Fundamental characterization of ion transfer capillaries used in Atmospheric Pressure Ionization sources

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Introduction

Atmospheric Pressure Ionization Mass Spectrometry (API-MS) has seen a dramatic performance and application increase over the past decade.

The overall ion transfer performance from the ion source throughthrough ion transfer stages into the mass analyzer generally suffers from severe losses of ion intensity. If the sites of ion losses are identified, basic optimization of instrument performance would be possible.

Several MS manufacutures have chosen capillaries to reduce the pressure from atmospheric pressure (AP) to the millibar regime in the first pumping stage of the instrument. Furthermore the charged particles have to pass the capillaries to enter the mass analyzer.

Little is known about the impact on ion transfer efficiency of such capillaries. The transmission of ions may vary by orders of magnitude, depending on various parameters and thus may heavily affect the overall performance of an instrument.

We present detailed investigations of the properties of transfer capillaries, such as:

- Fluid dynamic conditions in the capillaries
- Ion transfer efficiency
- Transfer times of individual ion packages

Methods

Transfer capillaries:

- Capillary types:
  - Home build glass capillaries,
  - Home build conductive capillaries (<100Ω, ~1GΩ)
- Inner diameter 0.5 - 0.6 mm
- Length: 10 - 30 cm

Laser systems:

- ATL ATLEX 300 SI, KrF* Excimer Laser, λ =248 nm;
- Quadrupled Nd-YAG Laser, (Spectron SI-401) λ=266 nm;
- Diode pumped quadrupled Nd-YAG Laser, (FQSS 266-50 Crylas GmbH, Berlin, Germany) λ = 266 nm;

Other Light sources:

- Custom build pulsed VUV Ar-discharge lamp (see also Poster TP610 for further details)
- Kr VUV discharge lamp

Analytes:

- Pyrene, Anisole, Toluene, Nitricoxide
- Bulkgas: Synthetic Air, Nitrogen

Ion detection was performed by measuring the ion current with a Microam- / Electrometer (Keithley Instruments 610C)

Experimental Setup

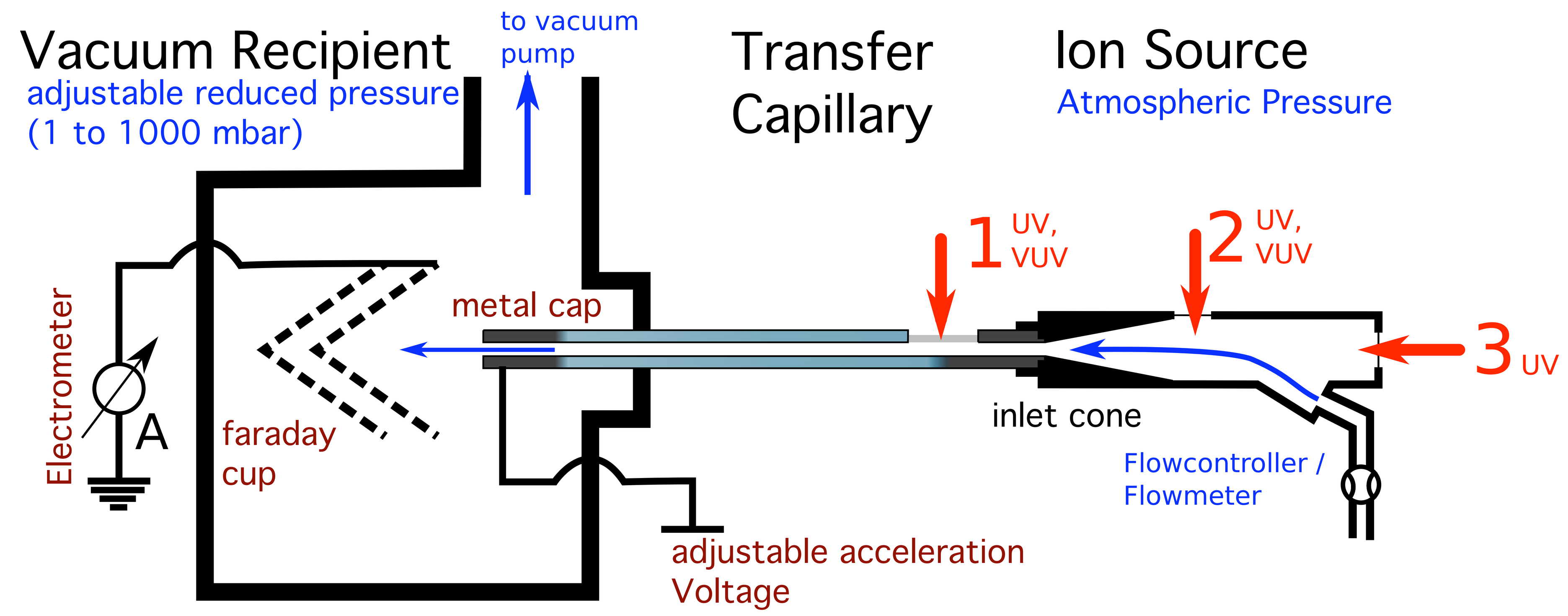

Fig. 1: Experiment Overview

- Ions are prepared in an AP ion source
- Ionization through direct Photoionization (PI) by VUV Light or Resonance Enhanced PI (REMPI) by UV Laser light
- The ion current through the capillary is detected by a Electrometer (sensitive ampere meter)
- Gas flow through the transfer capillary depends on pressure difference between ion source and vacuum recipient, pressure difference is monitored
- The gas flow through the system is monitored by a mass flow-meter

Photoionization Sites:

The custom build laminar AP - Ion Source allows the generation of ions via photo excitation at different sites (see Figure 1):

1. *Inside* the transfer capillary with UV laser or VUV lamp
2. In close proximity to the upstream inlet-cone to the capillary with UV laser or VUV lamp
3. Axial, along the main axis of ion source with UV laser

Results

Flow Dynamics: Choked Flow in Capillary

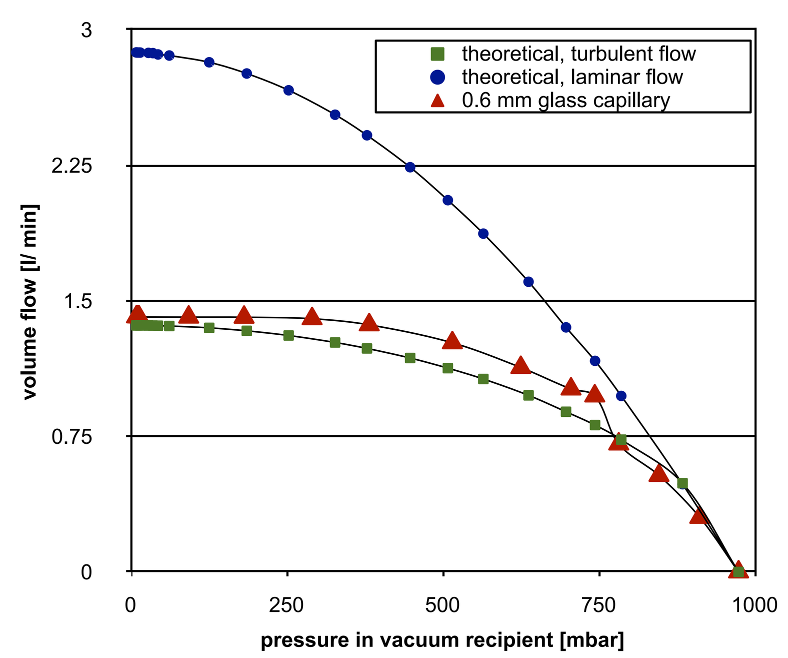

Fig. 2: *Flow vs. Pressure in vacuum recipient*

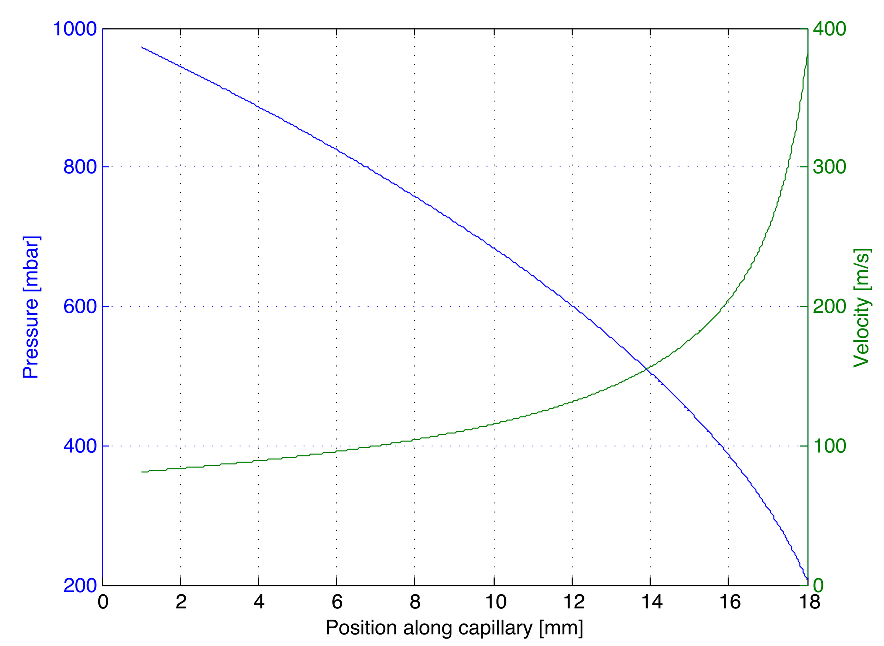

Fig. 3: *Pressure and flow velocity along the cap.*

- If a ***critical pressure difference*** is reached (Mach = 1 at capillary end), the flow through the capillary becomes ***choked*** (see area below 300 mbar in Fig. 2)
- The volume flow through the capillary becomes independent of the pressure difference in this state
- The fluid dynamic behavior of the flow is well described by theoretical models[1,2,3,4]

Transfer Times

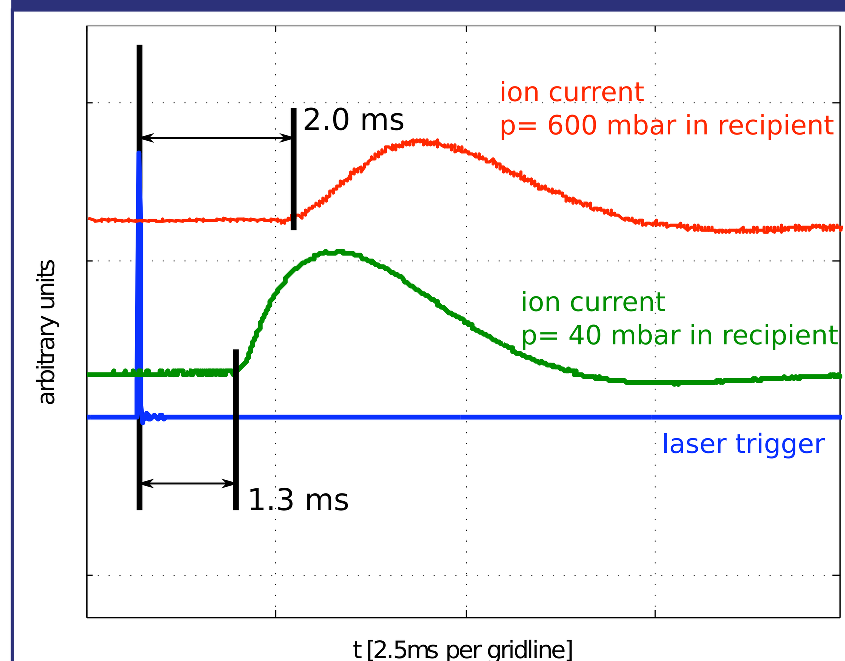

Fig. 4: *Temporal Ioncurrent, ionization at position 1 in fig. 1*

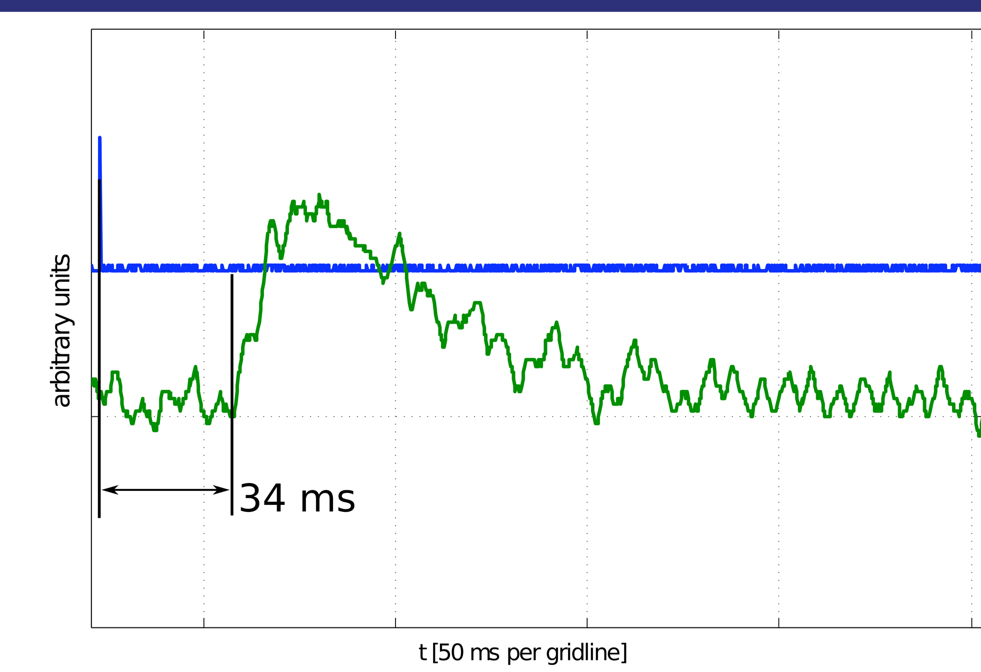

Fig. 5: *Temporal Ion-current, ionization at position 2 in fig. 1*

Gas Flow Dependence:

- The transfer time of the ion packet corresponds directly to the flow velocity
- The measured transfer times are consistent with the theoretical predictions

Different Ionization Position:

- The transfer time of the ion packet corresponds directly to the position where ions were generated

Selection of Ion Polarity

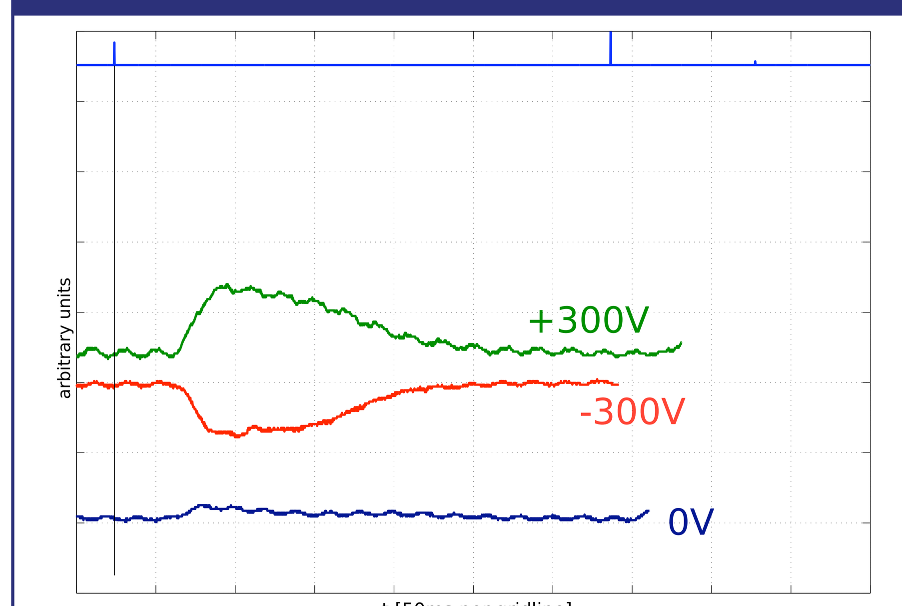

Fig. 6: *Ion Currents with different acceleration voltages on capillary exit*

- Polarity of detected ions is selected by the polarity of the acceleration voltage on the capillary exit
- The transfer times of anions and aations are virtually identical
- This suggests, that electrons generated by photoionization ($M + h\nu \longrightarrow M^{+} + e^{-}$) as well as irradiation of metal surfaces are rapidly converted to negative Ions, eg. $e^{-} + O_2 \longrightarrow O_2^{-}$

Ion Transfer Efficiency through Capillary

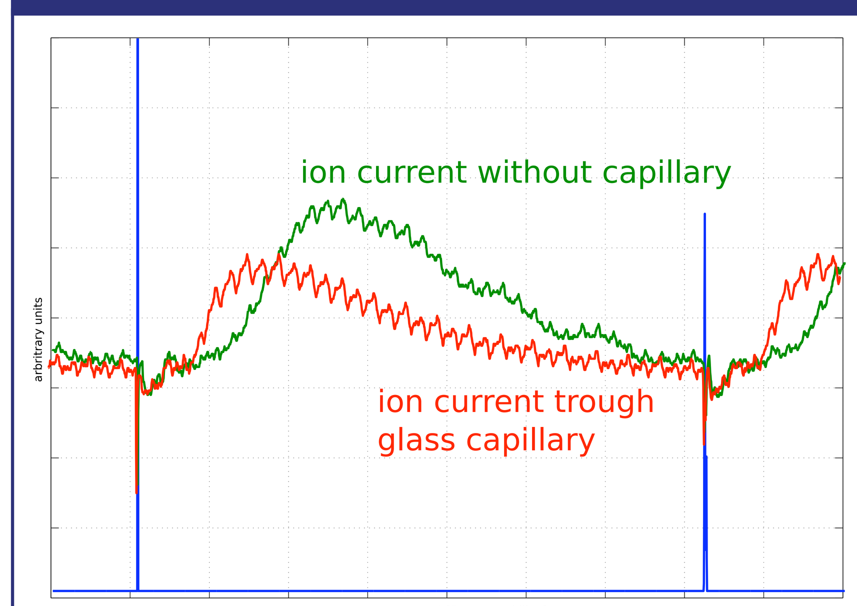

Fig. 7: *Comparison between ion current with and without transfer capillary*

- The experimental setup allows measurements with and without transfer capillary
- The ion current is generally ***not*** severely affected by the presence of the transfer capillary
- Transmission factors can reach values near 0.5 (see Fig. 7 on the left), minimal observed transmission factors are well above 0.1
- Transmission factors are ***not*** affected by strong electrical gradient along the main capillary axis (measured with conductive capillary, not shown here)

Conclusions

- Experimental setup allows detailed insight in the dynamical transport properties
- Fluid dynamic conditions are well modeled by theory
- Ion transfer times satisfy the predictions made by fluid dynamic theory
- Ion transfer through the capillaries is ***surprisingly high***, maximum ion loss in the investigated transfer capillaries is well ***below one order of magnitude***
- An electrical gradient along the capillary does not affect transfer times and transmission efficiency

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