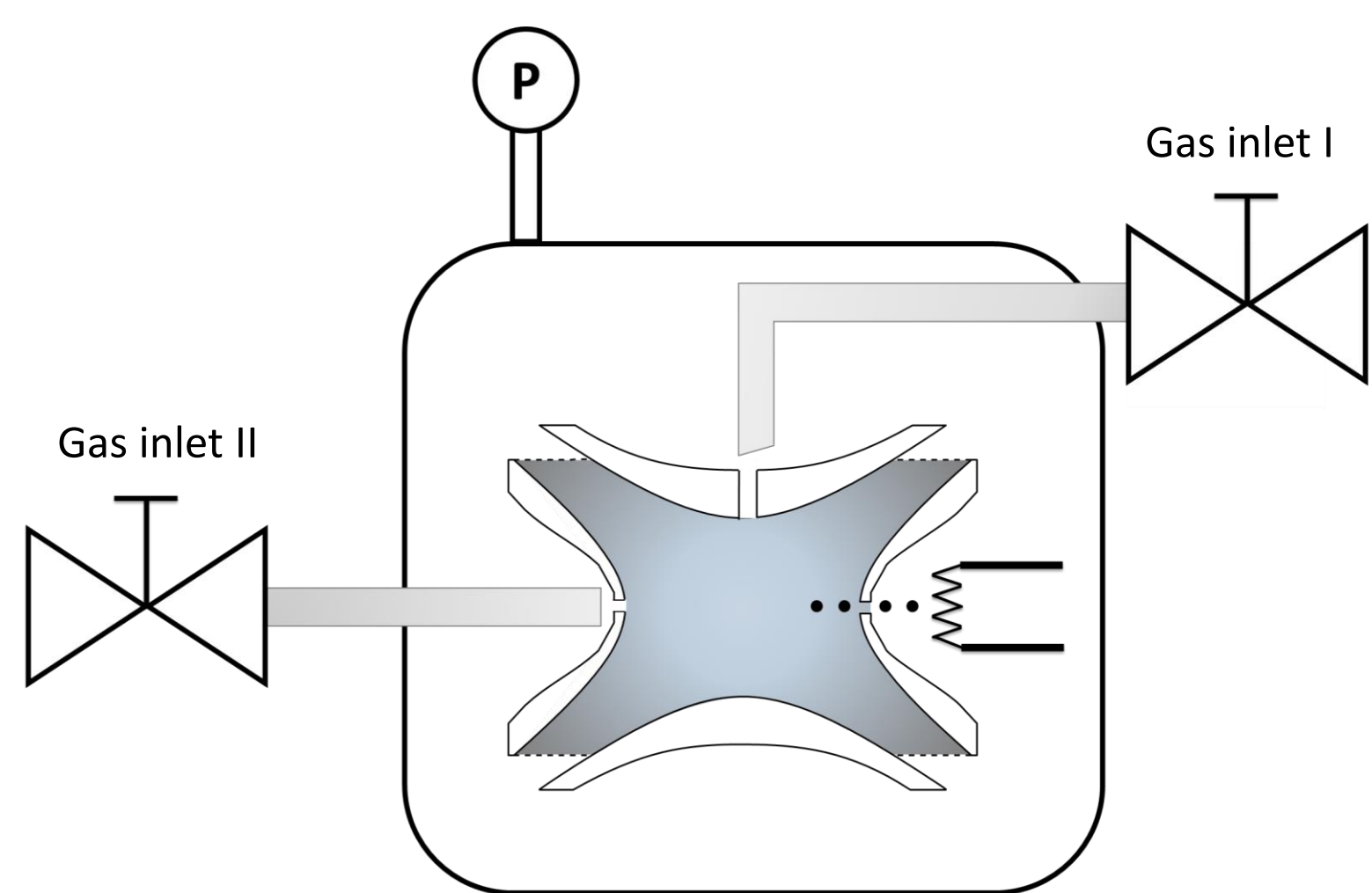


Figure 1: Schematic of the experimental setup with the ion trap mounted inside a vacuum recipient.

The experimental setup consists of a 3D ion trap with image current detection and subsequent FT analysis.

Gaseous samples are introduced into the ion trap via fast switching valves in a pulsed manner.

The gas sample is either directed by a bent metal tube pointing to a hole in one of the endcap electrodes (gas inlet I) or by a straight ceramic tube pointing to a hole in the ring electrode (gas inlet II).

Sample pressures are currently in the range of 0.1 – 10 mbar.

A filament driven 70 eV electron ionization source is used for in-trap ionization.

The recipient pressure is measured with a dual Pirani/cold cathode vacuum gauge.

Transient pressure profile

Methods for the examination of the transient pressure profile:

- Recording of the pressure in the vacuum recipient
- Recording of the analyte ion signal response
 - Toluene at high analyte mixing ratios up-to 1 ppmV
 - Short ionization time (1 ms)
 - Delay scan (see figure) of the expected pressure profile
 - Analysis of the analyte signal response

Gas Inlet I

Investigations on the transient pressure profile are carried out for gas inlet I. The recorded pressure profile and the ion signal response while sampling for 20 ms from 2.5 mbar are shown in Figure 3.

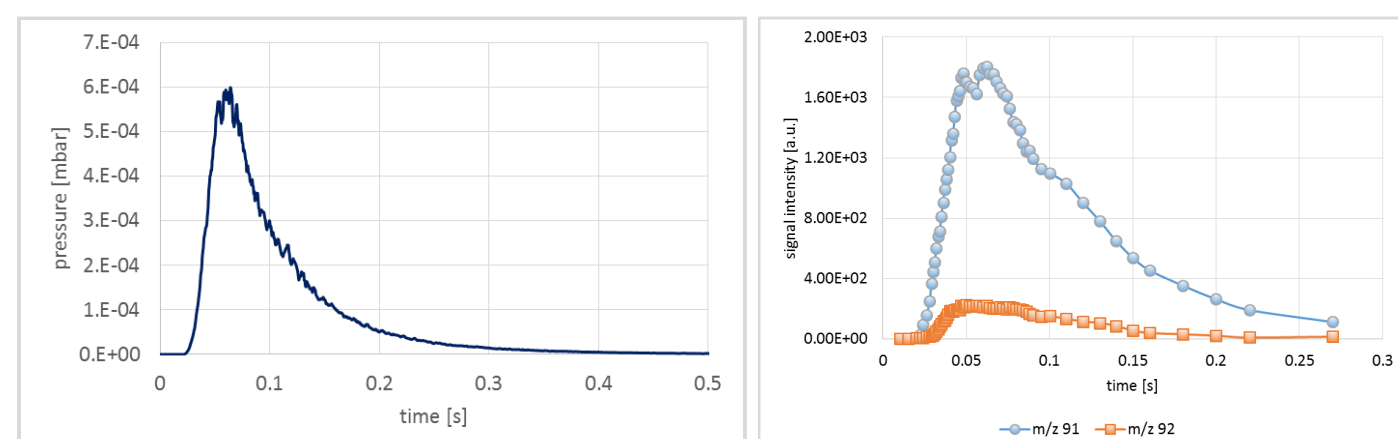


Figure 3: Reading of the pressure gauge (left) and analyte signal response (right) for a 20 ms gas inlet pulse at 2.5 mbar upstream pressure.

Analysis and comparison of the initial slopes and the shapes of the profiles shows a distinct shift between both data sets of about 10 ms. This shift is explained by the response time of the pressure gauge. Data of the pressure gauge and the ion signal are compared for different gas inlet lengths, sample pressures, and gas compositions.

Gas Inlet II

Why has the gas inlet been modified?

- Direct gas introduction into the ion trap
- Better defined and more intense pressure profile
- Greater ion yield and thus greater analyte ion signal abundances
- Shorter ionization times possible at smaller mixing ratios

But:

Ion signal pressure profile and reading of the pressure gauge are not directly comparable.

The pressure profile is examined for a 20 ms gas inlet pulse from 2.5 mbar upstream pressure.

Comparison of gas inlet I and gas inlet II

Conclusions:

- Reading of the pressure gauge for gas inlet I represents the transient pressure profile inside the ion trap
- The ion trap can be used for partial pressure measurements within the trap volume
- Pressure profiles of both gas inlets examined under identical measurement conditions are comparable
- The transient pressure obtained with gas inlet II is roughly a factor of 2 higher
- Pressure maximum for standard measurement conditions is about 1·10⁻³ mbar

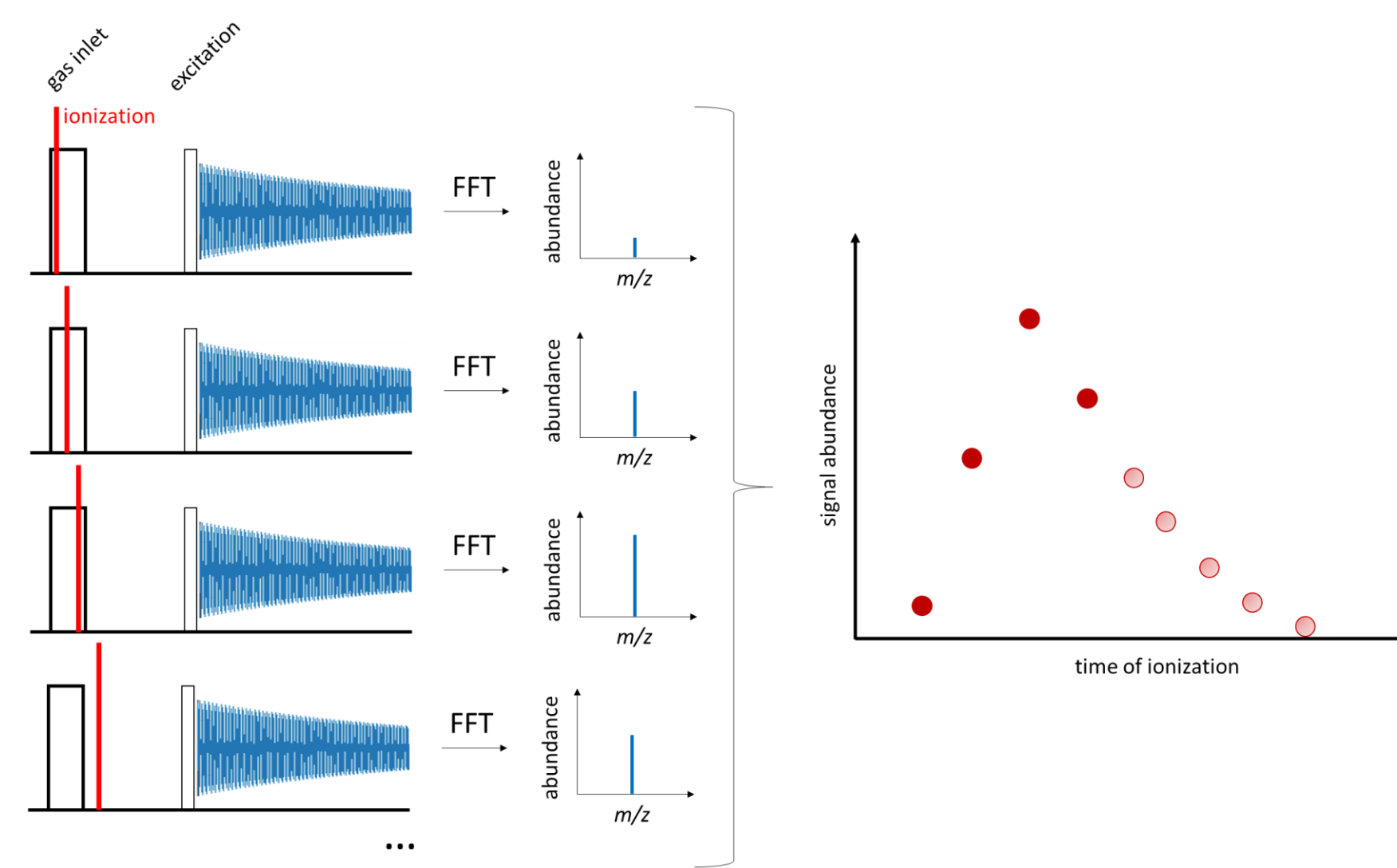


Figure 2: Sketch of the applied pulse sequence when recording the ion signal response of the ion trap.

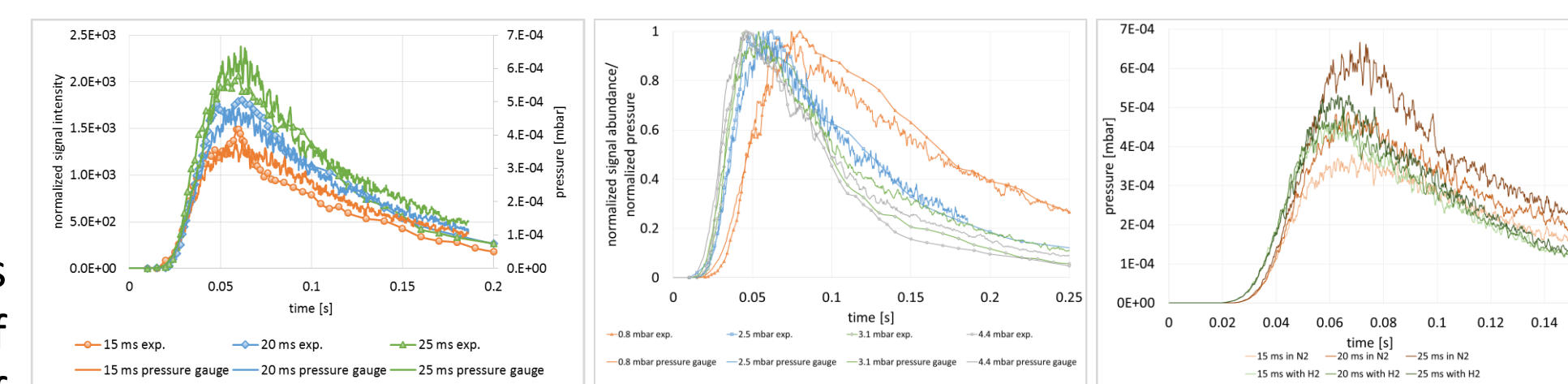


Figure 4: Transient pressure profiles investigated with both methods while varying the gas inlet length (left), the sample pressure (center) or the gas composition (right). All data are corrected by the 10 ms gauge shift.

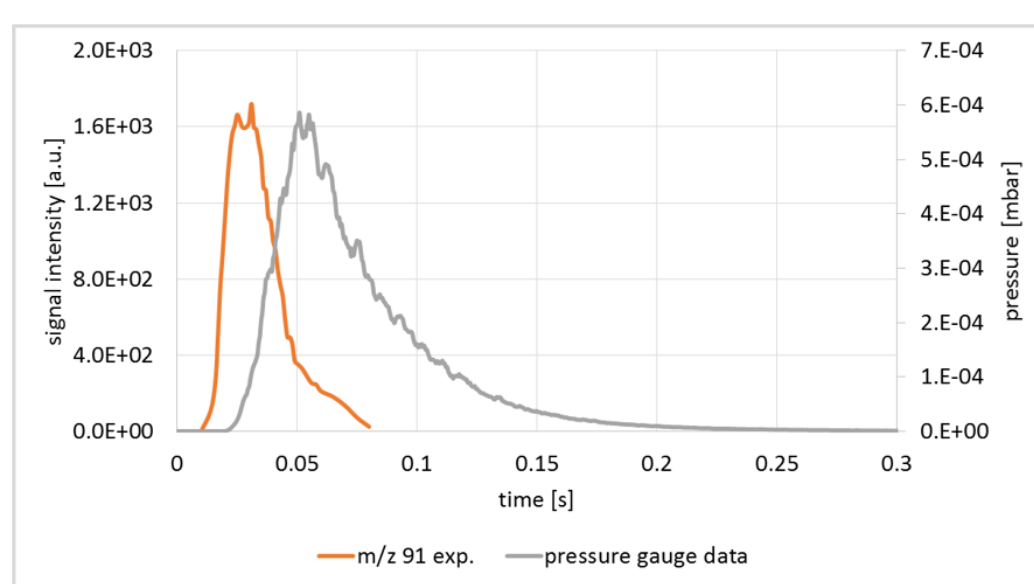


Figure 5: Comparison of both analysis methods for gas inlet II.

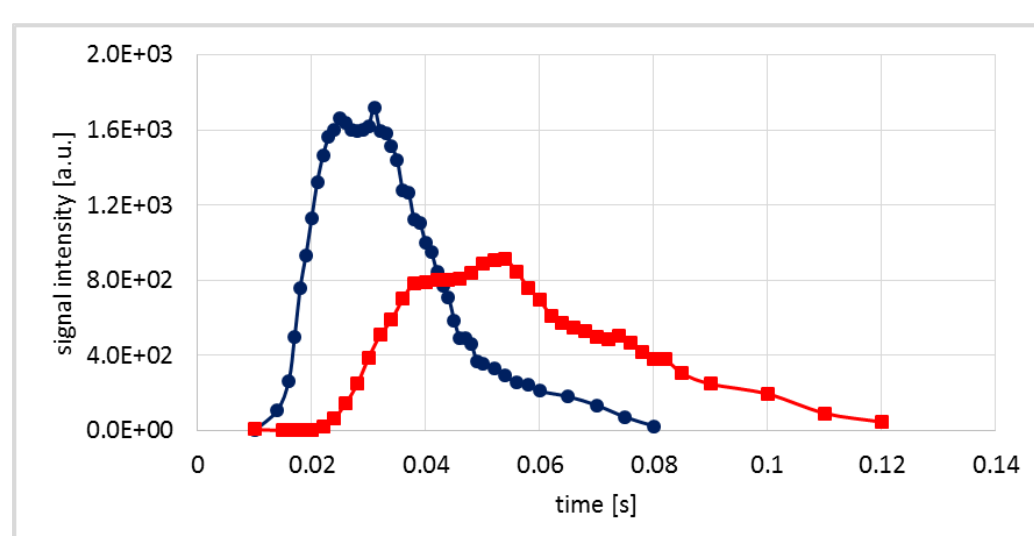


Figure 6: Comparison of both gas inlets sampling for 20 ms from 2.5 mbar upstream pressure.

Space charge induced effects

Increase of the total ion number

Within the present setup the total number of generated ions can be increased in three different ways:

- longer ionization times
- higher filament current
- higher sample gas pressure

The ion signal response of Toluene (500 ppbV diluted in nitrogen) at m/z 91 is observed while increasing the total ion number inside the ion trap. In all three cases a strong ion signal loss is observed at elevated ion loads instead of the expected increasing analyte ion signal response.

Note: Nitrogen ion species (N⁺, N₂⁺, ...) are present in 10⁶ fold excess.

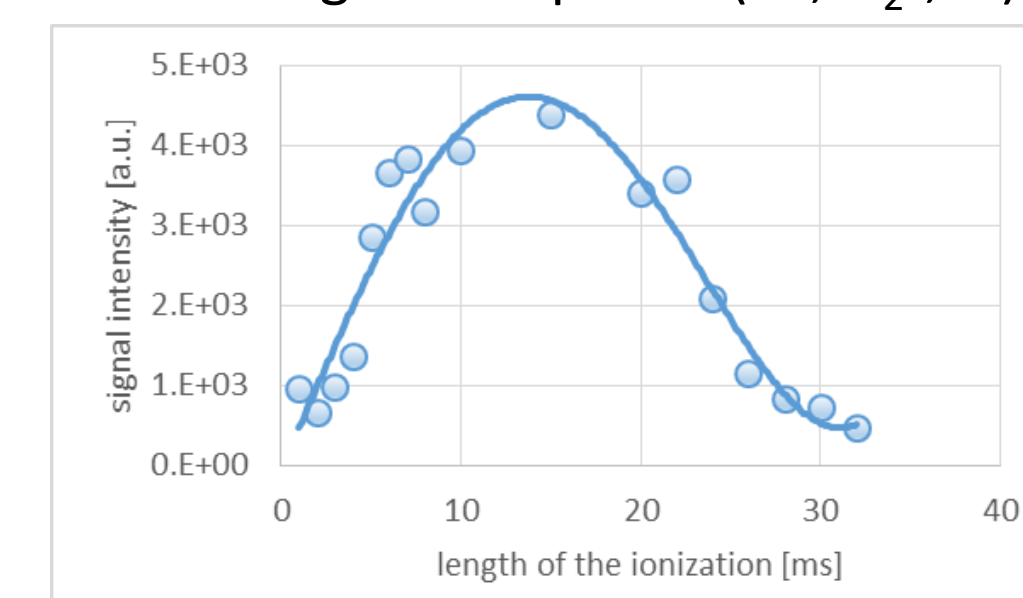


Figure 7: Ion signal response of m/z 91 in dependence of the ionization time.

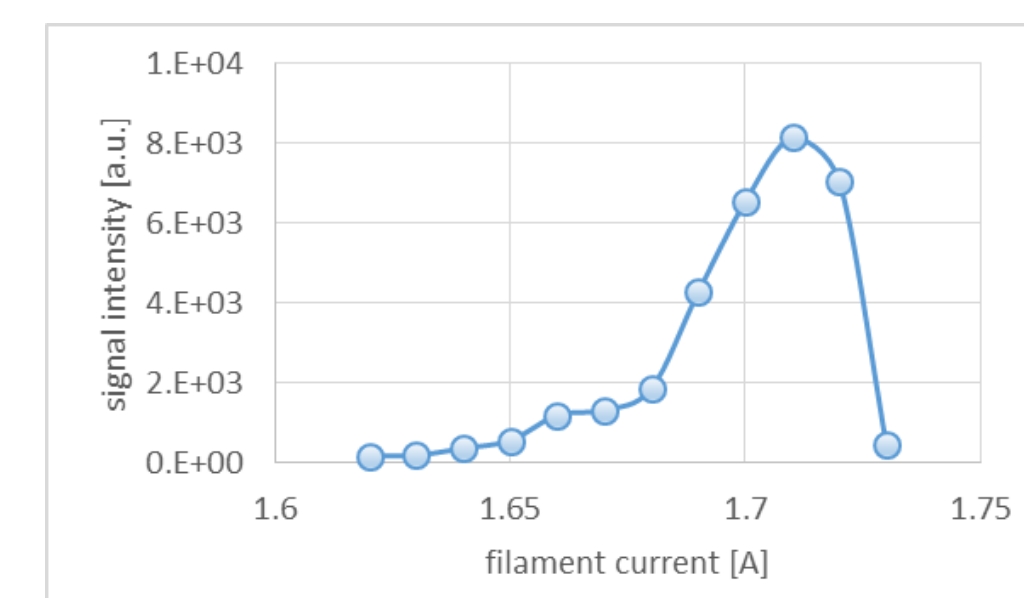


Figure 8: Ion signal response of m/z 91 in dependence of the filament current.

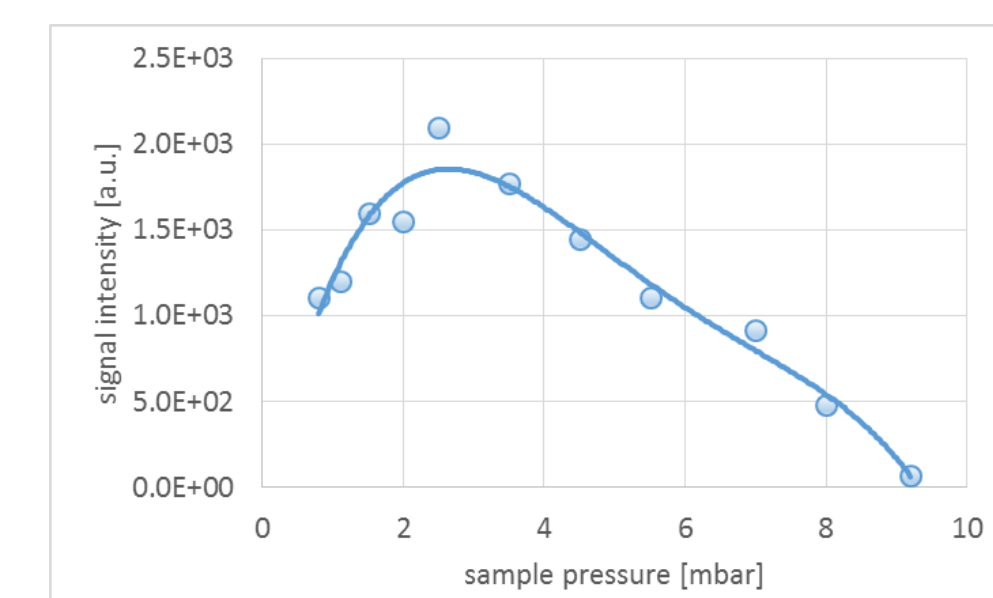


Figure 9: Ion signal response of m/z 91 in dependence of the sample gas pressure.

Ion signal loss / ion signal suppression

The ion signal loss at elevated total ion densities is examined using a simple gas mixture consisting of nitrogen and oxygen in a ratio of either 80/20 or 20/80. While increasing the ionization time the ion signal responses of m/z 28 and m/z 32 are recorded. Figure 10 shows mass spectra for short and eight times longer ionization times. In both cases the ion species that is present in larger excess entirely suppresses the minor component. Analogous, the ion signal suppression of Toluene shown in the above presented measurements is explained by the large excess of nitrogen ion species present inside the trap.

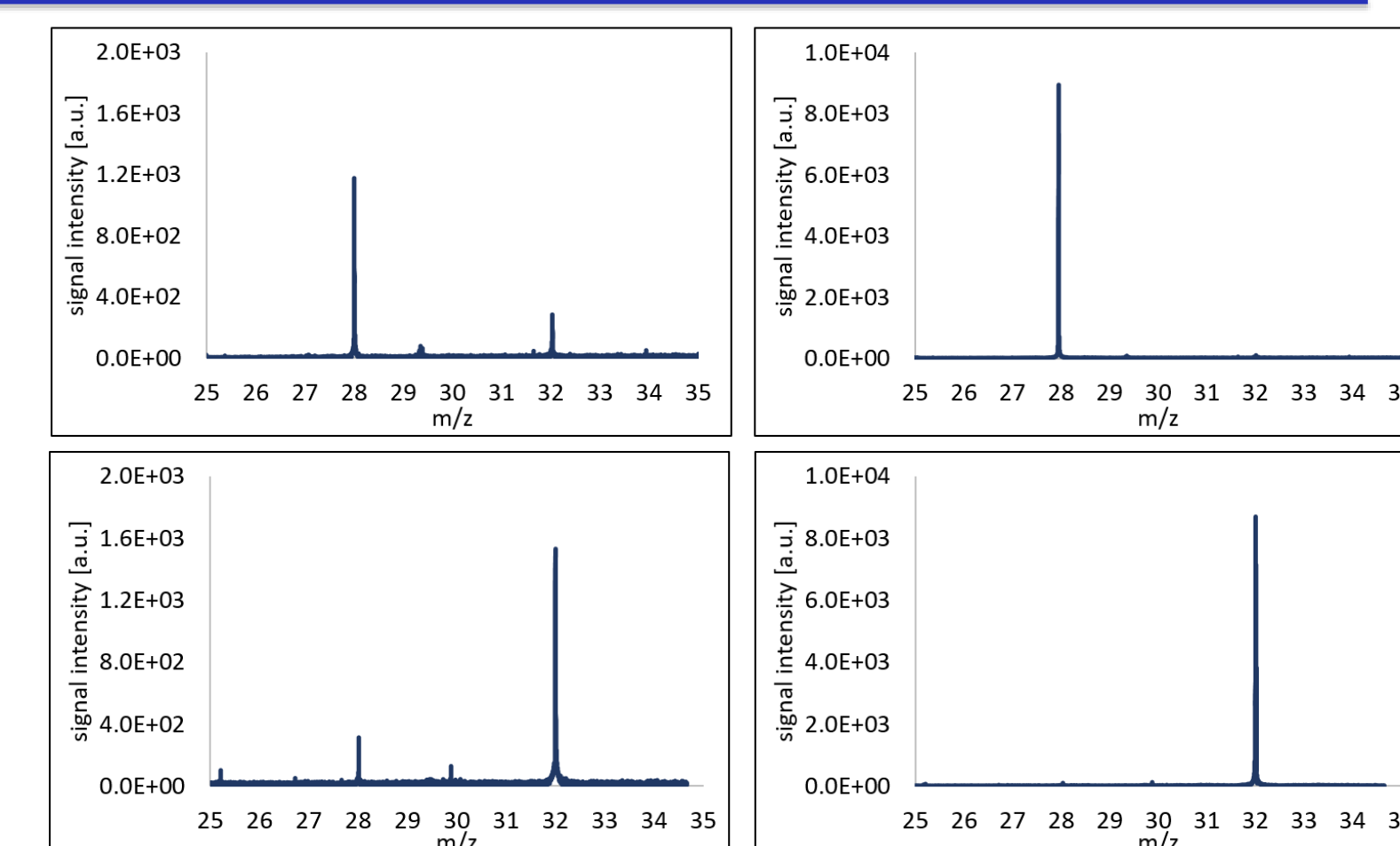


Figure 10: Top: Mass spectra obtained while sampling 20/80 nitrogen and oxygen at short and longer ionization time. Bottom: Mass spectra obtained while sampling 80/20 nitrogen and oxygen at short and longer ionization time.

Mass shifts

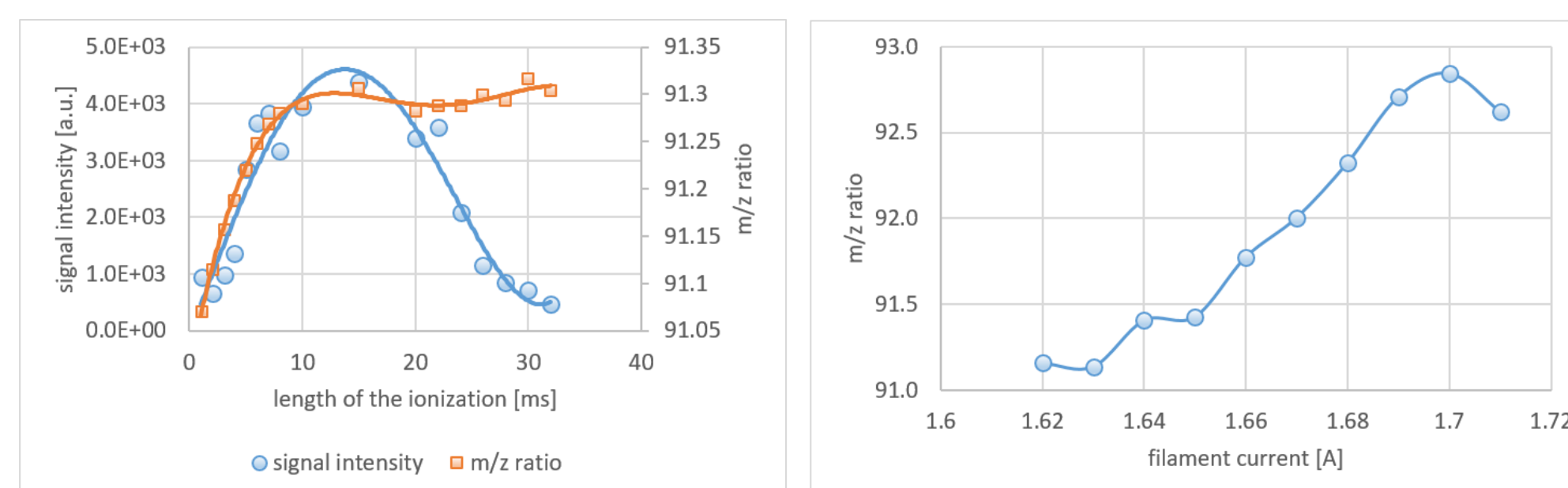


Figure 11: Observed mass shifts of m/z 91 while increasing the ionization time.

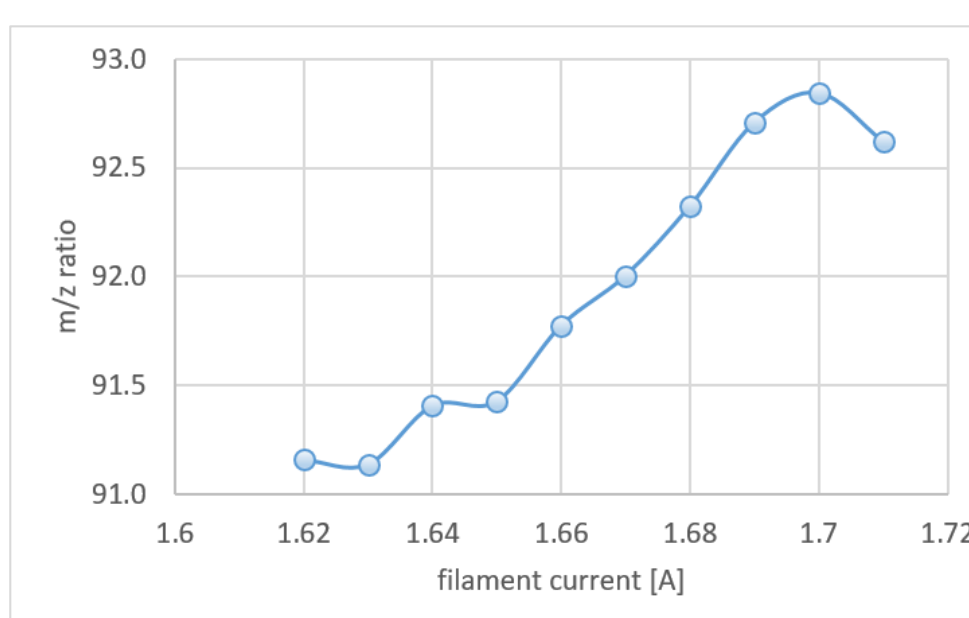


Figure 12: Observed mass shifts of m/z 91 while increasing the filament current.

In addition to ion signal loss and/or suppression a further space charge induced phenomenon is mass signal shift. An analysis of the recorded m/z ratios with increasing ionization time shows a total mass shift of 0.3 Da, which represents a m/z error of approx. 0.3 %. With increasing filament current a maximum mass shift of even 1.5 Da is determined, corresponding to a m/z error of 1.6 %.

Application of SWIFT

SWIFT is used for a resonant excitation of selected mass ranges or individual m/z ratios. Depending on the excitation energy, over-excitation and thus ion removal from the trap volume occurs. A broadband SWIFT pulse is used to remove matrix ions and hence to reduce the total ion load of the trap.

Using 500 ppbV Toluene in nitrogen increasing analyte ion intensities are obtained even at largely extended ionization times and increased filament currents. In addition, the ion signal mass shifts are strongly reduced due to the lowered total ion density within the trap.

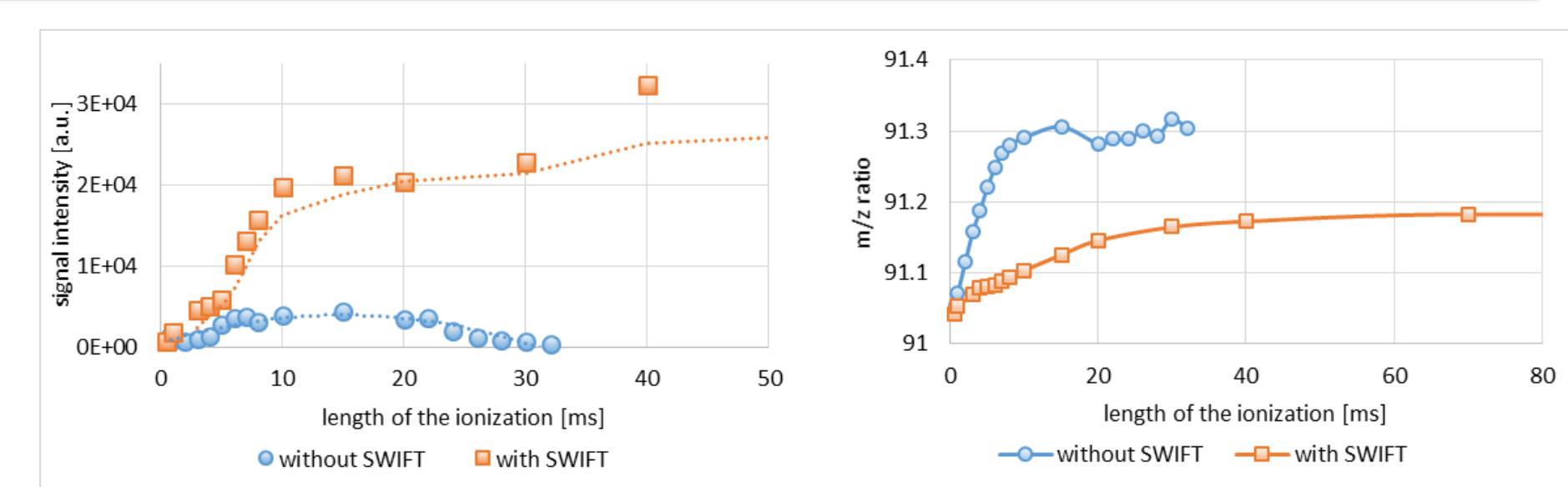


Figure 13: Increased signal intensities (left) and reduced mass signal shifts (right) due to the application of SWIFT while increasing the ionization time.

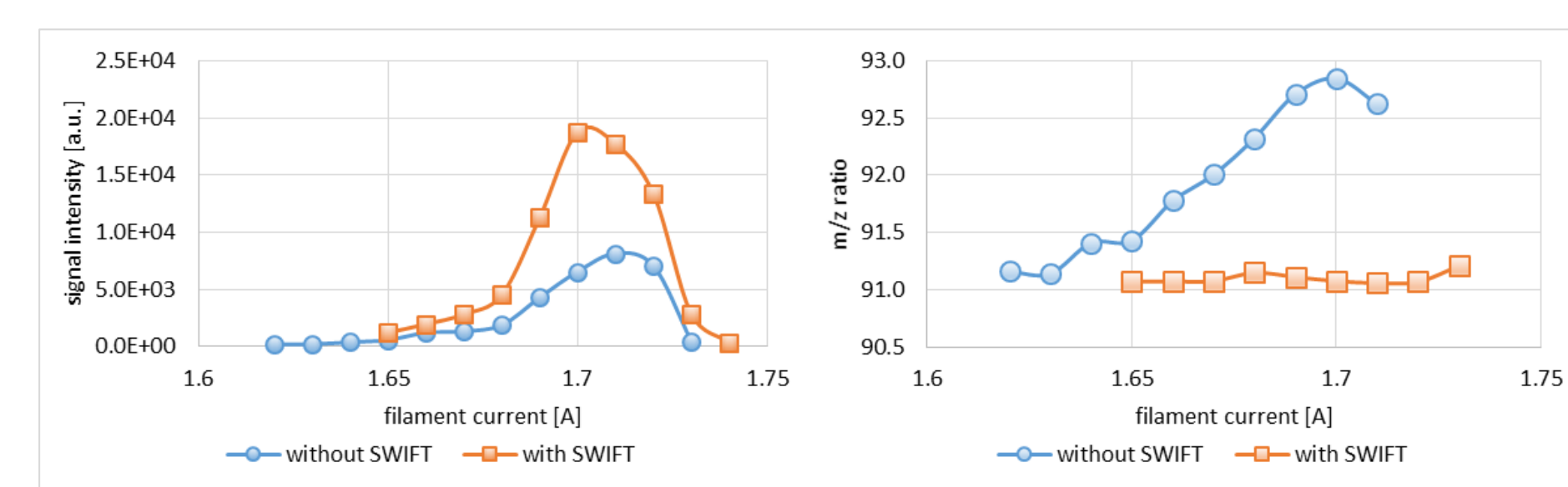


Figure 14: Increased signal intensities (left) and reduced mass signal shifts (right) due to the application of SWIFT while increasing the filament current.

Conclusions

Transient pressure profile

- Two approaches are used to investigate the pressure profile inside the ion trap
 - Reading of the pressure gauge
 - Examination of the analyte signal response in the mass spectrum
- By a temporal shift of 10 ms, i.e., the gauge response time, the pressure gauge data and analyte signal data become congruent for gas inlet I
- Hence, a determination of the trap pressure becomes feasible
- A direct comparison of pressure gauge data and ion signal responses results for gas inlet II is not possible
- The comparison of experimental signal profiles for both gas inlets, however, allows an estimation of the trap pressure for gas inlet II
- With typical sample gas pressures and valve opening times a maximum pressure of 10⁻³ mbar is reached inside the trap
- The known pressure profile allows an optimum adaption of the measurement sequence

Space charge induced effects

- Ion signal loss and ion signal mass shifts up-to several percent are observed in dependence of the number of ions present inside the ion trap
- Matrix ions, even if they are not trapped on stable trajectories, as well as other ion species present at elevated mixing ratios are supposed to cause the observed effects
- SWIFT is successfully applied for a reduction of the total ion number
- The application of SWIFT strongly reduces space charge induced effects and allows thus a more flexible adjustment of measurement parameters

Outlook

- Improvement of the pumping rate
 - Enhanced gas conductance by modification of the trap geometry (huge mechanical effort)
 - Increased analysis duty cycle
- Measurement of the ion load within the trap
 - Avoiding ion trap overload and thus
 - Avoiding space charge induced effects
- Optimization of SWIFT sequences: time of application, excitation energies, mass range, etc.

Literature

- Schmidt, M.; Brockhaus, A.; Brockmann, K.; Benter, Th.; Laue, A.; Aliman, M.; Using a Fourier transform quadrupole ion trap operating with advanced ion excitation methods for high performance mass analysis of organic hydrocarbons; 62nd ASMS Conference on Mass Spectrometry and Allied Topics; Baltimore, MD, USA (2014)
- Brachthaeuser, Y.; Mueller, D.; Kersten, H.; Brockmann, K.; Benter, Th.; Aliman, M.; Fedosenko, G.; Reuter, R.; Laue, A.; Derpmann, V.; Chung, H.Y.; Micro-plasma based pulsed direct charge transfer stage coupled to a FT-IT mass spectrometer; 63rd ASMS Conference on Mass Spectrometry and Allied Topics; St. Louis, MO, USA (2015)
- Brachthaeuser, Y.; Mueller, D.; Kersten, H.; Brockmann, K.; Benter, Th.; Derpmann, V.; Laue, A.; Reuter, R.; Aliman, M.; Development and characterization of an FT-QIT with in situ electron ionization for residual and trace gas analysis; 64th ASMS Conference on Mass Spectrometry and Allied Topics; San Antonio, TX, USA (2016)

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