Investigation of Gas- and Ion-Dynamics in Heated Glass and Metal Inlet Capillaries: Work in progress …

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Introduction

For an optimization of inlet interfaces for API mass spectrometers, a fundamental understanding of the flow dynamics in inlet capillaries is necessary. The change of the flow conditions with the temperature is of particular interest.

State of Knowledge:

- Commonly used first gas flow restriction stages in commercial API mass spectrometers are heated, critically operated glass or metal capillaries.
- For typical glass capillaries (inner diameter: 0.5 or 0.6 mm) operated at room temperature a number of investigations have been made, which are consistent with the assumption of a fully developed turbulent flow within the capillary.

Questions:

- Is the gas flow at higher temperatures in metal and glass capillaries comparable?
- Does the flow type, laminar or turbulent, depend on the length of the capillary?
- Are the flow condition different at higher temperatures and smaller inner diameters ?

Methods

Experimental Setup

Ionization:

- Within a custom ionization chamber, *upstream* of the capillary or *inside* a quartz capillary
- ATL Atlex KrF*-excimer laser (248 nm)
- Anisole as analyte

Detection:

- Within a custom detection chamber with a pair of electrodes mounted in parallel
- 6430 Sub-Femtoamp Remote SourceMeter® or 617 Programmable Electrometer, Keithley

Capillaries:

- In-house prepared glass capillaries (id: 0.5 and 0.6 mm / length: 60 – 1200 mm)
- In-house prepared metal capillaries (id: 0.15, 0.5, 0.7 mm / length: 60 –220 mm)
- In-house prepared quartz glass capillaries (id: 0.4 mm / length: 180 mm)

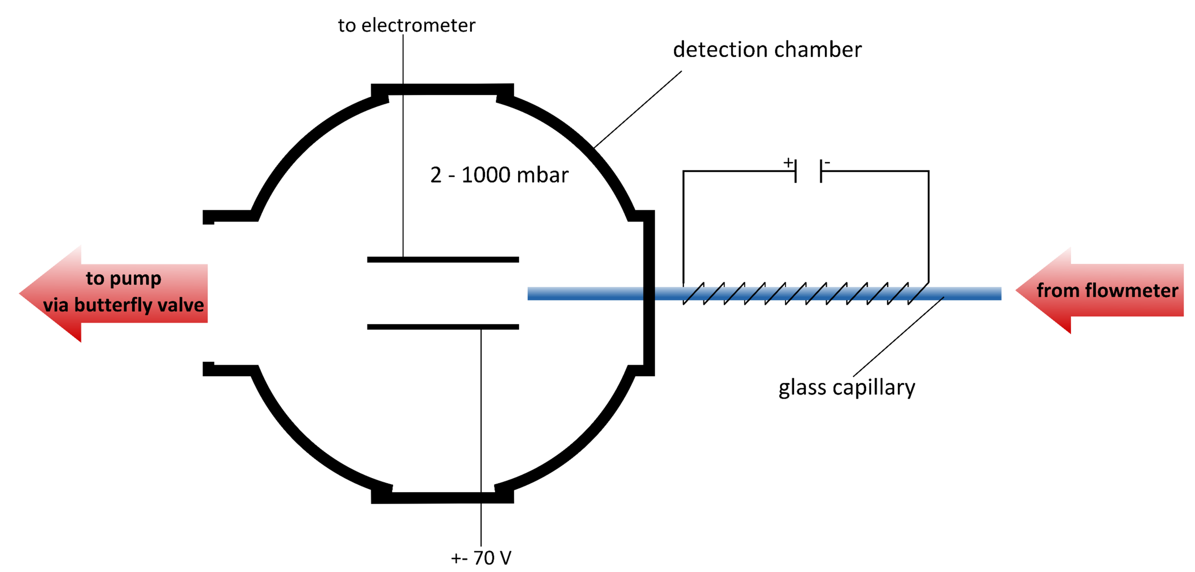
Flow Measurements:

- Ritter TG-1 Drum-Type gas flow meter or a custom bubble counter

Numerical Calculations

- Comsol Multiphysics 4.4
- Dell Precision T7400 Workstation (Xeon E5530 CPU)

Experimental Setup

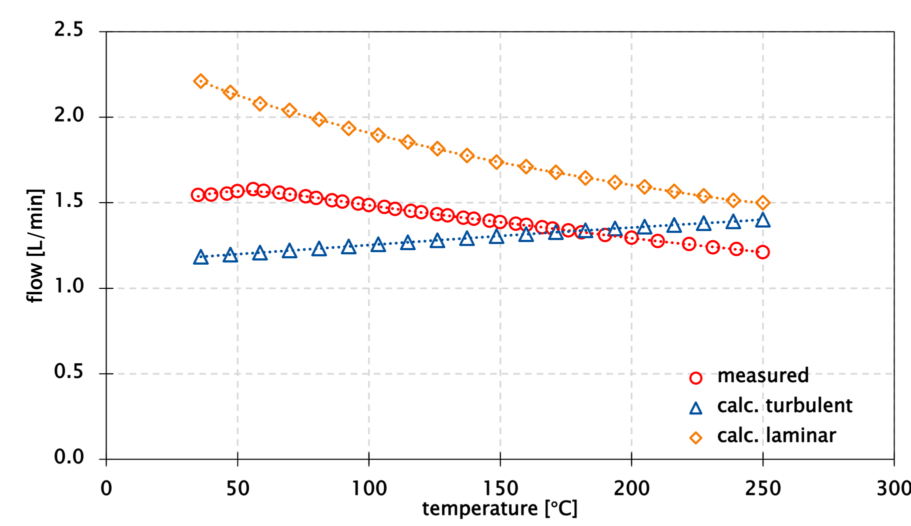


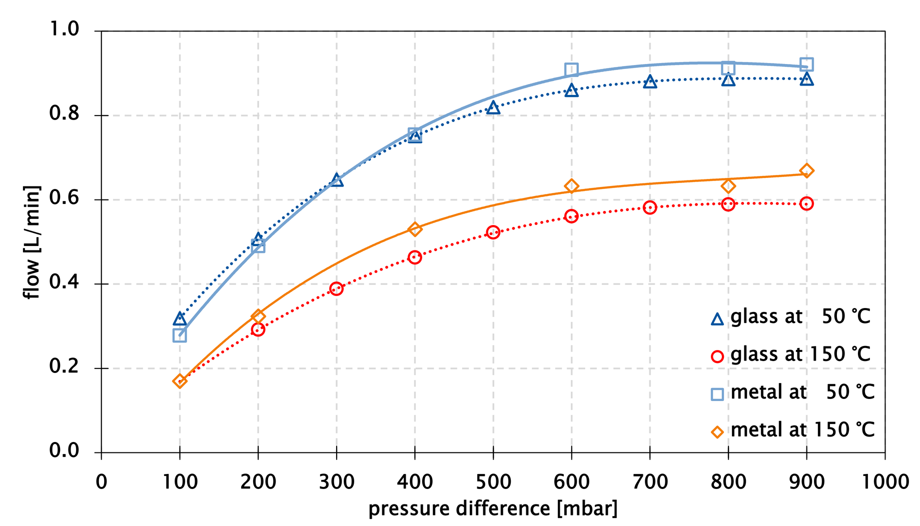
Capillaries:
For measurements of the temperature dependence of the flow, the capillaries are resistively heated either by a tantalum wire (glass capillary) or directly (metal capillary).

Detection Chamber:
The detection chamber is evacuated through a butterfly valve to a pressure between 1000 to 2 mbar. The flow through the capillary is measured as a function of the pressure within the detection chamber. A pair of parallel electrodes allows the detection of ions delivered through the capillary. By biasing one electrode the polarities in the ion current are separated and subsequently detected.
For measurements of the gas temperature a micro thermocouple (Type K: Ni/CrNi) id: 0.25 mm was used, mounted on a positioning stage downstream of the capillary exit.

Comparison between Metal and Glass Capillaries

Orbitrap measurements :
Initial measurements with metal capillaries (id: 0.5 mm) were carried out at constant pressure using an Orbitrap mass spectrometer. The gas volume flow was measured at different temperatures. A comparison between the measurements and calculated data shows an unexpected trend. As expected, the flow conditions change with increasing temperatures. There is however no way to determine whether the flow is laminar or turbulent with the conducted experiments.

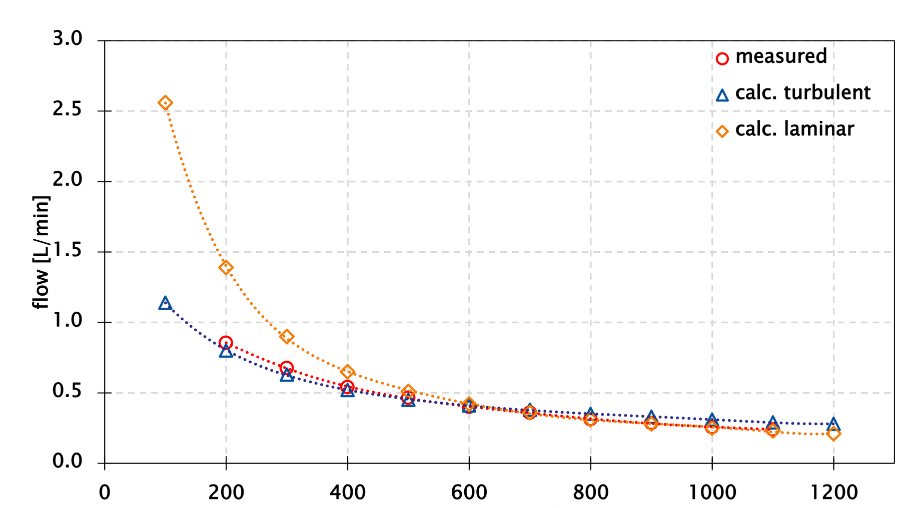




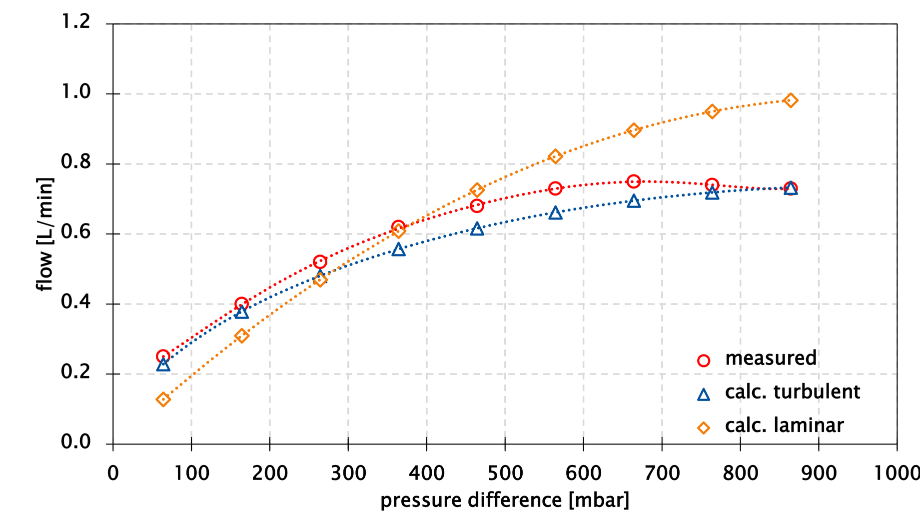
Measurements with experimental setup:
A systematic comparison between glass and metal capillaries with identical lengths and inner diameters was carried out using the experimental setup shown above. No difference between glass and metal capillaries in the temperature range between 20 - 150 °C was observed. The figure (left) shows data for a length of 14 cm and an inner diameter of 0.5 mm.

Variation of Capillary Length

A systematic investigation of the flow characteristics of capillaries with different lengths shows good agreement of the modeled and the measured data. For a capillary length of <500 mm, the measured flow matches well with the turbulent model. For >700 mm the models are indistinguishable. Nevertheless, it seems that the flow coincides more with the laminar model.



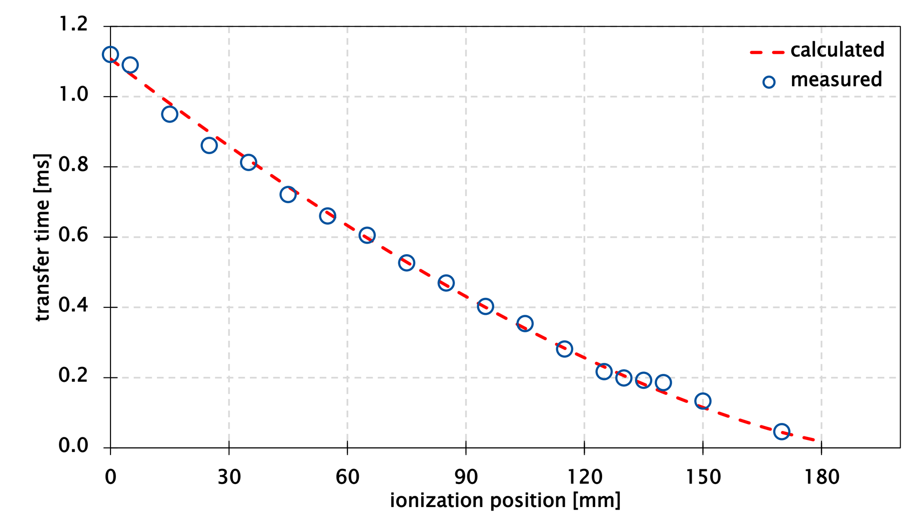
Capillaries at Standard Conditions



Laminar vs. turbulent gas flow:
For standard conditions, the pressure dependent flow through a capillary with an inner diameter of 0.4 - 0.6 mm and a length of 6 - 220 mm is in good agreement with the turbulent model data.

Shown left is a comparison of the data for a glass capillary (id: 0.5 mm / length: 220 mm).

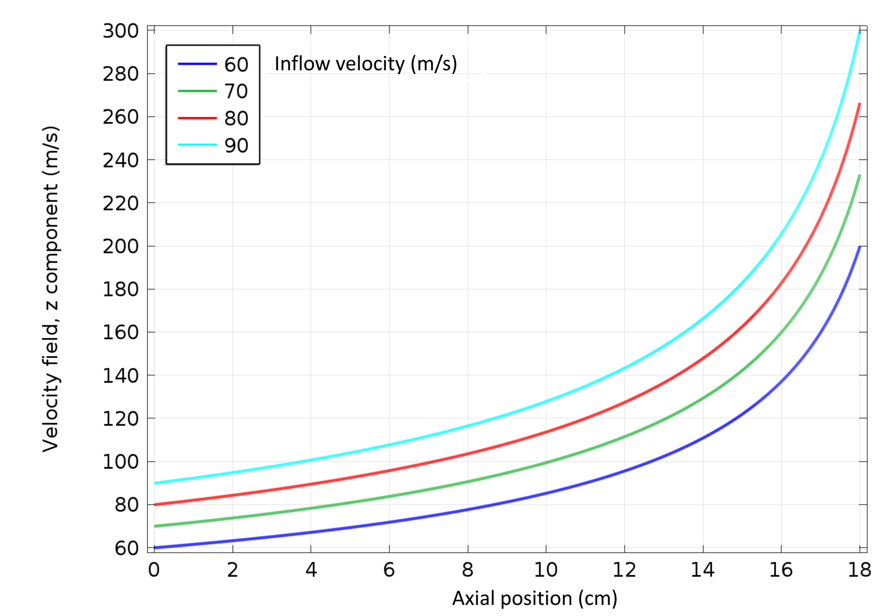
Ion transfer times:
Quartz glass capillaries allow spatially resolved ionization with a laser inside the capillary. Therefore, the transmission time can be measured as a function of the distance between ionization and the exit of the capillary.
For a 0.4 mm quartz capillary, the measured times match with the calculated times using the turbulent model at room temperature.

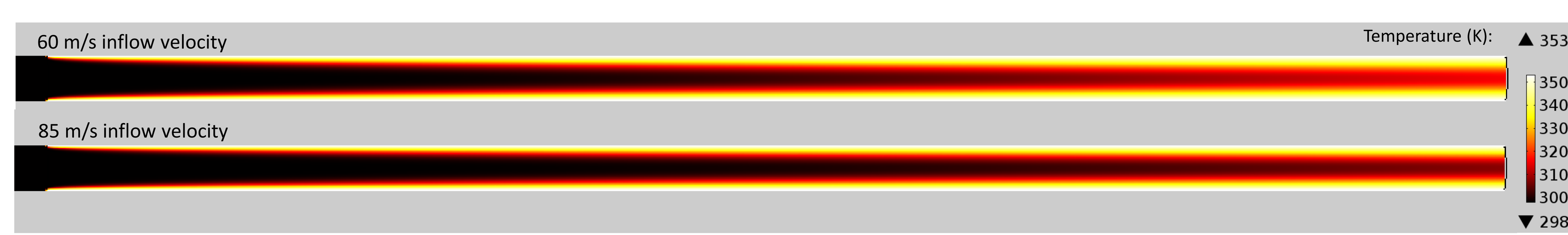


Numerical Modeling: Temperature and Concentration

Basic numerical modeling of the inlet capillary:
The available model for laminar flow was used for a basic numerical assessment of the flow dynamics in the inlet capillary: A simplified flow field in the inlet capillary was assumed and the temperature distribution in the estimated gas flow was simulated.

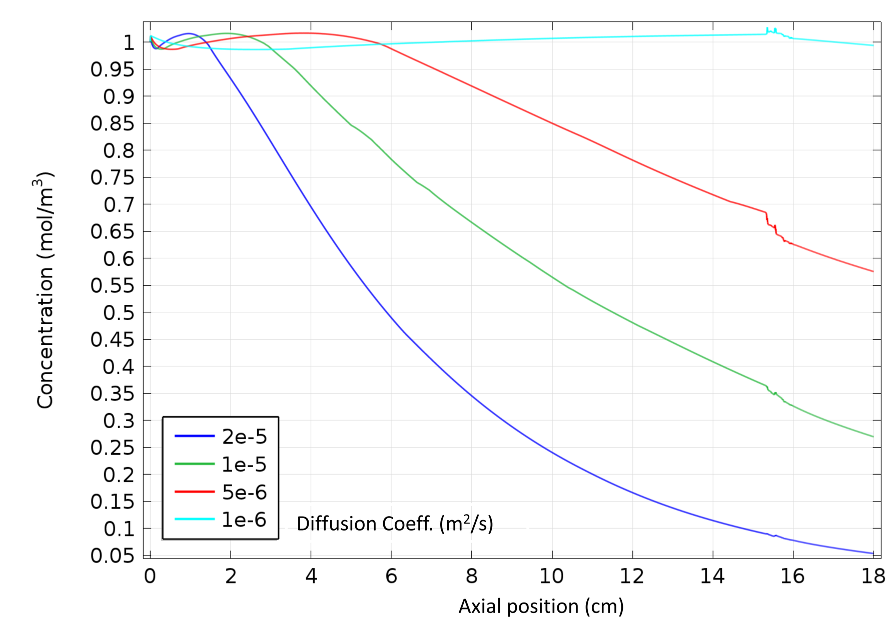
Right: The assumed axial velocity distribution of the gas flow for different inflow velocities.
Below: Calculated gas temperature for different inflow velocities. A segment (2 cm) at the end of the capillary was heated in the model. The resulting mean temperature at the capillary end is lower than that observed experimentally.





Analyte depletion model:
A common assumption is that inlet capillaries show a good ion transmission due to an essentially laminar gas flow in the capillary.
A convection and diffusion model was used to estimate the depletion of a generic molecular analyte in the modelled laminar gas flow with the assumption of complete analyte loss on the capillary walls.

Right: The calculated axial concentration profile indicates nearly complete analyte loss for small analyte molecules in a laminar gas flow within the capillary which is solely due to molecular diffusion.



Conclusions

- The experimental setup allows measurements of pressure dependent gas flows, ion transmission and, with heating of the capillary, temperature dependence of gas the flow.
- At *standard conditions*, the flow types of capillaries with an inner diameter of 0.4 - 0.6 mm and a length of 60 - 300 mm are in good agreement with the theoretical model for turbulent flow. The axial velocity profile matches as well.
- For capillary lengths exceeding 500 mm, the flow characteristics at standard conditions converge for both models, turbulent and laminar. Therefore, a differentiation between both flow types can not be made.
- The flow characteristics in metal or glass capillaries are similar even at higher temperatures.
  - A difference in parameters, for example, wall roughness is thus not observable.
- For higher temperatures, neither the turbulent nor the laminar model can describe the flow characteristics.
  - It appears as if that the models are invalid for these conditions.
- The metal capillary used in the Orbitrap mass spectrometer and the capillary used in the present setup behave differently (nominal identical dimensions!)
  - A clarification of the observed difference is work in progress.
- The basic numerical assessment of the capillary suggests an essentially turbulent state of the gas flow in the capillaries.

Literature

1) Venerus, D. C.; Laminar capillary flow of compressible viscous fluids, J. Fluid Mech., 555, 59 – 80, 2006.
2) Michalke A.; Beitrag zur Rohströmung kompressibler Fluide mit Reibung und Wärmeübergang, Ingenieur Archiv 57, 377 – 392, 1987.
3) Wutz, M.; Adam, H., Theorie und Praxis der Vakuumtechnik; Vieweg+Teubner Verlag: Braunschweig, 1988.
4) Klopotowski, S.; Brachthaeuser, Y.; Mueller, D.; Kersten, H.; Wissdorf, W.; Brockmann, K.; Benter, T. Characterization of API-MS Inlet Capillary Flow: Examination of Transfer Times and Choked Flow Conditions, *60th ASMS Conference on Mass Spectrometry and Allied Topics,* Vancouver, BC, Canada, 2012.
5) Klopotowski, S.; Brachthaeuser, Y.; Mueller, D.; Kersten, H.; Wissdorf, W.; Derpmann, V.; Klee, S.; Brockmann, K.J.; Janoske, U.; Gregor, H.; Benter, T. API-MS Transfer Capillary Flow: Examination of the Downstream Gas Expansion, *59th ASMS Conference on Mass Spectrometry and Allied* Topics, Denver, CO, USA, 2011.
6) Brockmann, K.J.; Wißdorf, W.; Hyzak, L.; Kersten, H.; Müller, D.; Brachthäuser, Y.; Benter, T. Fundamental characterization of ion transfer capillaries used in Atmospheric Pressure Ionization sources, *58th ASMS Conference on Mass Spectrometry and Allied Topics,* Salt Lake City, UT, USA, 2010.