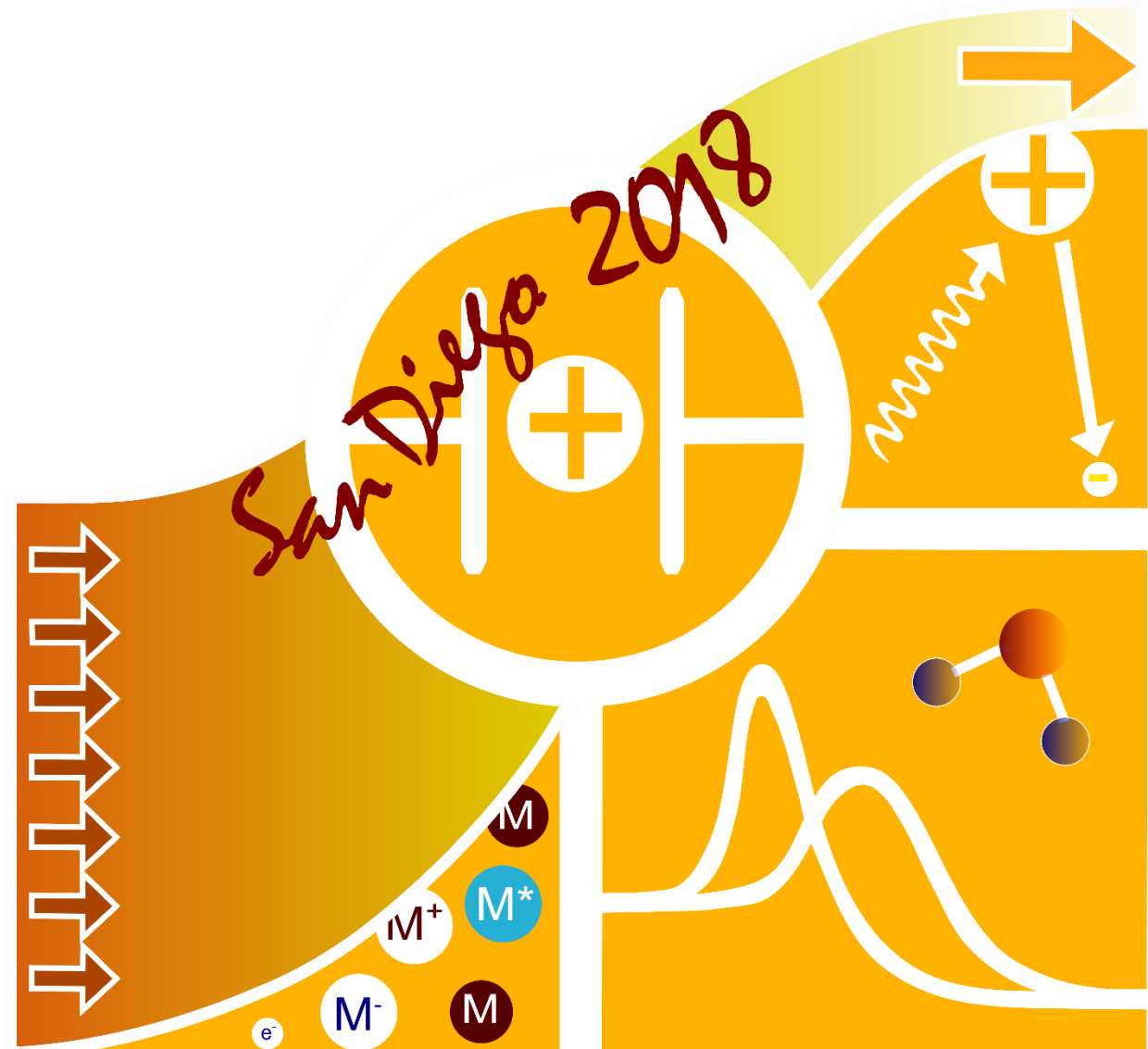
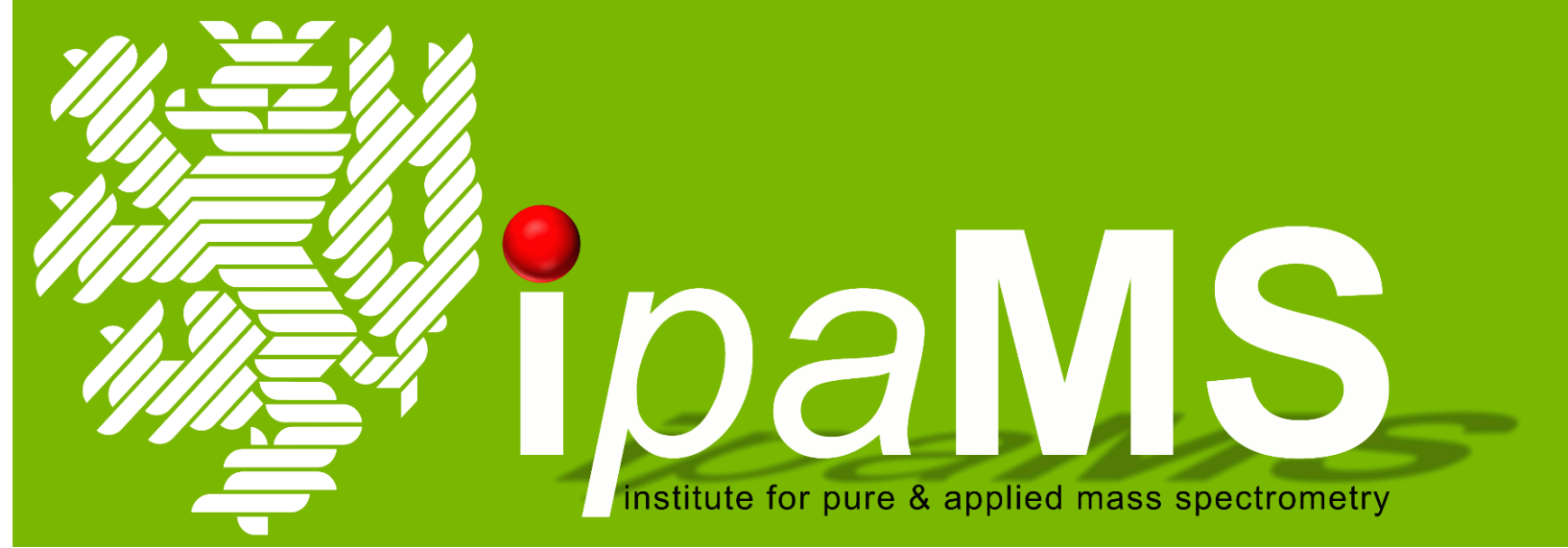




Progress in the development of a kinetically controlled chemical ionization setup



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Introduction

Ion transformation processes in regions of mass spectrometers with high collision probabilities and elevated collision energies generally alter the detected ion distribution. In particular, the ionization process perturbs the neutral equilibrium and induces a rich ion-molecule chemistry leading into a new equilibrium state. After a sufficient number of reactive collisions, thermodynamics governs the final ion distribution, which may differ significantly from the neutral composition. Recently, a chemical ionization setup was introduced, which aims to reflect the neutral analyte mixing ratios [1] through kinetical control or complete titration of neutral analyte by abundant primary reagent ions. In this contribution we present an enhanced version of this setup, in particular the improvement of the low-pressure RF discharge as the primary ionization source will be discussed.

Approach:

- Application of one of the strongest known gas phase acids, H_3^+ , as the main primary charge carrier.
- Subsequent quantitative transformation of H_3^+ into reagent ions (N_2H^+) for less exothermic analyte protonation.
- Maintaining the protonation reactions of the analyte under kinetic or titration control.

Methods

Chemical ionization setup

MS	HTOF with custom ion transfer optics (TOFWERK AG, Thun, Switzerland)
Ion Source	Custom low pressure RF discharge source
Gases	Hydrogen 5.0 and Nitrogen 5.0 (Messer Group GmbH, Krefeld, Germany)
Analytes	Custom gas mixtures: Benzene, toluene, o-xylene in nitrogen (1 -10 ppmV) All gases were used without further purification
Gas Flows	All gas flows are controlled by mass flow controllers (MKS Instruments Deutschland GmbH, Berlin, Germany)
Ion current setup	
Electrometer	Model 602 Solid-State Electrometer, (Keithley Instruments Inc., Cleveland, OH, USA)
Power Supply	Model 456 High Voltage Power Supply (EG&G Ortec, TN, USA)
Gas	Hydrogen 5.0 (Messer Group GmbH, Krefeld, Germany)

Ion current setup

Experimental setup

The dependence of the primary ion currents on various plasma source parameters was measured with the setup as shown in fig. 1. A sealed stainless steel vacuum chamber (1), equipped with an assembly of two facing electrodes, one for deflection (2) and one for detection (3). A glass tube (5) connects the custom low-pressure RF discharge (4) with the vacuum chamber.

The continuous RF discharge effluent is aligned on the center axis of the electrode assembly with the gas flow passing between them.

The ion current was measured on the detection electrode (2) with an electrometer. For polarity separation a deflection voltage was applied on the deflection electrode (3).

The pumping speed of a connected rough pump and thus the pressure was adjusted with a needle valve (0.2 – 10 mbar).

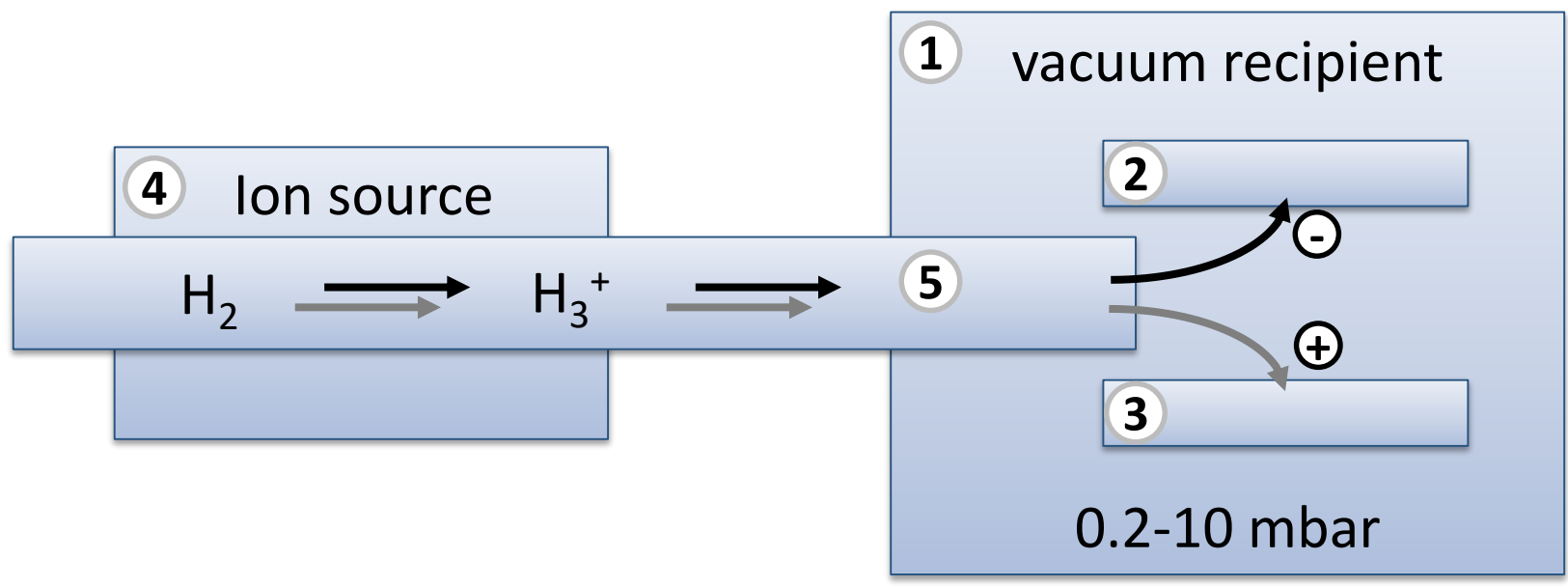


Figure 1: Schematic of the ion current measurement setup

Results

Figure 2, right:

The ion current as a function of the distance from the RF discharge to the detection electrode for four different pressures in the range from 0.6 to 4.3 mbar, without deflection voltage.

A common trend is visible: A steep ion current incline with increasing distance starting at negative ion currents and ending in a positive ion current maximum, followed by a less pronounced fall off, whereby the ion current stays positive. The maximum shifts to lower distances with increasing pressure. Note that the observed ion current without deflection voltage is due to charge diffusion and potentially photo electrons.

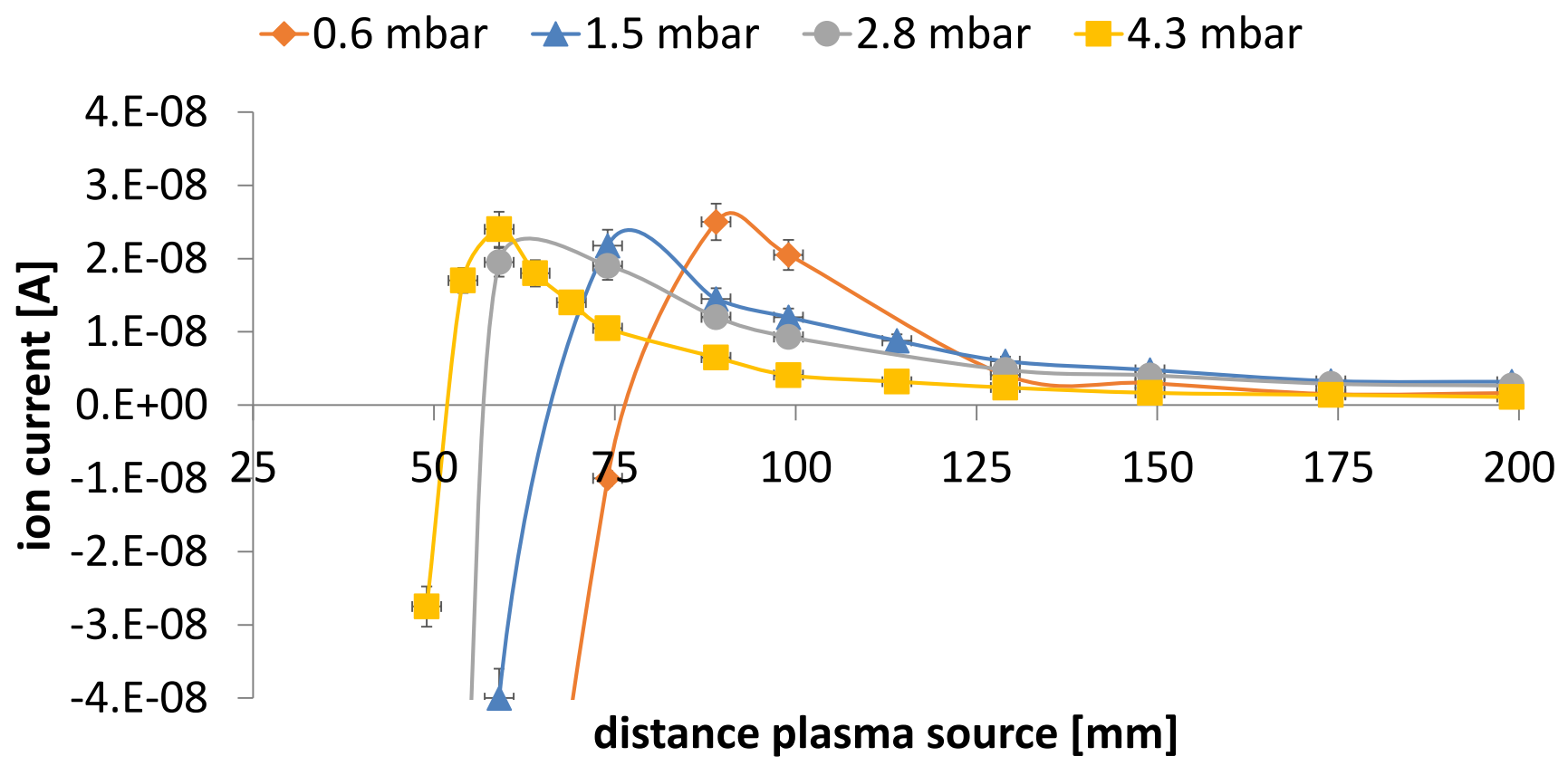


Figure 3, right:

Ion current in dependence of the distance between the RF discharge and the detection electrode for four different pressures in the range of 0.2 to 2.6 mbar. A deflection voltage of 50 V was applied.

The logarithm of the ion current declines linearly at a pressure of 0.2 mbar. With increasing pressure, the curves deviate from a linear trend, the slope decreases with increasing distance. A linear trend of the logarithmic ion current is in accordance with a first order charge loss mechanism. Curved signals indicate the occurrence of secondary effects, e.g. gas phase ion chemistry or recombination.

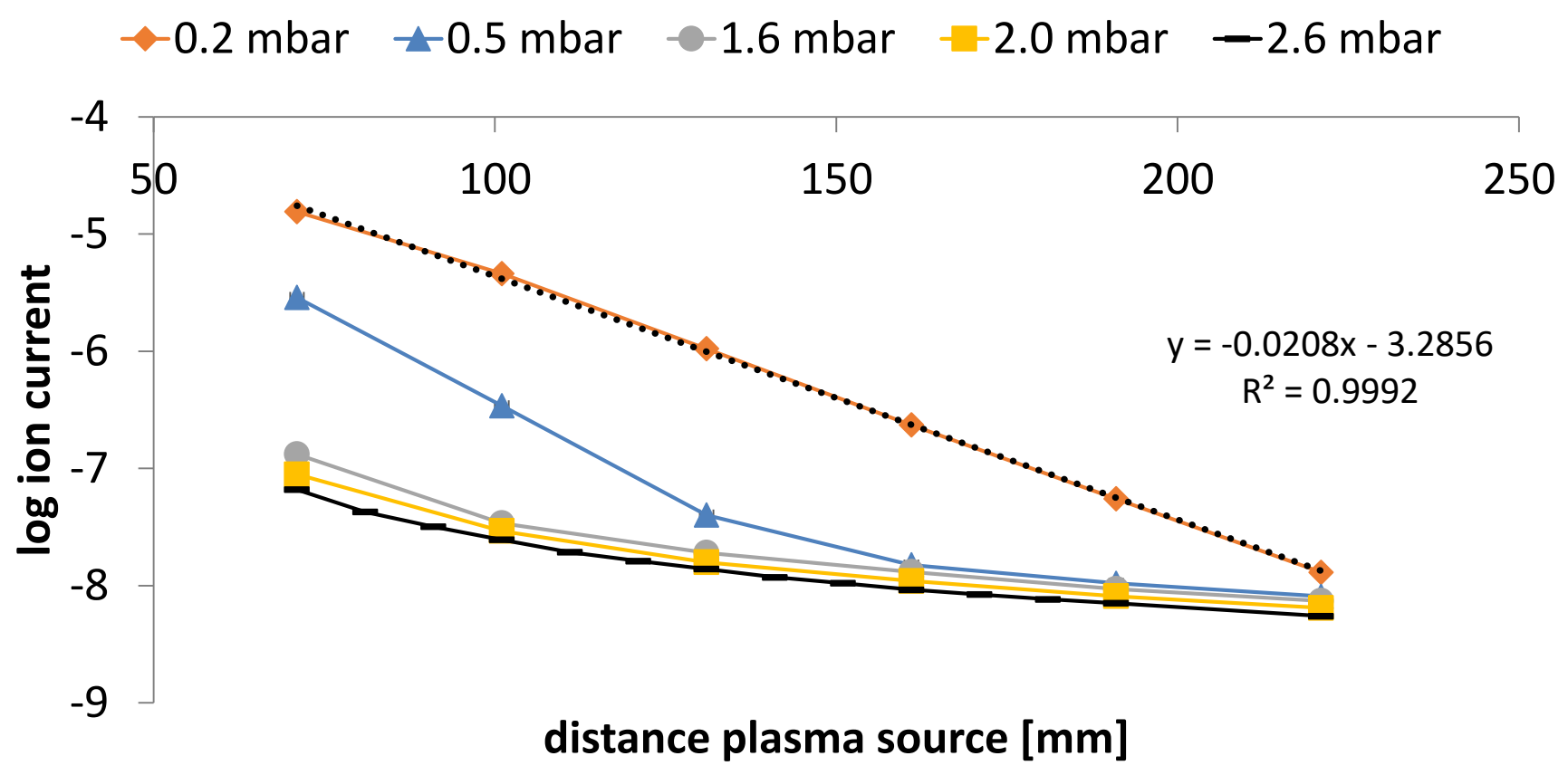


Figure 4, right:

Ion current for both polarities measured at a distance of 109 mm as a function of the deflection voltage at a pressure of 3.2 mbar. Both polarities show the same behavior. This indicates, that after 109 mm of gas flow anions and cations are still present in virtually equal concentrations.

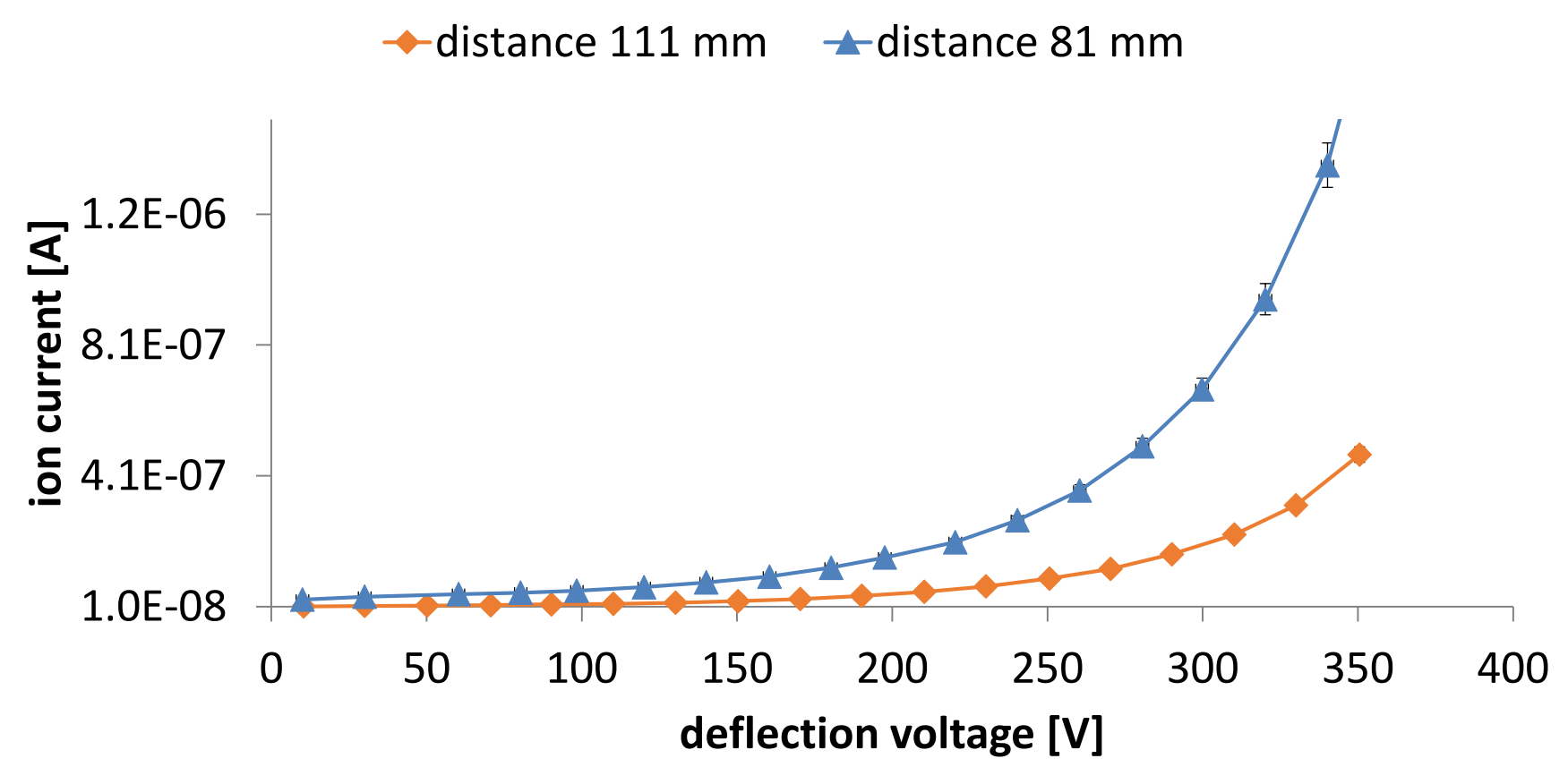
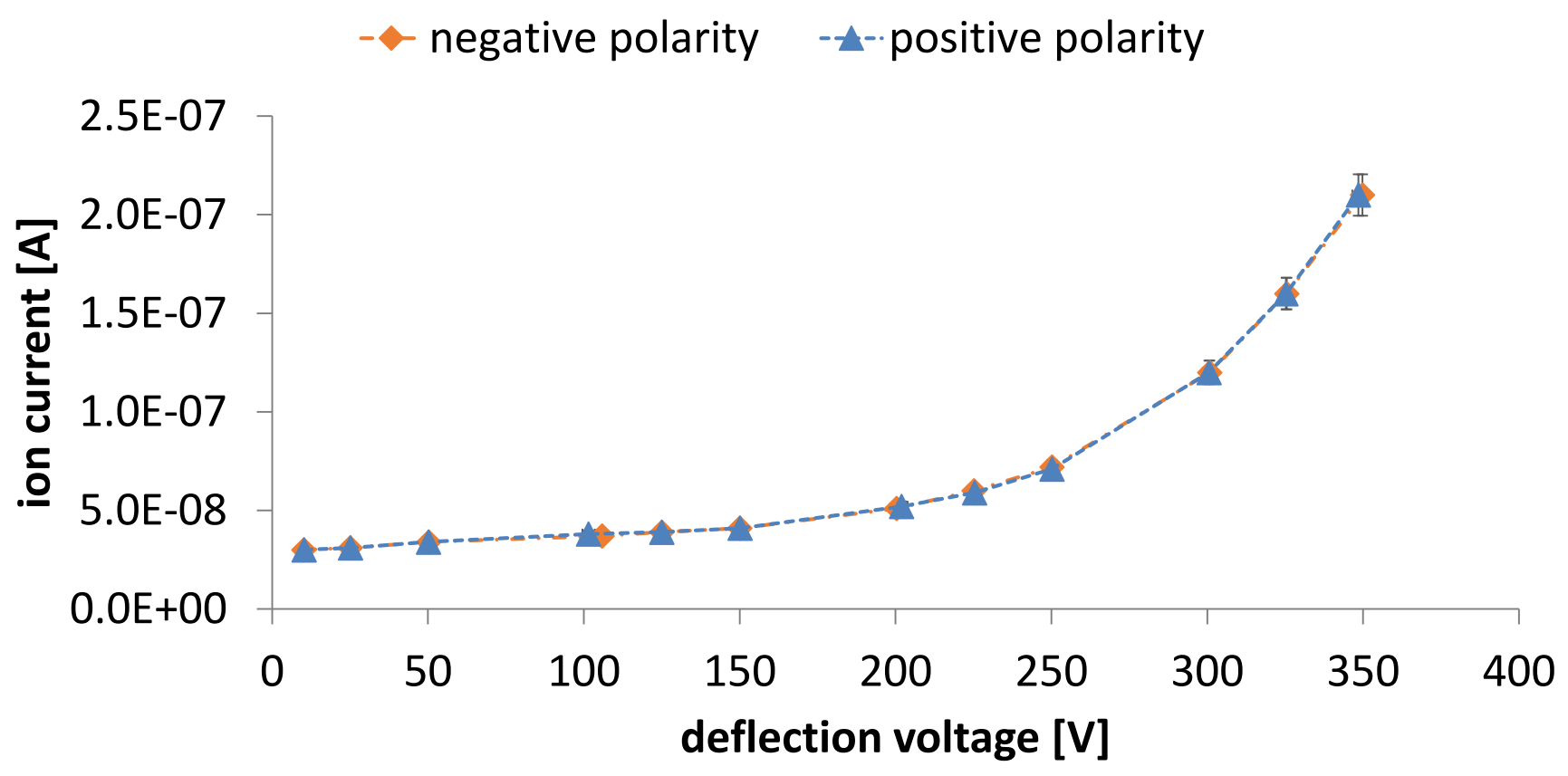


Figure 5, left:

Ion current in dependence of the deflection voltage for two different distances between the RF discharge and the detection electrode at 3.2 mbar.

The ion current increases similarly with deflection voltage in both cases, but the charge loss with distance to the RF plasma is clearly visible. The charge loss is independent from the deflection voltage.

Chemical ionization setup

Experimental setup

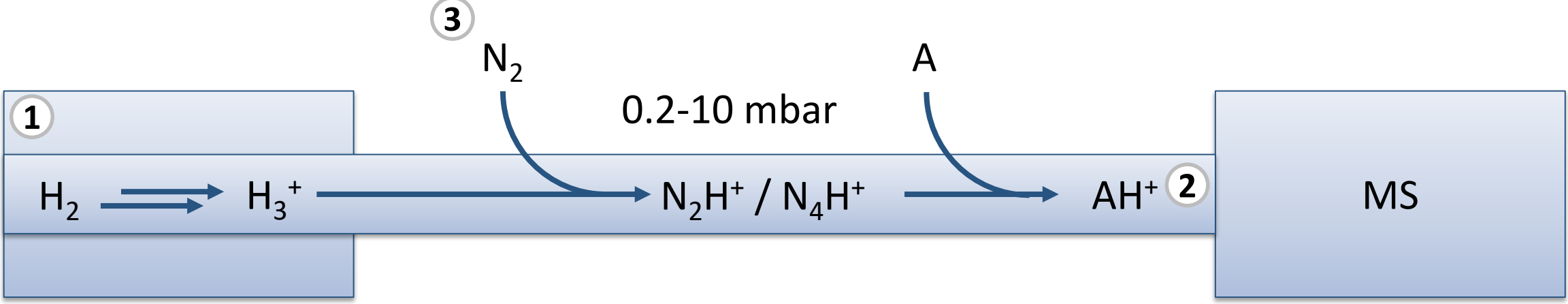


Figure 6: Schematic of the chemical ionization setup

A custom low-pressure RF discharge generates the reagent ions (H_3^+) within a hydrogen plasma fed by a continuous gas flow (1) [2]. The discharge source consists of a helical coil resonator (HCR) providing the RF energy to sustain the discharge. The steady flow of primary reagent ions is transported through a glass tube within the first differentially pumped pressure region (0.2 – 10 mbar) of a Time-of-Flight mass spectrometer (2). A second gas flow containing the gaseous sample is introduced into the primary reagent ion flow (3). Due to the presence of nitrogen as bulk gas, the primary protonating species for analyte ionization is (ideally and by theory) N_2H^+ .

Results

Figure 7, right:

Degree of protonation for a benzene/toluene/xylene mixture as function of the distance of the low-pressure RF discharge to the sample inlet at 3.1 mbar.

The degree of protonation is determined by the ratio of the molecule ion relative to the protonated molecule ion. The protonation degree increases with distance and reaches a maximum around 65 mm, followed by a less pronounced decline. The maximum is approximately located at the same position as the maximum of the measured ion current (cf. Fig. 2). Note the overall high level of protonation at all distances.

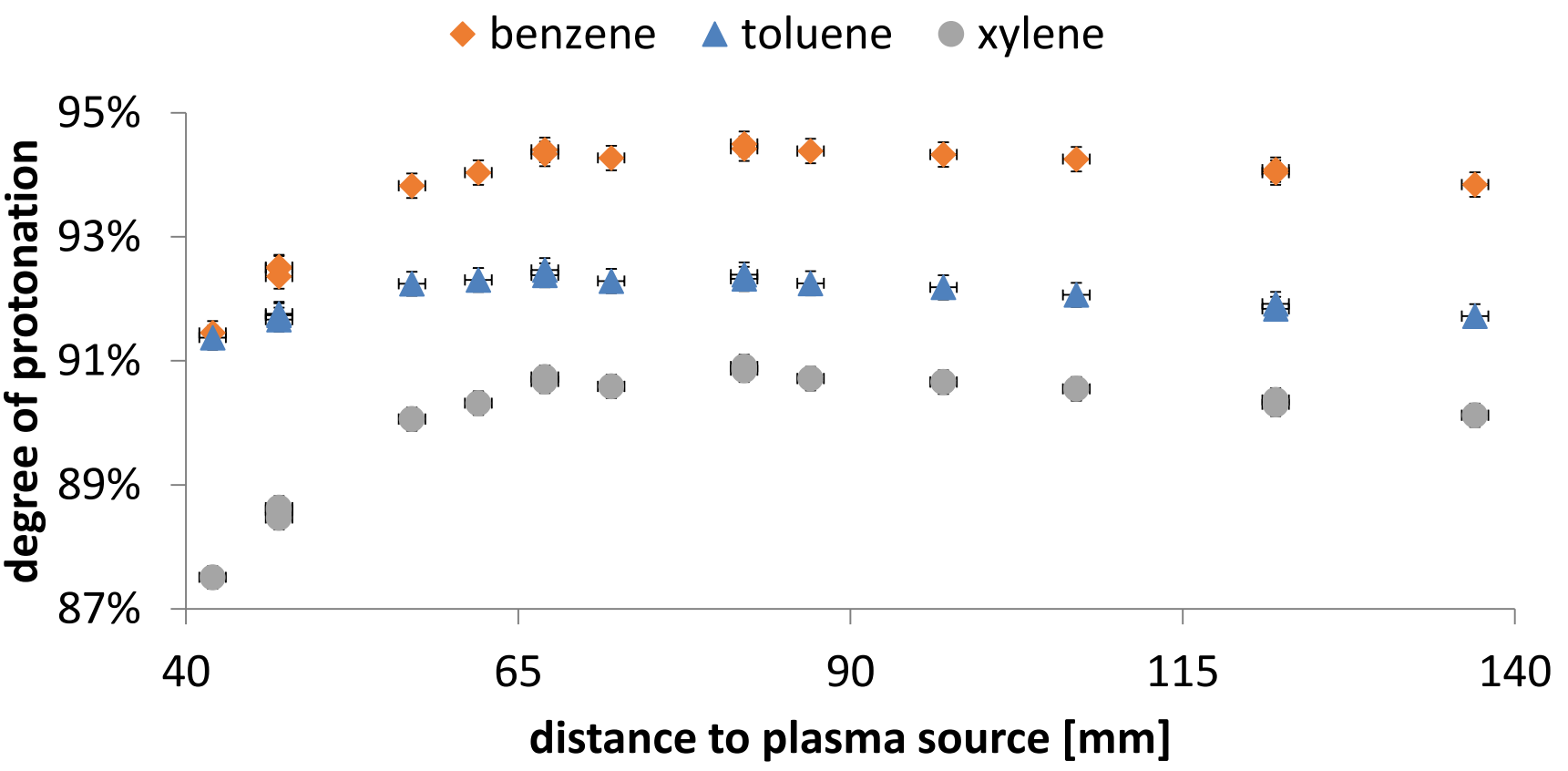


Figure 8, right:

Degree of fragmentation of toluene in dependence of the distance of the RF discharge to the sample inlet at 3.1 mbar.

The degree of fragmentation is determined by the ratio of the tropylium fragment ion ($m/z = 91$) relative to the protonated molecule ion. The degree of fragmentation decreases with increasing distance to the RF discharge. This indicates, that a direct exposure of the analyte to the plasma afterglow leads to fragmentation and should be avoided.

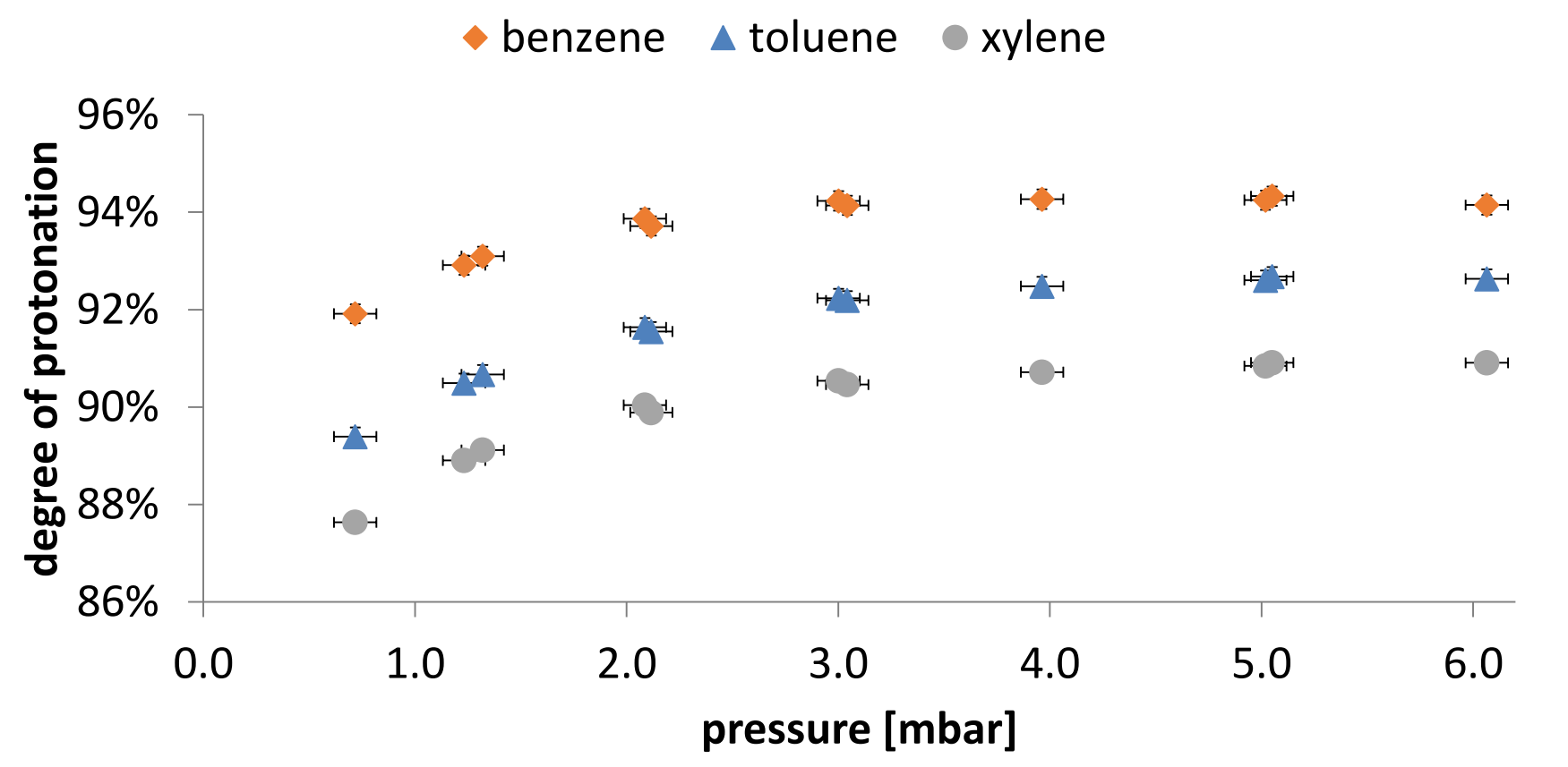
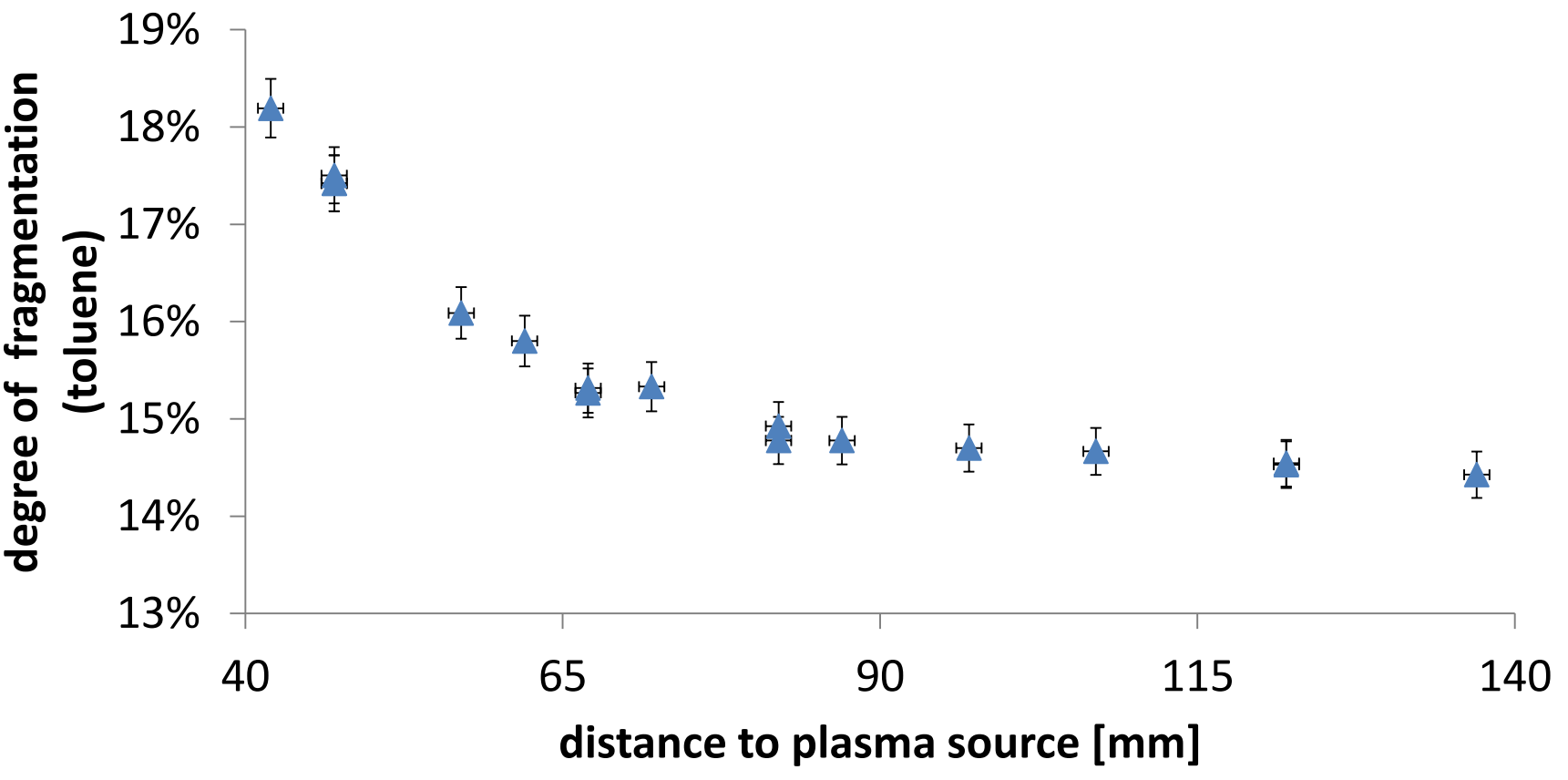


Figure 9, left:

Degree of protonation for a benzene/toluene/xylene mixture as a function of pressure. The mixture was introduced at a distance of 72 mm to the RF discharge.

The degree of protonation is determined by the ratio of the molecule ion relative to the protonated molecule ion. The degree of analyte protonation increases with pressure and levels off at 3 mbar. The observed maximum of protonation for benzene is 94 %, for xylene 93 % and for toluene 91 %.

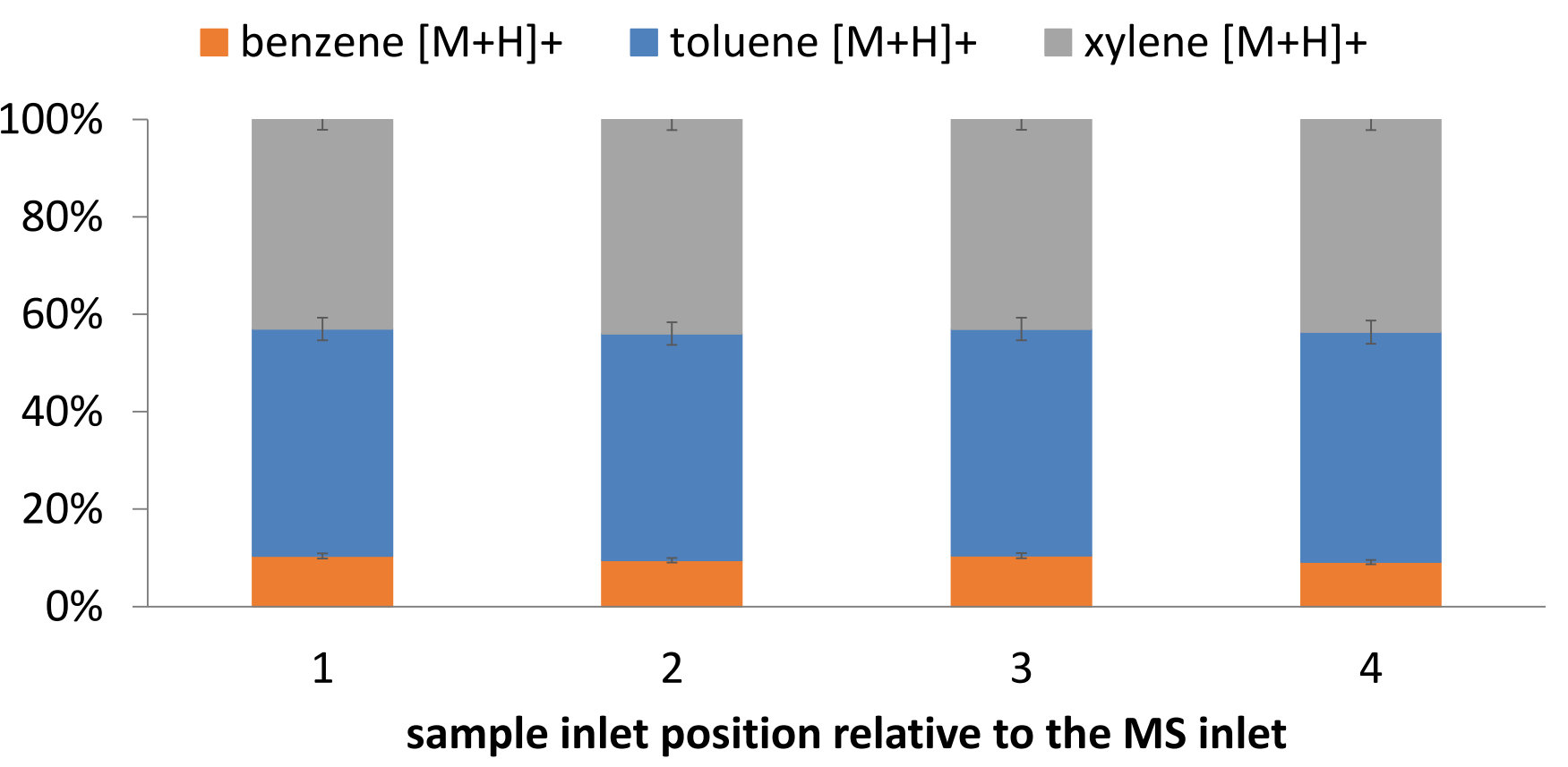


Figure 10, left:

Signal distributions for a benzene/toluene/xylene mixture introduced at different sample inlet positions relative to the MS inlet at 3.1 mbar. The reaction time between the primary reagent and the sample gas varies with the sample inlet positions (cf. fig. 6; #3). The position numbers 1-4 indicate the reaction time in ascending order.

The observed signal distributions are not sensitive to the sample inlet position, which could indicate that the system is in kinetic or titration control.

Conclusions

Ion current measurements:

- Observed ion currents are in the μA region.
- Significant charge loss at the walls of the glass tube.
- Occurrence of additional charge loss effects.
- Surprisingly similar results for positive and negative ion polarities.

Analyte fragmentation/ protonation:

- Kinetic and/or titration control of the ionization process for all investigated ion source parameters.
- Overall high degree of protonation for benzene, toluene and xylene.
- In close proximity to the plasma source (afterglow region): occurrence of analyte fragmentation.

Outlook

- Minimizing wall loss effects of primary reagent ions.
 - Investigation of different glass types for ion transport and ion generation.
 - Applying additional electric fields for charge transport, manipulation and minimizing wall loss effects.
- Further investigation of occurring processes in the plasma afterglow with extensive ion current measurements and mass spectrometric investigations.
- Further verification of a kinetic control of the chemical ionization setup.
- Simulations of the chemical kinetics based on the results of the ion current measurement.

Literature

- [1] Kroll, K.; Erdogan, D.; Kutsch, T.; Kersten, H.; Benter, T. Evaluation of a kinetically controlled chemical ionization setup, *65th ASMS Conference on Mass spectrometry and Allied Topics*, Indianapolis, IN, USA (2017)
- [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)

Acknowledgement

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