Charging effects in ion transfer capillaries: An in-depth study

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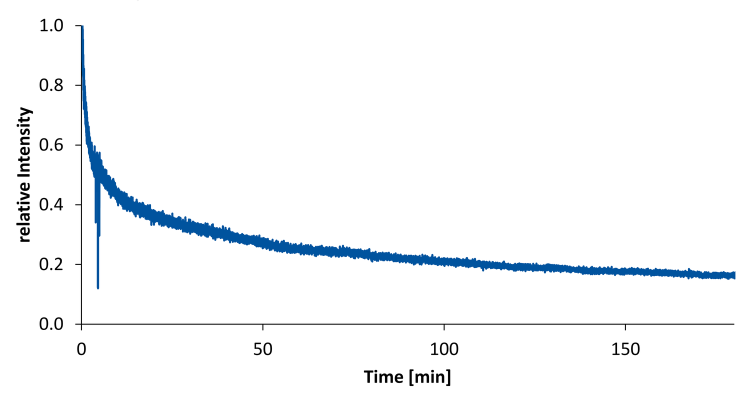
Introduction

Challenge:

In cAPECI, modified inlet capillaries lead to a pronounced decrease of the recorded ion signal intensity with time.



Decreasing mass signal of the cAPECI-source

To minimize the adverse effects on the transfer efficiency of modified inlet capillaries it is necessary to study and fundamentally understand the physical and/or chemical change that gives rise to such behavior.

State of Knowledge:

- Inlet capillaries are frequently used as first pressure restriction stages in many commercial API mass spectrometers
- The gas flow within the capillaries is fully developed turbulent
    - It was experimentally shown that irregularities in the flow channel do not affect the overall flow characteristics
- Capillary ionization sources, e.g., capillary Atmospheric Pressure Photo Ionization (cAPPI) and capillary Atmospheric Pressure Electron Capture Ionization (cAPECI), significantly reduce the extent of ion-molecule/radical reactions by reducing the ion transfer time to < 1 ms
- Ionization *within* the capillary duct necessitate modifications, e.g. adding quartz windows or inserting metal sections
- Different material properties, e.g. electrical conductivity, may lead to "charging effects" which potentially affect the ion transfer efficiency

Methods

Experimental Setup

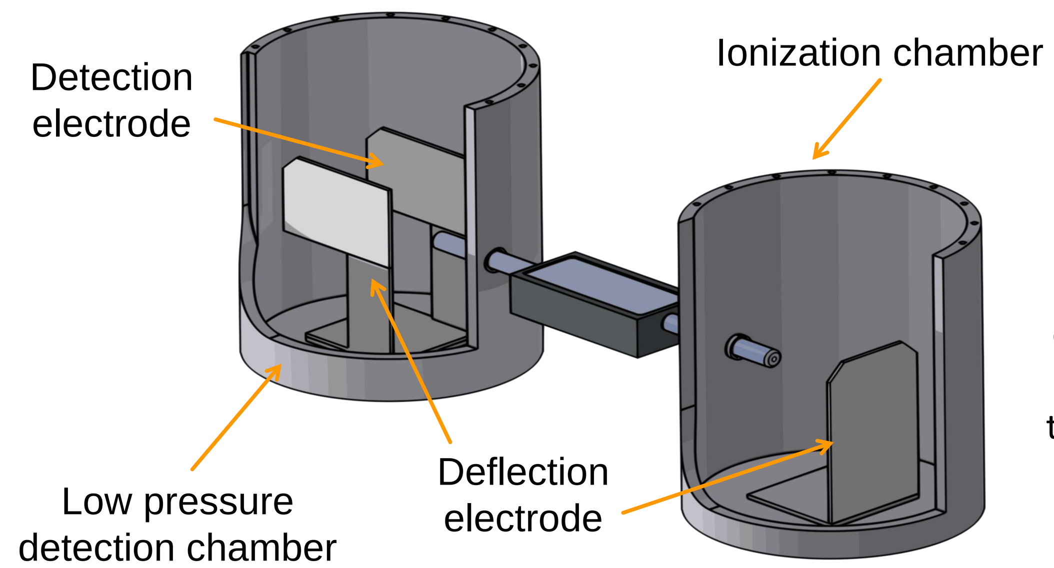
Ionization: **APLI:** ATL Atlex KrF^*-excimer laser (248 nm) upstream of the capillary, anisole as analyte

cAPECI: custom capillary ion source with photoelectrode and a PenRay Mercury low pressure UV lamp (185 nm and 254 nm)

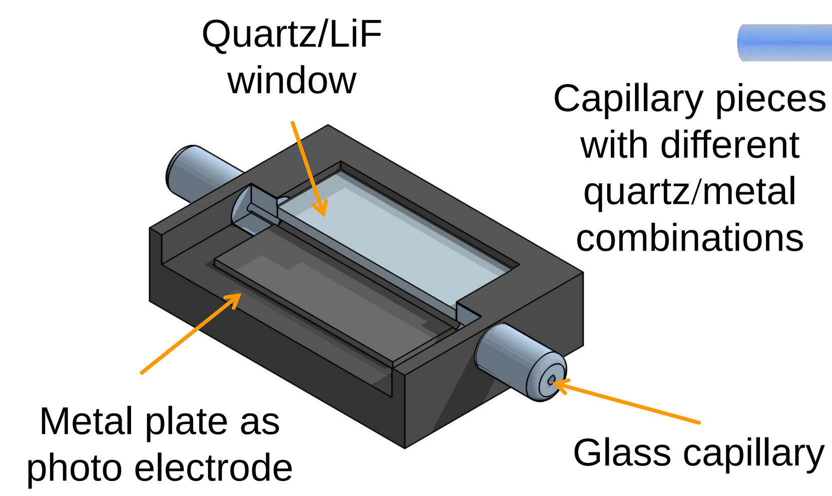
Detection: 6430 Sub-Femtoamp Remote SourceMeter® or 617 Programmable Electrometer, Keithley

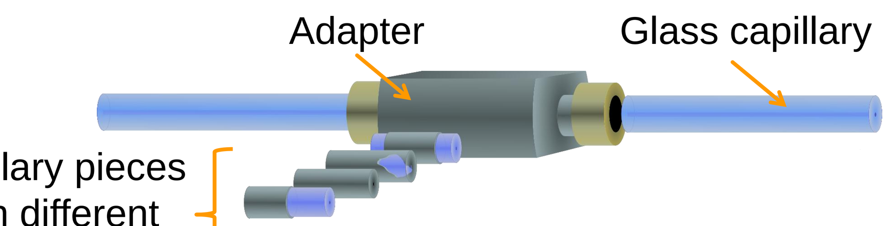
Experimental Setup

A sealed ionization chamber is connected via interchangeable transfer capillaries to a low pressure detection chamber. The parallel orientation of the detection and deflection electrodes in the detection chamber allows for polarity separation of a bipolar ion current. By changing the polarity of the deflection electrode the unipolar nature of the ion current is clearly demonstrated.



Ions are generated by Atmospheric Pressure Laser Ionization (APLI) upstream of the capillary or by cAPECI via an UV-Lamp mounted on top of the ion source. A deflection electrode opposite to the capillary entrance may be used to charge separate the ion cloud. Thereby an unipolar or a bipolar ion current can be delivered through the capillary.

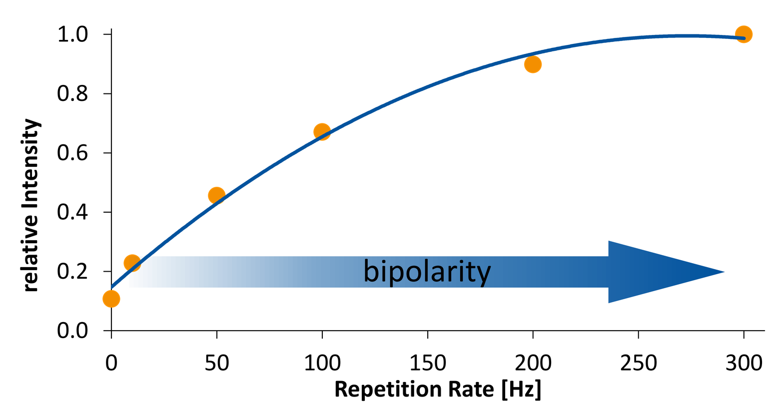




Capillary pieces with different quartz/metal combinations

To study of the impact of various *material combinations* on the ion transmission efficiency of the cAPECI-source, two glass capillaries were combined with a metallic adapter. Small capillaries of different materials were placed between the two glass capillaries inside the adapter

Polarity of the Ion Current



Transmission ion signal of the cAPECI-source (**neg. charge**) as a function of the repetition rate of the laser (**pos. charge**)

bipolar ion current = no charging effects = no signal decrease

- Transmission factor of the cAPECI-source depends on the extent of "bipolarity" of the ion current (Def.: net positive = net negative charge = 100% "bipolarity")
- Transmission of negative ions (unipolar) is increased by adding positive ions (produced by APLI upstream of the capillary entrance)
- Repetition rate of the laser determines the total amount of positive ions and thus the extent of "bipolarity" of the ion current

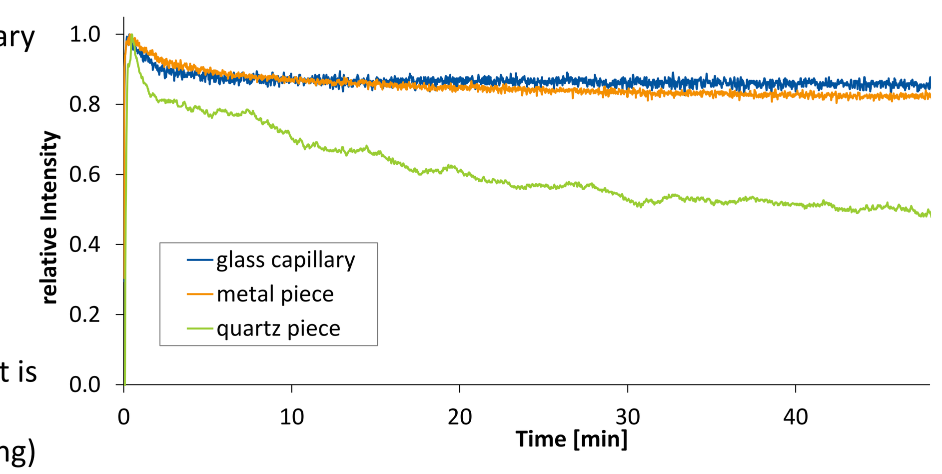
Material

The extent of the signal decrease depends on the capillary material.

After a few minutes standard glass capillaries show a constant ion transmission with time. Because of the turbulent flow conditions the combination of two glass capillaries has only an influence on the total flow and therefore on the intensity but not on the signal *trend* (see also poster #MP277).

To generate thermal electrons inside the capillary duct it is necessary to combine

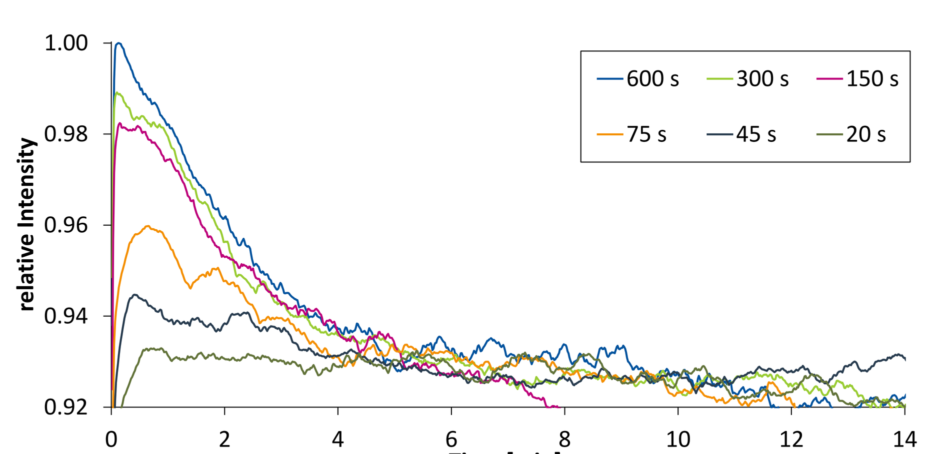
- UV-transparent material (electrically "non"-conducting)
- Photo emissive material (electrically conducting)



Transmission signal of different capillary pieces

For unipolar ion currents the use of quartz results in a pronounced long term decrease of the ion signal (green trace) with time. In contrast, inclusion of metallic material in the capillary duct does not give any additional trends (orange trace).

It is assumed that the electric resistivity of the materials are responsible for the different characteristics in ion transmission. If the *difference* of the resistivity of the used materials is too large, the contact resistance causes an asymmetric charging of the capillary. Thus, an equilibrium situation is hardly established.



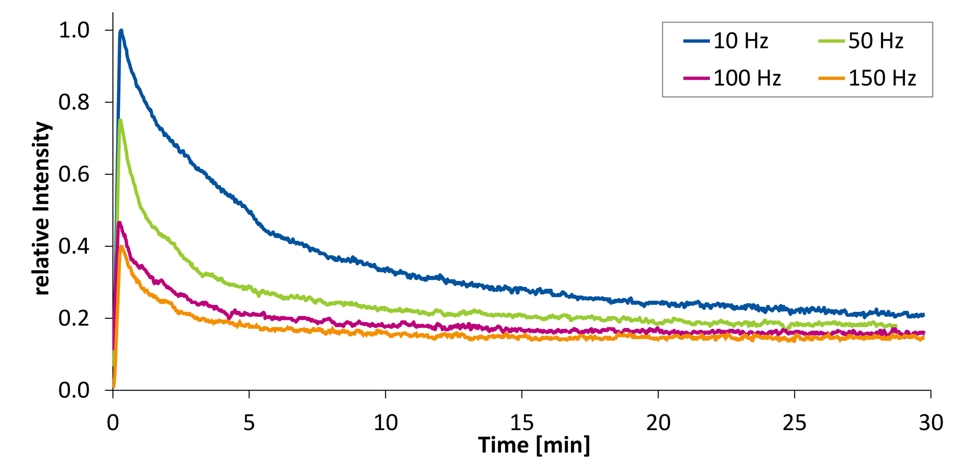
Ion transmission signal of glass capillaries as a function of time were the laser was switched off.

For glass capillaries, a transient charging effect is also observed but only in the very first minutes

When the laser is switched off the ion signal *decreases* initially *after* switching on the light again. The magnitude of the signal decrease is dependent on the length of the dark time. Therefore, it is assumed that the ion transmission of the capillary is determined by the charge on the wall. By changing the dark time, the charge amount on the wall is changing as well.

It is thus assumed that the charge flux to the wall of the capillary and the charge loss are swiftly reaching equilibrium.

Conditioning



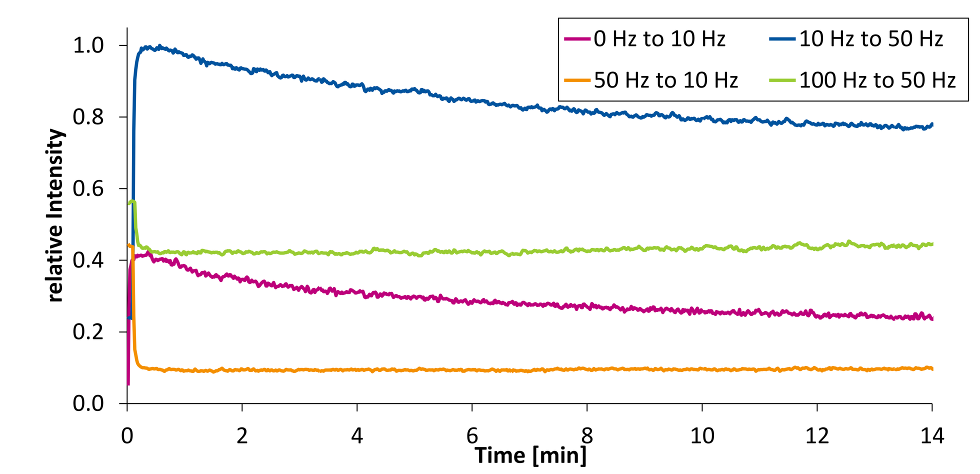
cAPECI-signals after delivering different amounts of ion flows

The transmission efficiency of the capillary depends on the total amount of charges delivered through the capillary.

By adjusting the repetition rate of the laser the total amount of ion current through the capillary is changing. After delivering different ion currents through the capillary the signals produced by cAPECI are detected. It is observed that for small amounts of charge on the capillary wall the transmission in the first minutes is higher than for high charge on the wall.

As shown for the glass capillaries the total amount of charge on the wall is the result of an equilibrium between the efflux from the wall and the fresh supply from the ions delivered through the capillary.

If the charge on the wall is higher than the charge in equilibrium the signal trend increases (green and orange traces). Otherwise, the signal decreases with time until equilibrium is reached.



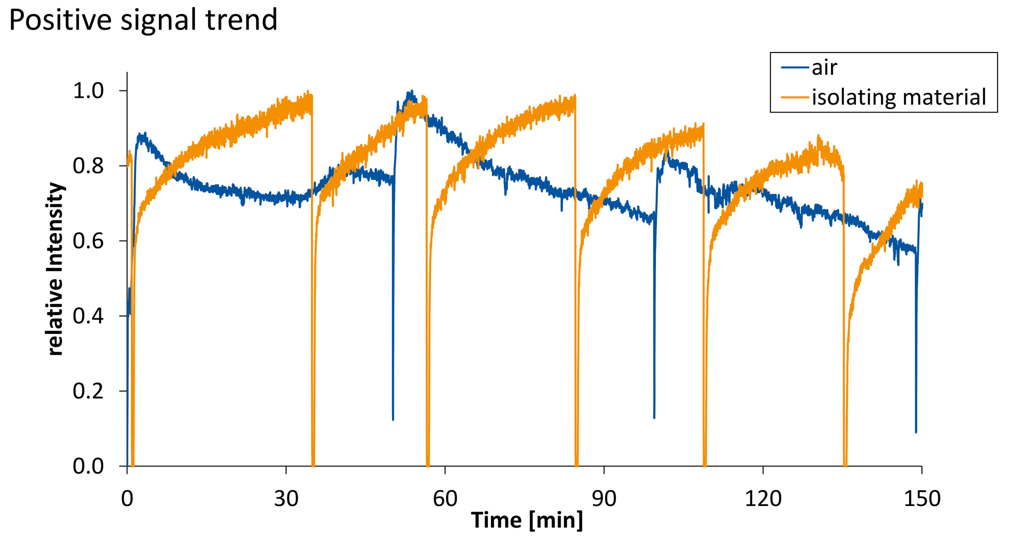
Transmission ion signals observed when changing the total amounts of ions delivered through the capillary

Ion signal drop outs

If the contact resistance is high enough, as is the case for an interface between glass and quartz and the quartz is electrically isolated from the surrounding grounded mounts, ion signal drop outs can occur.

The discharges occurred in two different ways:

- Through the air (blue trace), so that the charge on the wall drops below the equilibrium level.
    - Negative signal trend
- From the quartz piece to the glass capillary (orange trace), so that the charge on the glass wall exceeds that at equilibrium.
    - Positive signal trend



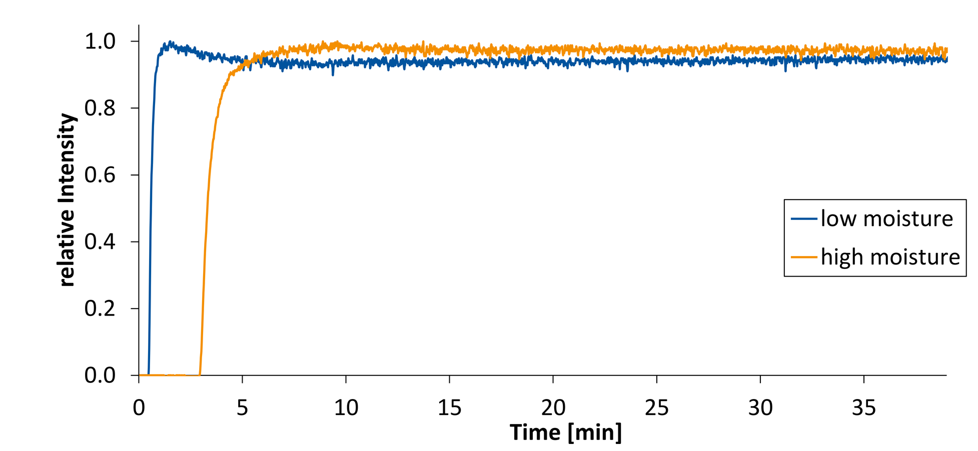
Relative Humidity (RH)

Treatment of the capillaries with air containing different amounts of water affects the transient ion transmission efficiency.

- Low RH: The ion signal response is fast, transmission swiftly reaches maximum values
- High RH: The ion signal response is significantly delayed and the transmission increases slowly
    - In addition to the wall charge equilibrium, the "thickness" of the surface water layer affects the transient ion signal

Further investigations are necessary to gain a more detailed understanding of this phenomenon.
Possible reasons are:

- Surface conductivities
- "Capacity" of the water layer(s) with respect to ion uptake



Conclusions

- Ionization *within* the capillary duct necessitates modifications to the capillary material
- Delivery of unipolar ion currents through capillaries results in charging of the inner wall, which leads to a loss of transmission efficiency with time
- Efflux and afflux of charges on the inner wall results in an charge equilibrium which depends on the electrical conductivity of the material
- Combination of materials with different resistances results in asymmetric charging of the capillary wall
- *Especially,* non-conductive materials lead to decreasing signal trends
    - Possible reasons are contact resistances and different surface conductivities
- Water vapor has a huge impact on the transmission of ions
    - Further investigations are necessary to understand the role of water
    - Possible reasons are changing surface conductivity and/or the high uptake rate of ions

References

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2) Brockmann, K. J.; Wissdorf, W.; Hyzak, L.; Kersten, H.; Mueller, D.; Brachthaeuser, 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.
3) Kersten, H.; Derpmann, V.; Barnes, I.; Brockmann, K.; O'Brien, R.; Benter, T.: A Novel APPI-MS Setup for In Situ Degradation Product Studies of Atmospherically Relevant Compounds: Capillary Atmospheric Pressure Photo Ionization (cAPPI). J. Am. Soc. Mass Spectrom., DOI: 10.1007/s13361-011-0212-y (2011).