Investigation of Ion Transfer Times in a commercial Atmospheric Pressure Ion Source

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Introduction

At atmospheric pressure (AP) ions are subject to a high frequency of collisions with bulk gas particles and other species present. Due to the high number of collisions, even relatively slow chemical reactions may become relevant in an AP ion source. The length of the ion migration path is directly correlated with the absolute number of collisions, therefore it may serve as a figure of merit to estimate the relevance of individual chemical interactions.

In addition the experimental investigation of ion transfer times allows the verification of complex numerical models, which consider transport due to electrical fields and viscous gas flow.

Methods

Numerical Methods

Ion Trajectory Simulation:

SIMION charged particle simulator (v8.01) with Statistical Diffusion Simulation (SDS) Extension

Computational Fluid Dynamics Solver:

Ansys CFX v. 12.0 with Shear-Stress-Transport (SST) turbulence Model Extension and convection/diffusion simulation for neutral analyte distribution simulation

Experimental Methods

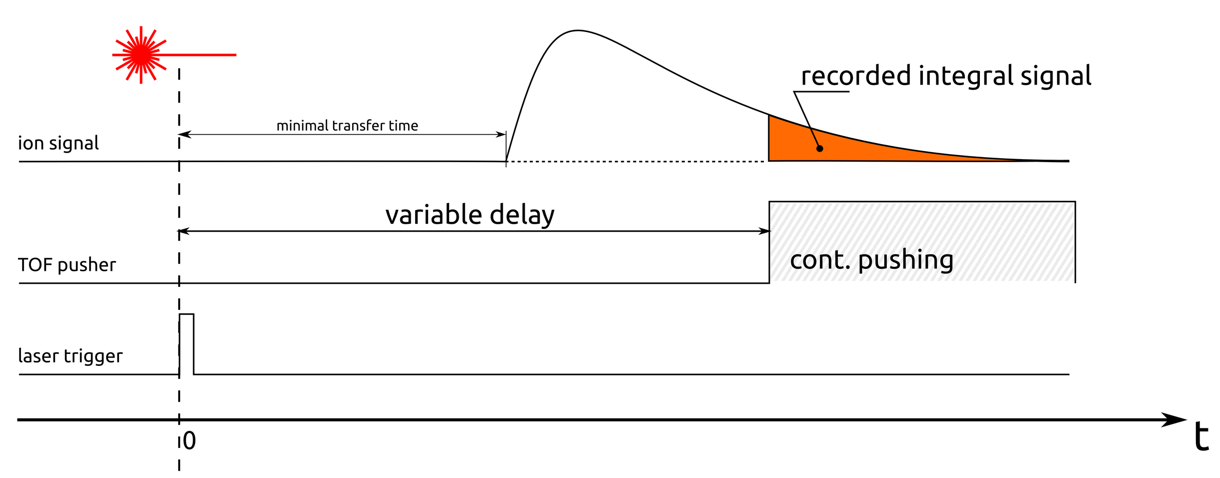
Particle Image Velocimetry Setup:

- 2D PIV (LaVision, Goettingen, Germany) with New Wave 120mJ YAG double pulse laser (ESI, Portland, USA)
- Seeding generator: DEHS oil, >108 particles/cm³ (Topas, Dresden, Germany)

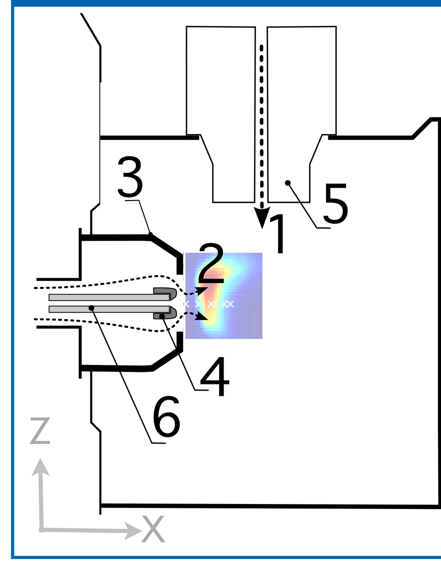
Temporal and spatial resolved ion measurements:

- 2-Photon laser ionization (APLI) with ATL Atlex KrF* Excimer Laser (λ=248nm)
- Mass analyzer: Bruker microTOF (ext. triggered)
- Analyte: 1 µmol Benzo[a]pyrene in ACN

Integral Ion Transfertime Measurement



AP Ion Source (MPIS)



1: Nebulizer / Analyte gas flow
2: Dry-gas flow
3: Spray-shield
4: Capillary cap
5: Vaporizer block
6: Inlet capillary

Ion Source Parameters:

U_{Cap}: Voltage on capillary cap
U_{Shield}: Voltage on Spray-Shield
Q_D / T_D: Dry-Gas flow / temp.
Q_N / T_N: Nebulizer gas flow / temp.

Figure 1) Multi Purpose Ion Source (MPIS) schematic

Conclusions

- The currently available numerical ion motion model significantly underestimates the width of the experimentally observed temporally resolved ion signal in the MPIS.
- The ion transfer times in the tubular ion source as well as the spatially resolved ion signal in the MPIS are at least qualitatively reproduced by the numerical model.
- The model is valid for simplified conditions as present in the tubular ion source and in terms of the averaged flow field and the averaged neutral analyte distribution in the MPIS.
- At the current development stage, the model does not consider effects which lead to significant broadening of the temporally resolved ion signal caused by the complex conditions in the MPIS.
- Diffusive effects presently not considered by the numerical model are:
  - Flow oscillations
  - Effect of flow turbulence on ions (turbulent diffusion)
  - Space charge diffusion / Space charge repulsion
- To model the ion transfer times in the MPIS, diffusive effects have to be considered. Envisioned further development steps are:
  - Development of a non-static fluid dynamical model of the MPIS
  - Development of a valid model for the effects of turbulence on the ions (Development of a transfer function from turbulence model parameters as the turbulent kinetic energy (TKE) to parameters of the SDS ion migration model)

Transfer Times: MPIS (axial variation)

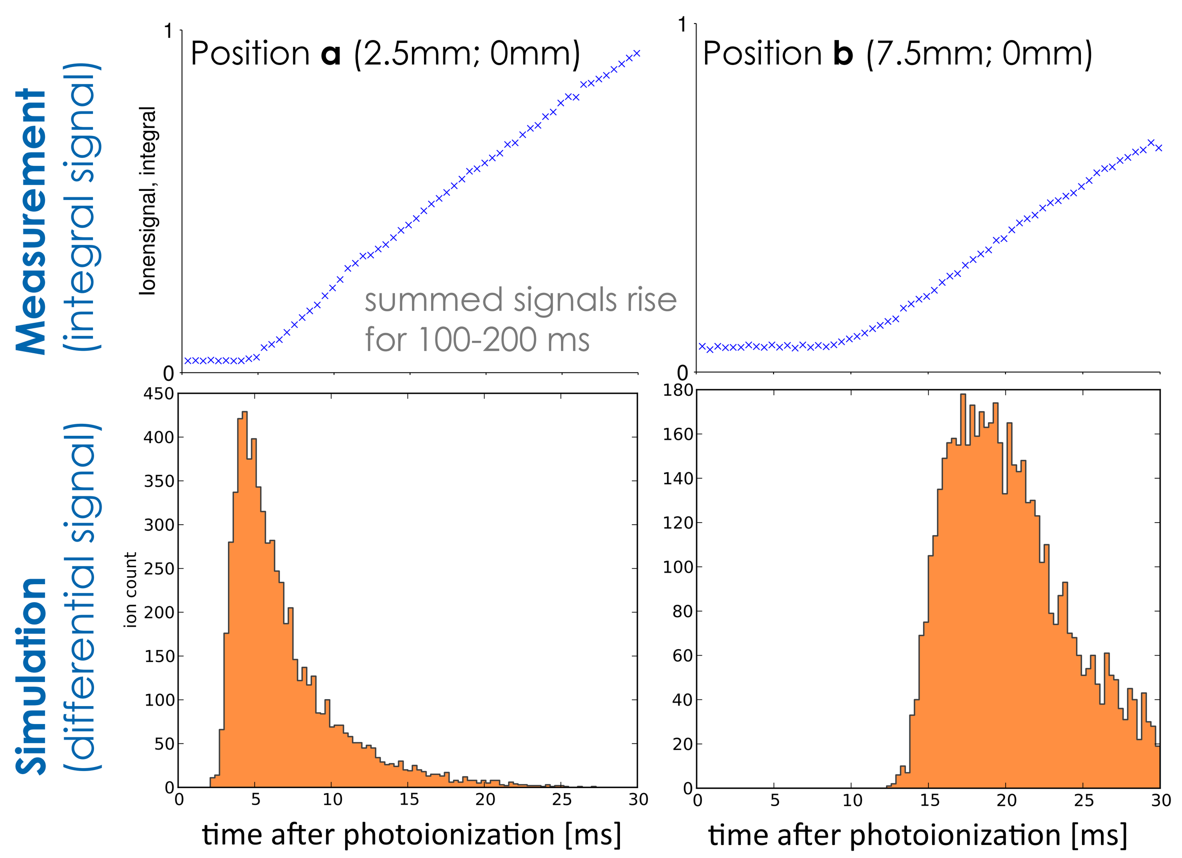


Figure 2) Simulated and measured temporally resolved ion signal in an MPIS

The comparison between simulated and measured ion signal reveals:

- The simulation predicts a relatively sharp ion pulse which is not observed in the experiments.
- The simulated pulse width is in the range of 10-30 ms, experimentally ion pulses of least 100 ms length are observed
- This suggests that the simulation does not consider essential effects which lead to significant ion diffusion and peak broadening

Spatial resolved ion signal (DIA):

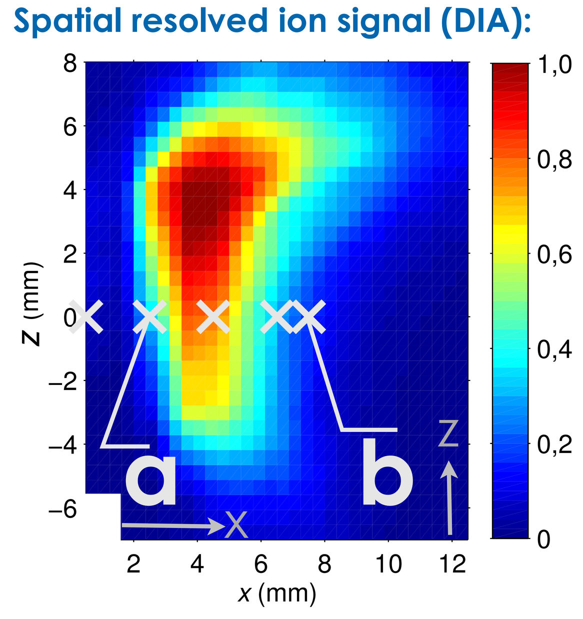


Figure 3) Spatially resolved ion signal (Distribution of Ion Acceptance - DIA), with the ionization positions of the temporally resolved data shown to the left

Minimal ion transfer times:

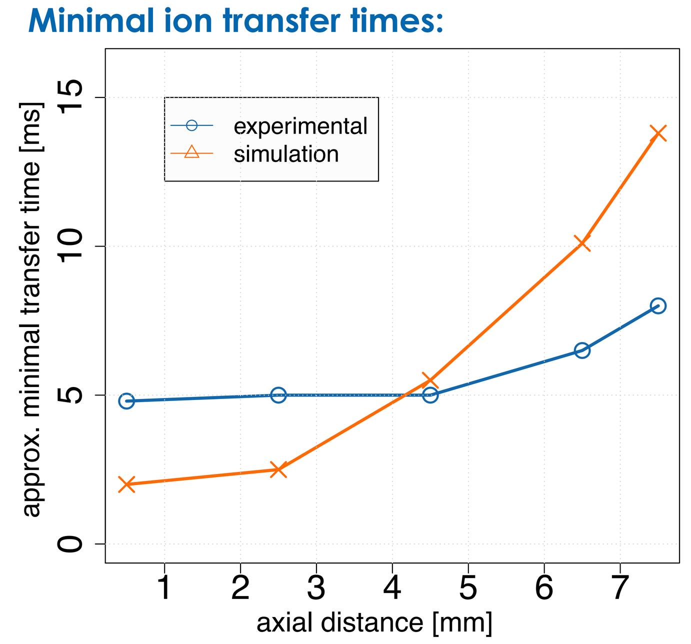


Figure 4) Comparison of the simulated and experimentally observed minimal ion transfer times

The analysis of all 5 ionization positions shows:

- The simulation reproduces the increasing *minimal ion transfer times* with increasing distance to the MS inlet
- The experimentally observed slope of the dependence of the minimal transfer time is **not** reproduced by the simulation, even if the *spatially* resolved ion signal distribution is well reproduced by the simulation method (shown in former ASMS contributions [3])
- A relatively high level of uncertainty is observed in experiments and simulations, due to the poorly defined initial signal increase for each individual ion pulse

AP Ion Source (MPIS): Complex Fluid Dynamics

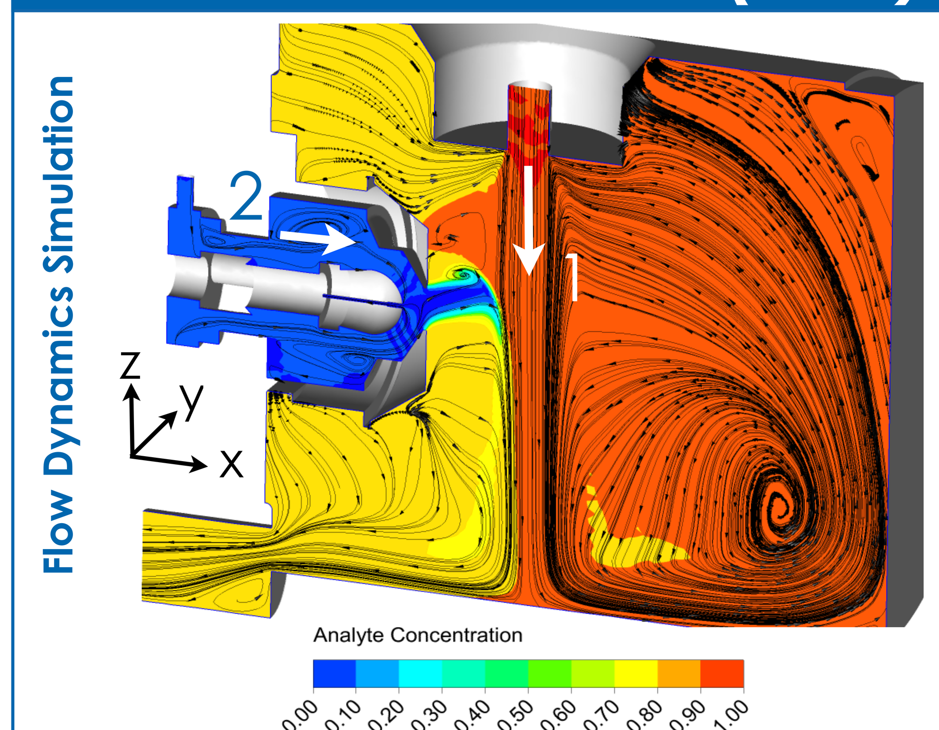


Figure 5) Simulated static gas flow and neutral analyte distribution in MPIS [4]

- Complex flow dynamics in MPIS; Complex convergence zone of nebulizer gas (1) and dry gas (2) flow
- CFD simulation shows *static* flow field (flow oscillations averaged)
- Nearly isotropic neutral analyte concentration in MPIS, with exception of the volume "washed out" by the dry gas flow

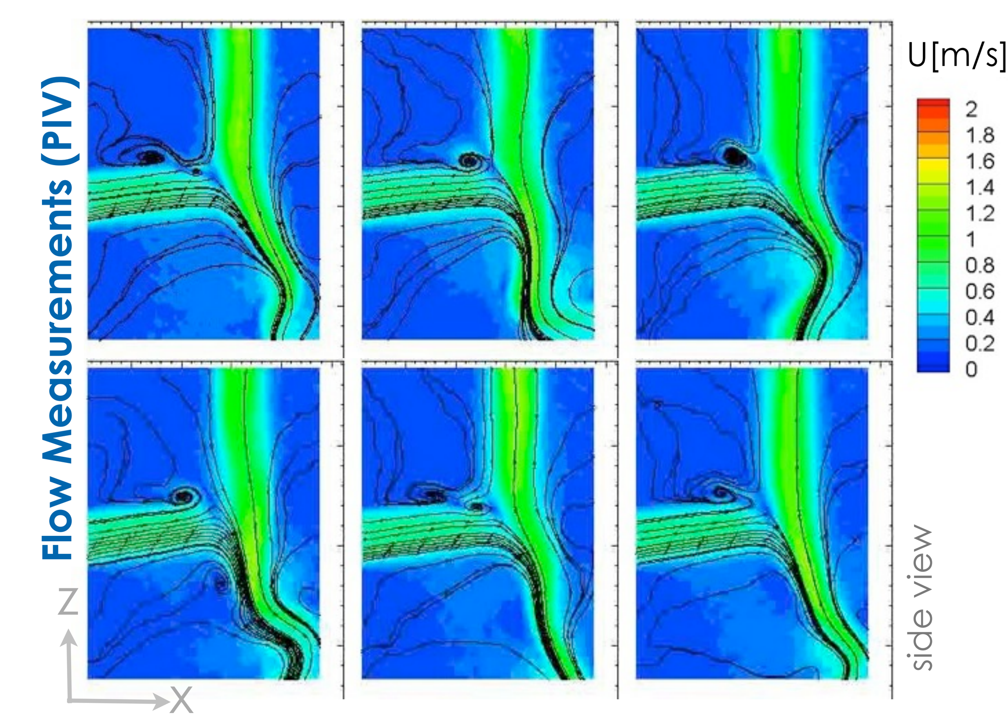


Figure 6) Single frames of particle image velocimetry (PIV) frames (color encoded: flow velocity magnitude "U")

- Single PIV frames show significant oscillations in gas flow
- The position and shape of critical flow features (vortices in the convergence zone, borders of gas streams) swiftly changes temporally

Transfer Times: Tubular Ion Source

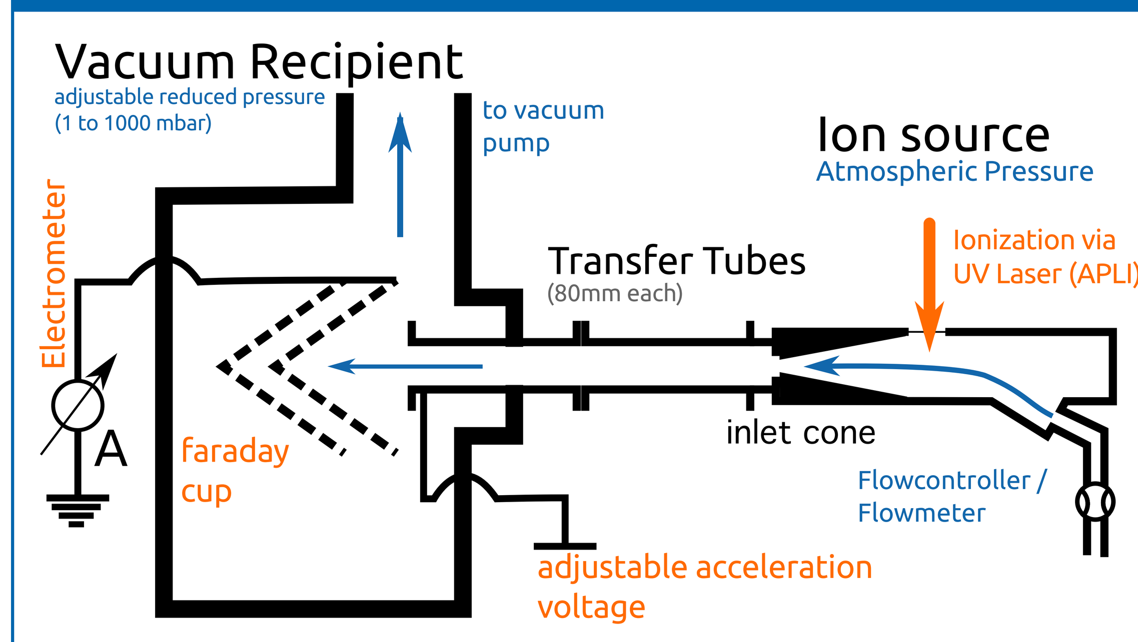


Figure 7) Schematic of the experimental setup for determination of transfer times in ion transfer tubes

- Ion current detection with a Keithley Instruments 610C Electrometer

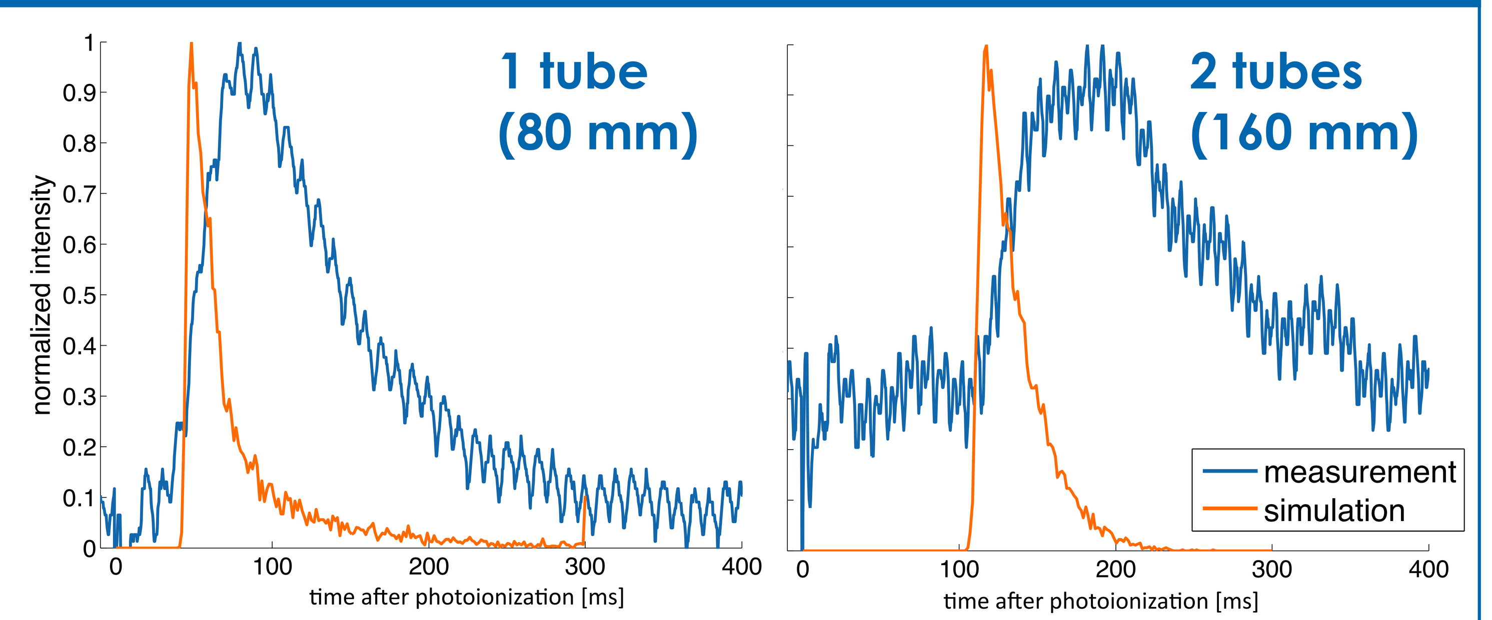


Figure 8) Simulated and measured temporally resolved ion signals in a tubular ion source

- The simulation method correctly predicts the minimal transfer times
- Considering the significant peak broadening caused by the detection system (electrometer) and the additional turbulent diffusion which was not modeled, the agreement in terms of peak width is substantially better than in the case of the MPIS

AP Ion Source (MPIS): Simulated Ion Trajectories

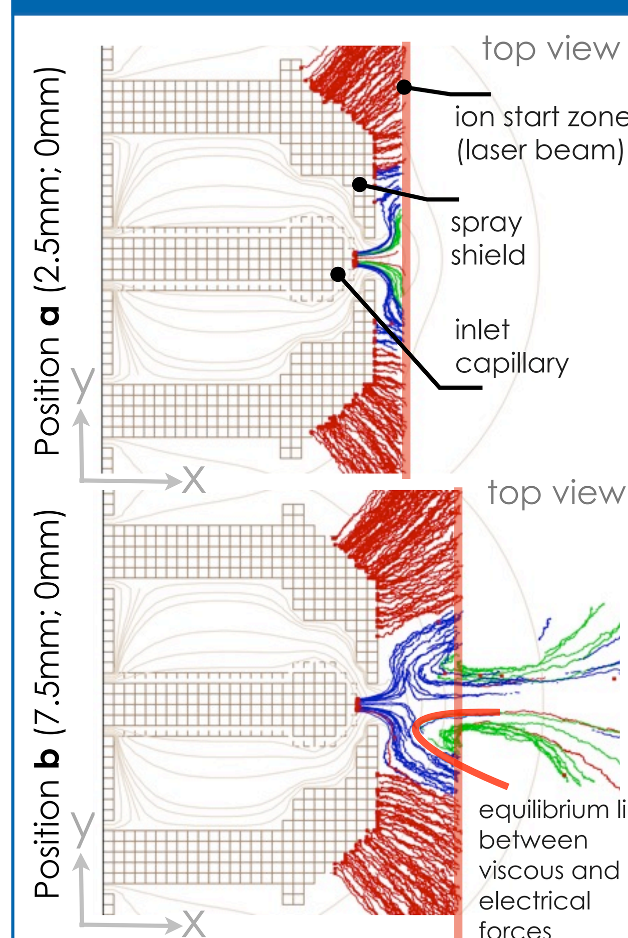


Figure 9) Detailed view of ion trajectories (simulation conditions and ionization positions according to fig. 2, U_{Cap}: -500V, U_{Shield}: -50V)

Left:

- The detailed analysis of simulated ion trajectories reveals that the ion motion in the MPIS is governed by the gas flows and the present electrical fields in a complex manner
- The shape of the zone from where the ions reach the MS inlet is strongly dependent on the electrical fields and the gas flows (see Pos. b on the left)
- Due to the fluctuations in the gas flow (see Figure 6 above) the boundaries of this zone fluctuate as well
- These fluctuations are not considered in the present numerical model based on a static flow simulation

Right:

- Ions directed into the bulk ion source volume have a long residence time in the ion source
- A significant additional diffusion of these ions in combination with the gas flow oscillations would probably lead to a significant broadening of the modeled temporally resolved ion signal

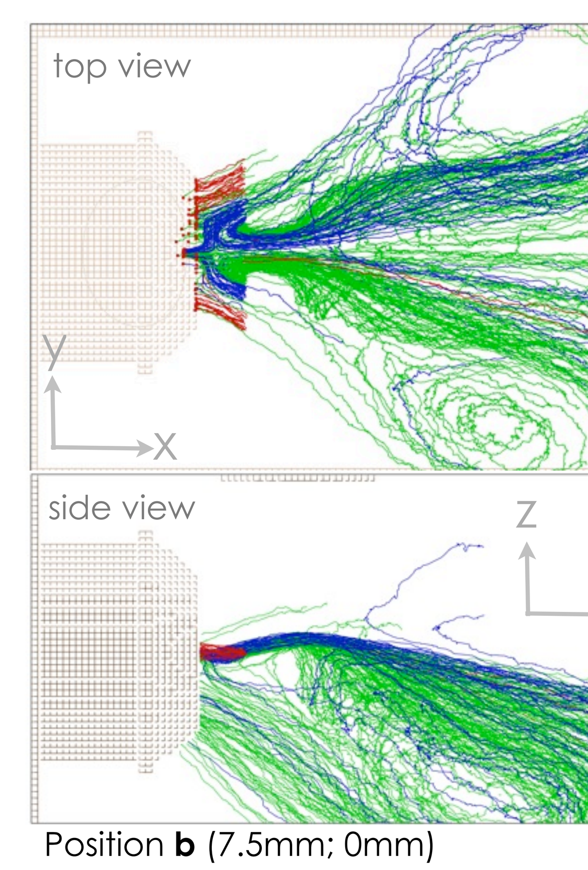


Figure 10) Overview of ion trajectory simulation (simulation conditions and ionization positions according to fig. 2, U_{Cap}: -500V, U_{Shield}: -50V)

Literature

1) Appelhans, A D.; Dahl, D A. *SIMION ion optics simulations at atmospheric pressure.* Int. J. Mass Spectrom. **2005**, 244, 1-14.
2) Wissdorf, W.; Pohler, L.; Klee, S.; Müller, D.; Benter, T. *Simulation of Ion Motion at Atmospheric Pressure: Particle Tracing Versus Electrokinetic Flow.* J. Am. Soc. Mass Spectrom. **2012,** 23(2), 397-406.
3) Wissdorf, W.; Lorenz, M.; Benter, T. *Numerical Simulation of the Distribution of Ion Acceptance (DIA) in a Commercial API Source.***,** poster contribution, ASMS annual meeting, Denver, **2011**
4) Poehler, T.; Kunte, R.; Hoenen, H.; Jeschke, P.; Wissdorf, W.; Brockmann, K. J.; Benter, T. *Numerical simulation and experimental validation of the three-dimensional flow field and relative analyte concentration distribution in an atmospheric pressure ion source* J. Am. Soc. Mass Spectrom. **2011,** 22(11), 2061-2019

Acknowledgement

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