

Development of a New Ion Source for Capillary Atmospheric Pressure Electron Capture Ionization (cAPECI)



Physical & Theoretical Chemistry
Wuppertal, Germany

Institute for Pure and Applied Mass Spectrometry

Valerie Derpmann; Walter Wissdorf; David Mueller; Thorsten Benter

Introduction

Challenge:

Development of an ionization method for analytes with high electron affinity (e.g. nitro-compounds, oxygenated PAH) *within* the transfer capillary of an API mass spectrometer

→ Minimized reaction time for ion transformation processes

Approach:

→ Use of the photoelectric effect at atmospheric pressure

→ UV-light interaction with metal surfaces yields low energy electrons

→ Electron capture forms exclusively negative ions

→ No interaction with oppositely charged species possible

Use of two half shells:

- Photoemissive material; exchangeable
- UV transparent material (Quartz/LiF)

Replaces part of the glass transfer capillary

- Possible because of turbulent flow present in virtually all ion transfer capillaries
- Nearly identical flow through cAPECI ion source and standard capillary

Sectioned cAPECI ion source provides

- Compatibility with most mass spectrometers
- Simultaneous use of standard ion sources

• Characteristics of transfer capillaries are now well established; the determination of rate constants of reactions between primary ions and analytes becomes thus feasible

Methods

Experimental Setup

MS: Esquire 6000 QIT, Bruker Daltonic
Ion Sources: cAPECI: Custom capillary ion source with silver as photoemissive material and LiF-window
ESI: Apollo ion source, Bruker Daltonic
Radiation Source: PenRay Mercury low pressure UV lamp ($\lambda = 185$ nm and 254 nm)

Note: All measurements described here were performed when the ion signals became nearly constant, i.e., after some hours of operation.

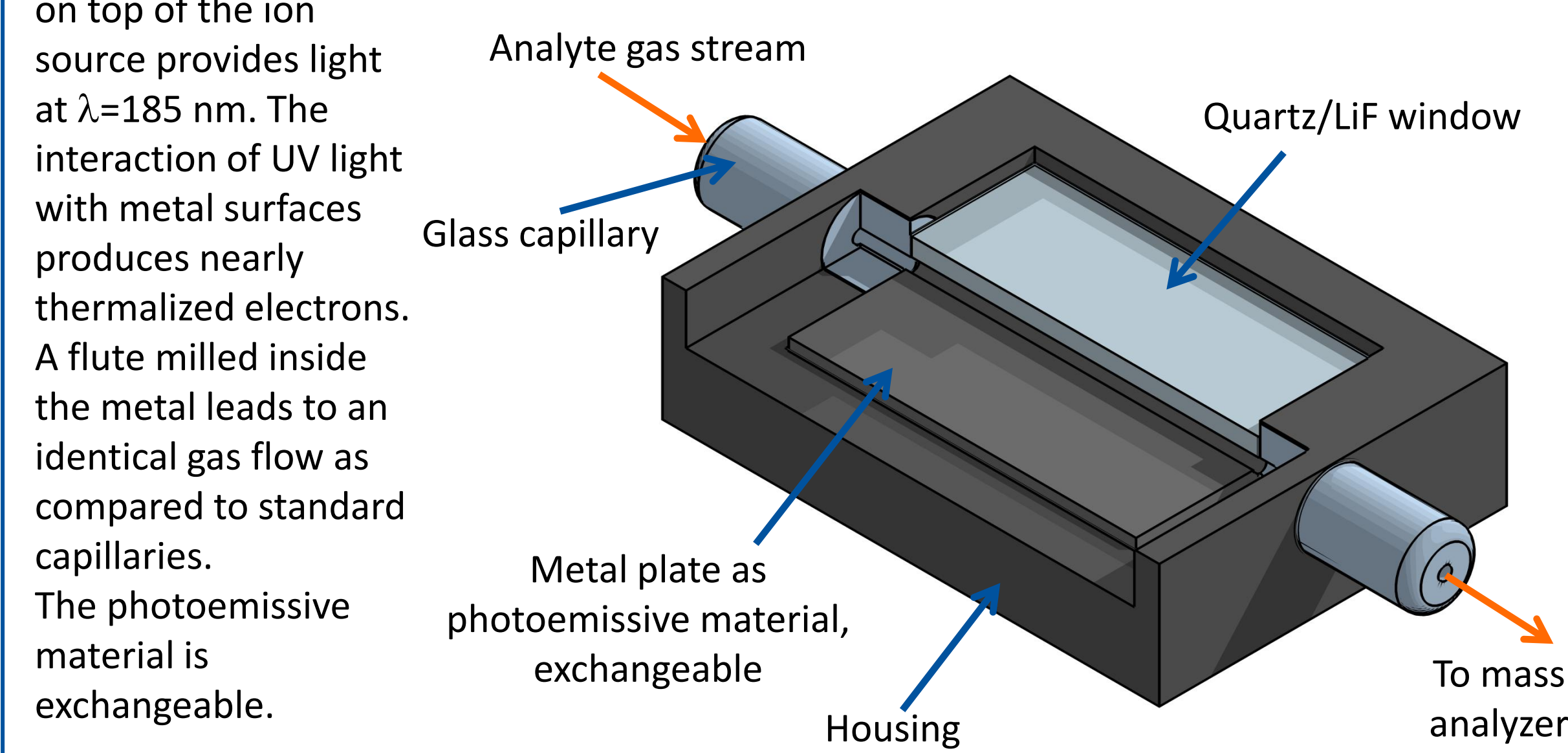
Numerical Simulation

Monte Carlo Reaction Simulation
See also Session MP29 Poster #670

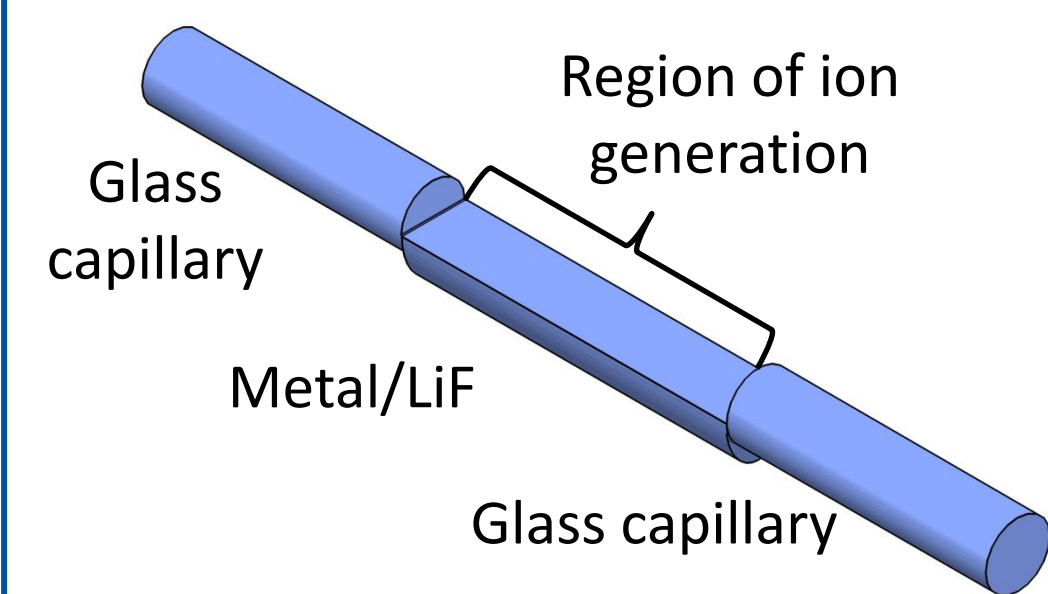
Ion Source

A UV-lamp mounted on top of the ion source provides light at $\lambda = 185$ nm. The interaction of UV light with metal surfaces produces nearly thermalized electrons. A flute milled inside the metal leads to an identical gas flow as compared to standard capillaries. The photoemissive material is exchangeable.

Schematic of the Ion Source

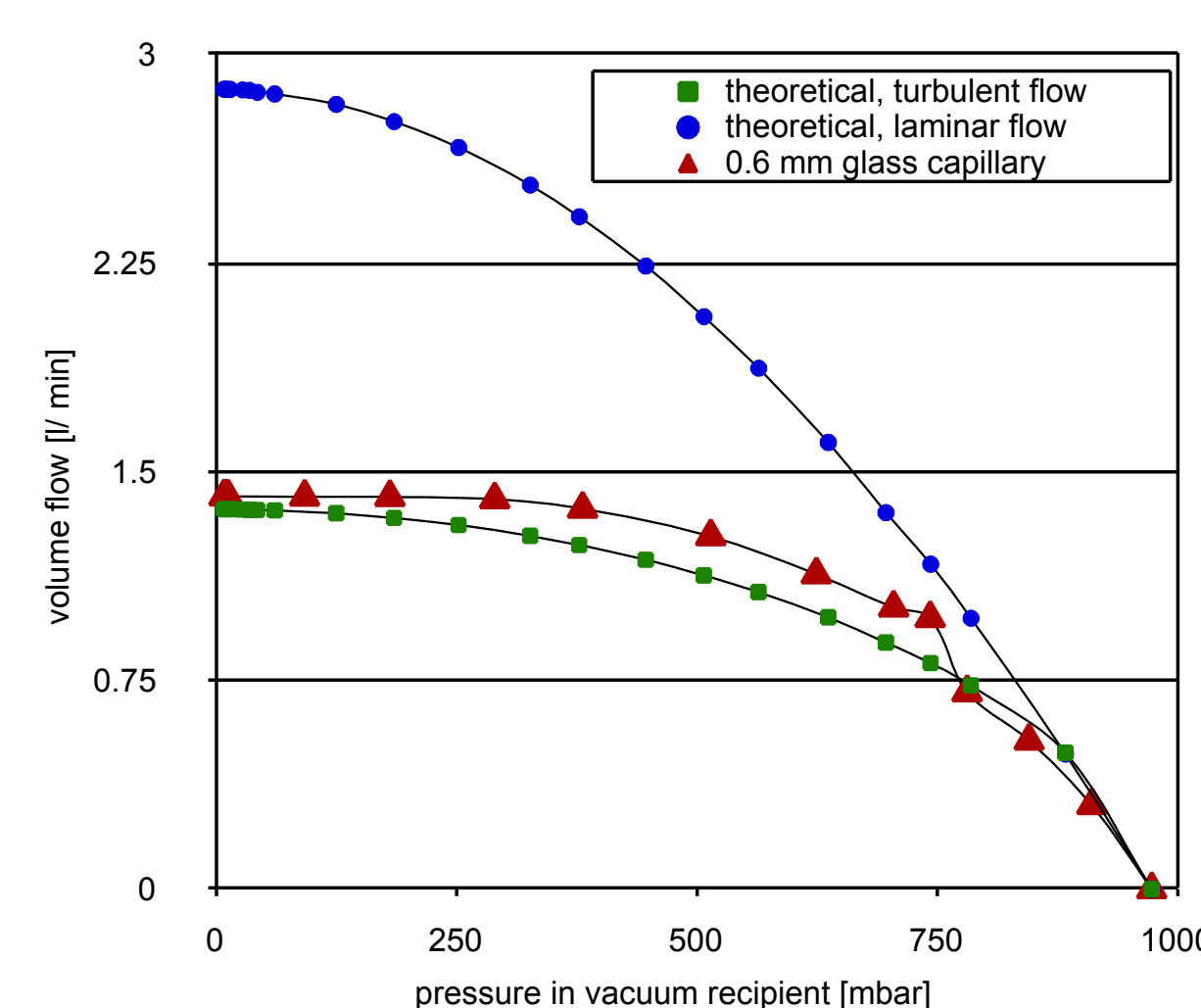


Inner Profile of the Capillary Channel



How can that work?

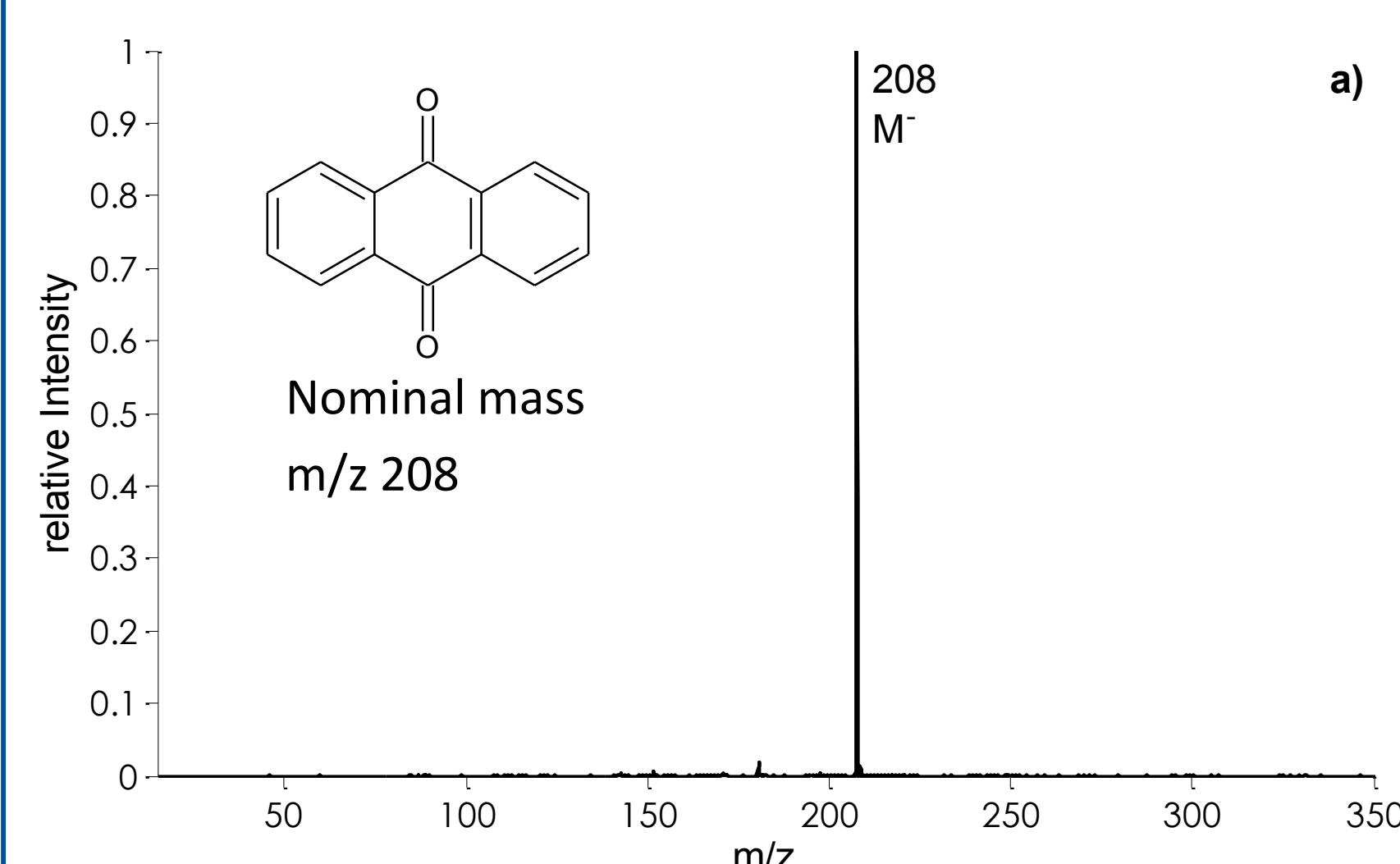
The gas flow inside the transfer capillary is fully developed turbulent. Thus the transitions between metal and capillaries do not change the flow and the ion transfer characteristics.



Dependence of the calculated and experimental volume flow through a standard capillary on the pressure in the vacuum recipient.

Mass Spectra

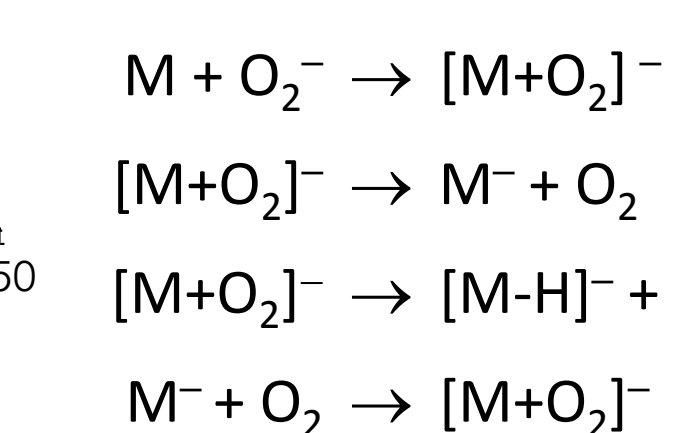
Mass spectra of a) an oxygenated PAH (1,4-anthraquinone) and b) 3-methyl-2-nitrophenol (approx. 120 ppbV) in synthetic air



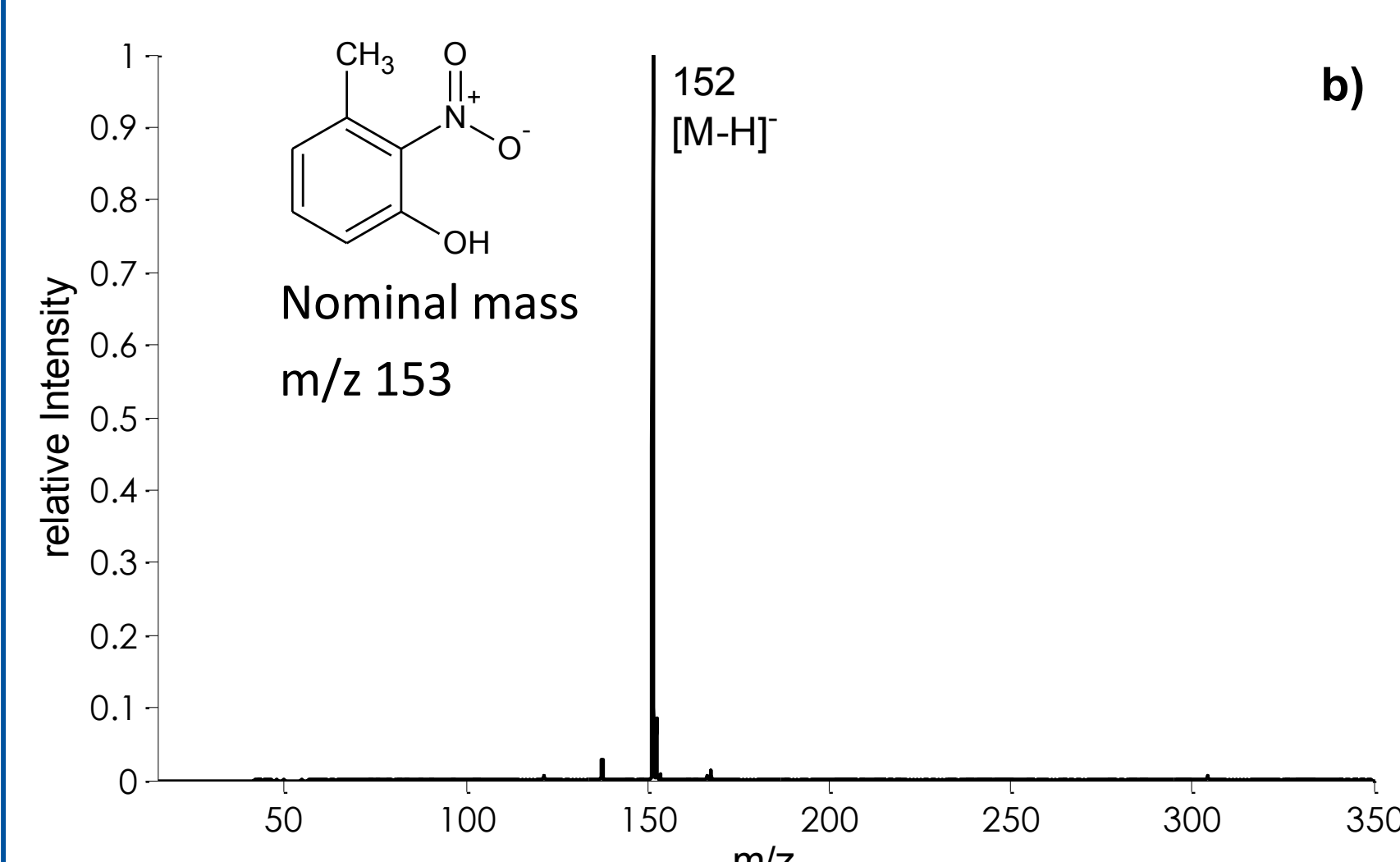
a) **Mechanism:**
Thermal electrons are captured by oxygen

M⁻ formation
 $M + O_2^- \rightarrow M^- + O_2$

[M-H]⁻ formation



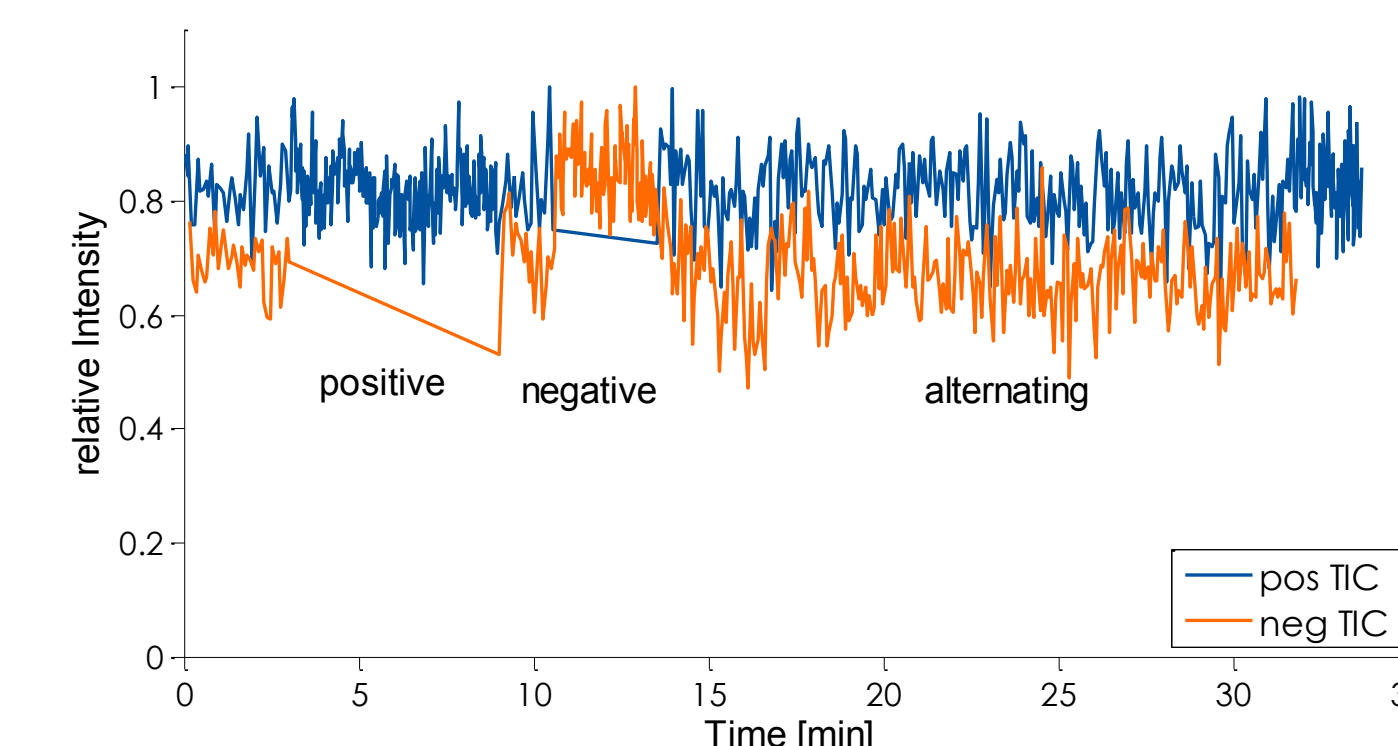
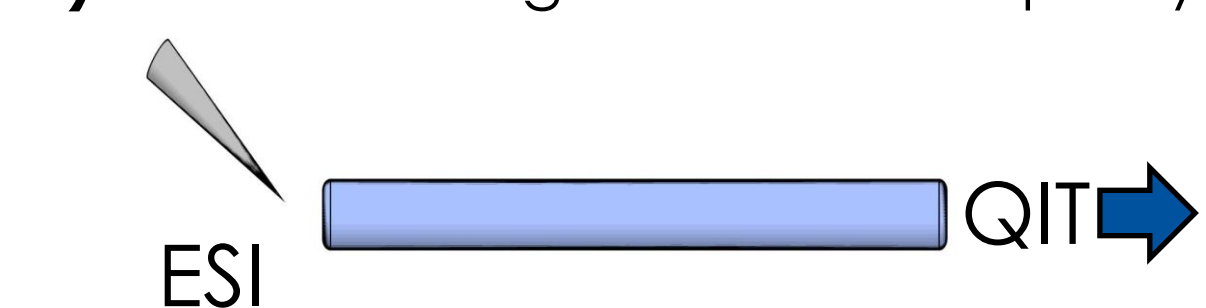
b) See also Session MP29 Poster #672
For 3-methyl-2-nitrophenol a limit of detection (3 σ) of approx. 250 pptV (1 ms acquisition time) is established.



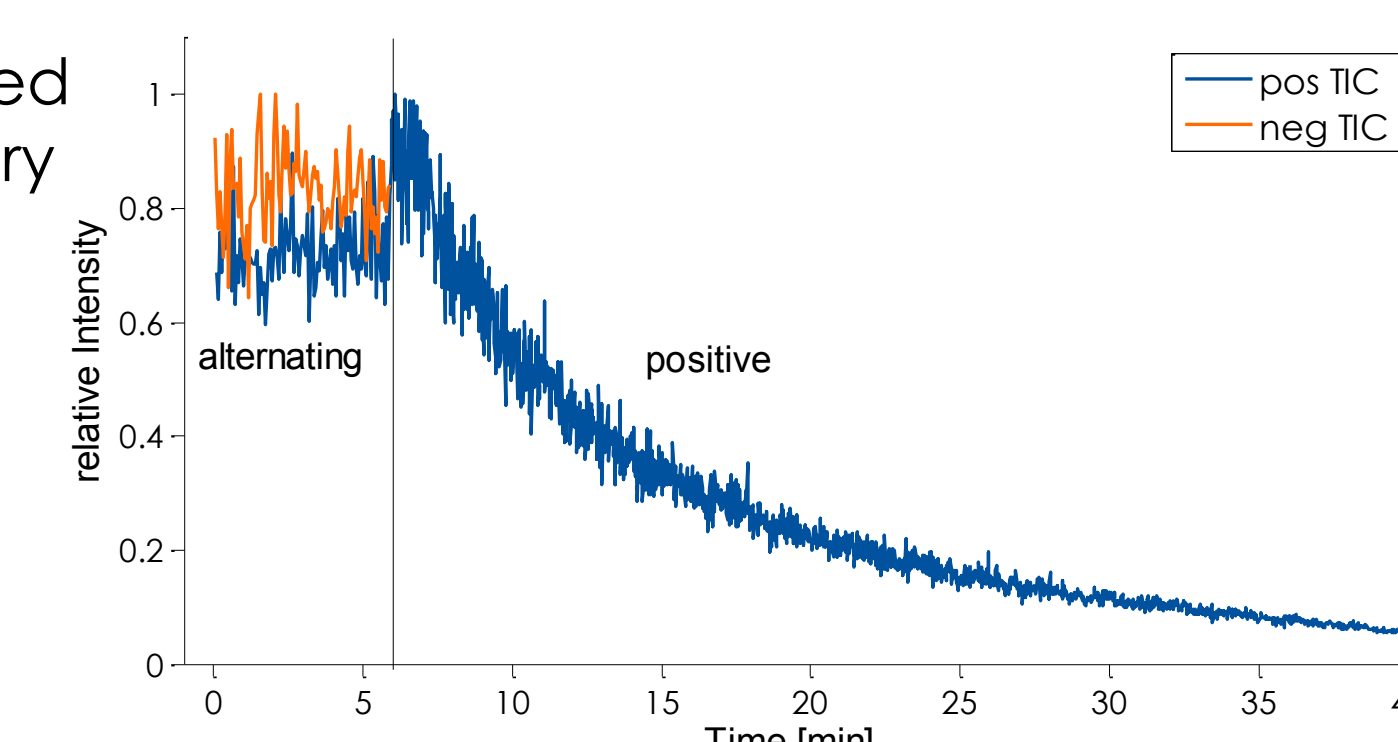
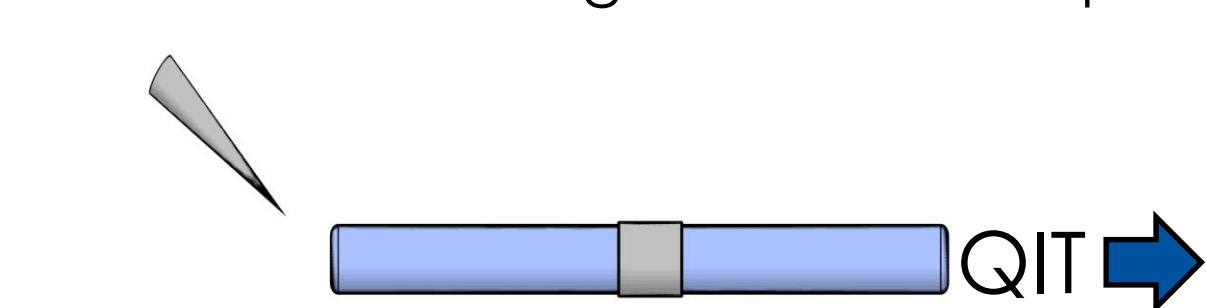
General Discussion on Charging Effects

ESI measurements

a) Standard glass transfer capillary

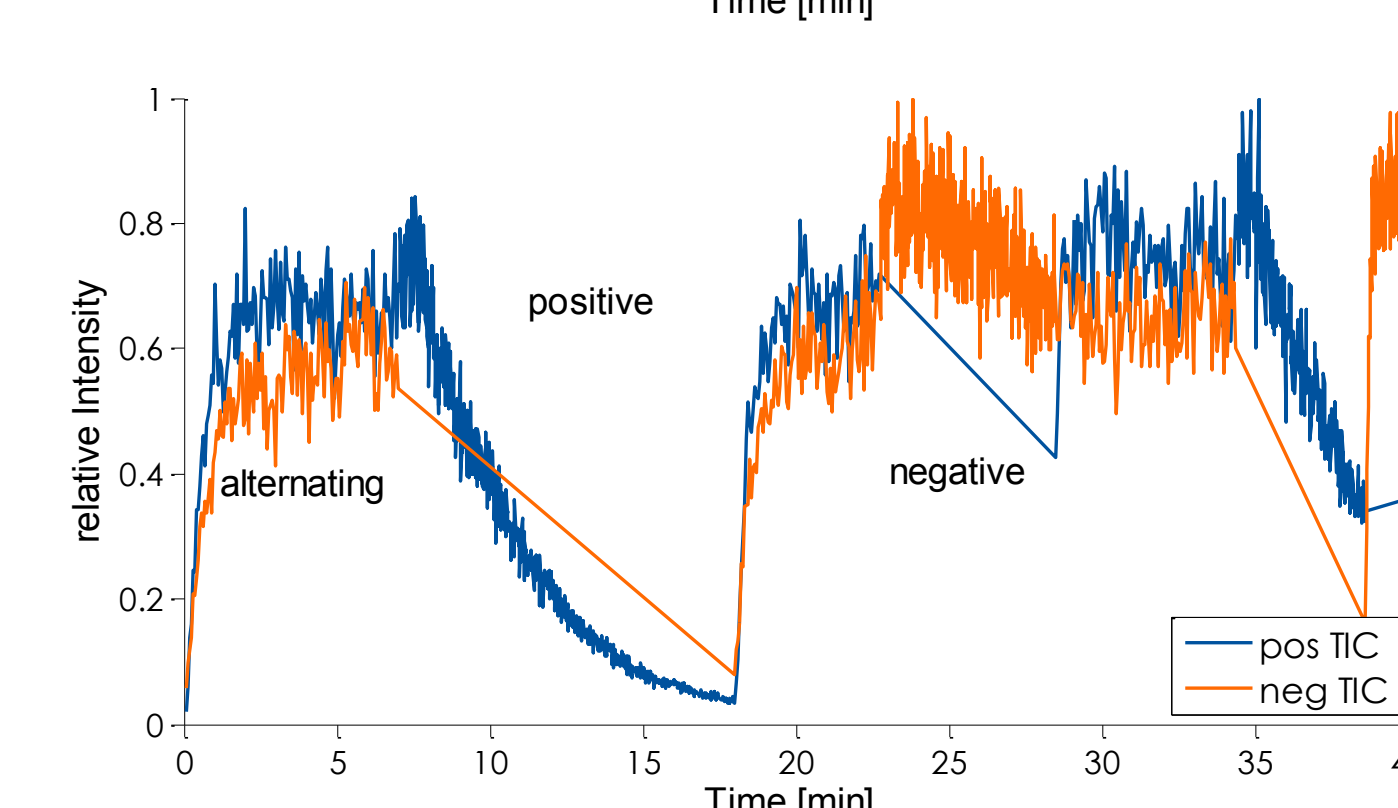
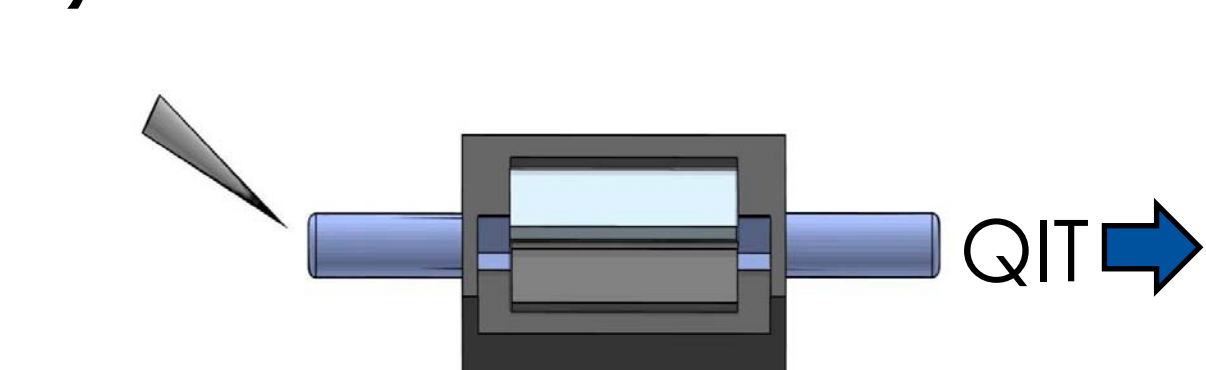


b) Grounded aluminum foil wrapped around the glass transfer capillary

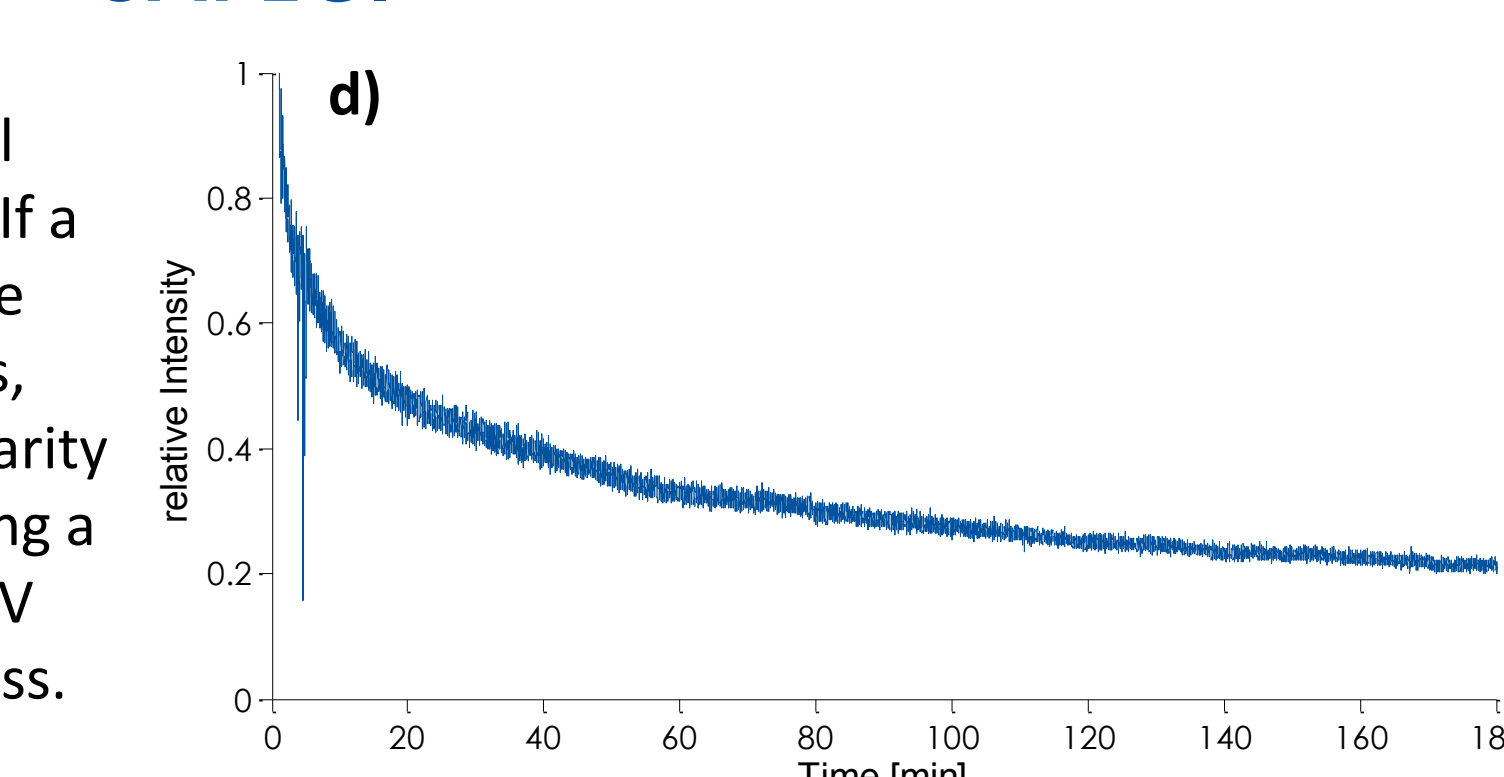


With non-grounded aluminum foil the signal decreases only slightly. If a voltage is applied on the foil the signal decreases, independent of the polarity of the potential. Applying a voltage of approx. ± 2 kV leads to a total signal loss.

c) cAPECI ion source



cAPECI



Switching on the UV lamp of the cAPECI ion source yields a higher signal level for positive ESI. Removal of the negative ions by switching off the UV lamp results in a continuous decrease in signal intensity.

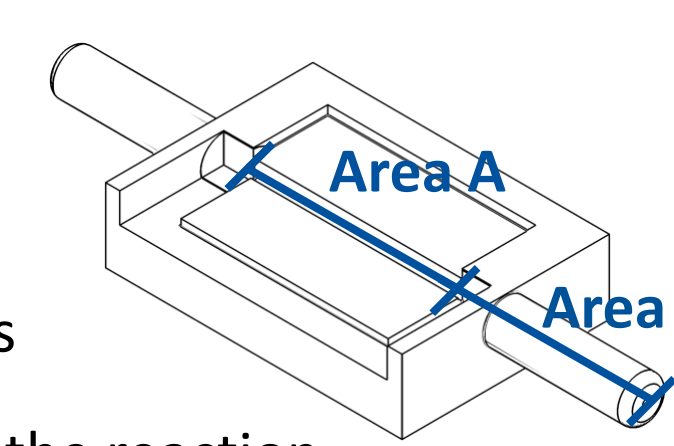
Determination of Rate Constants

With the cAPECI ion source rate constants of reactions involving O_2^- can be determined:

- Oxygen is in excess, the rate constant for electron attachment is collision controlled
→ Quantitative formation of O_2^- within nanoseconds
- < 100 pptV electrons are generated, analyte mixing ratio is > 10 ppbV
→ Pseudo first order kinetics with respect to analyte and reaction products
- Characteristics of the transfer capillaries, e.g., the transfer time and pressure profile are well known (see also Session MP29 Poster #667)

Challenge:

- No specific position where the reactants are mixed
→ **Area A:** O_2^- is uniformly generated and reacts with the analyte
→ **Area B:** reaction with the analyte
- The residence times of both areas are similar
- Pressure inside the transfer capillary decreases
→ Change of particle density in the course of the reaction



Calculation:

The production rate of product P for pseudo first order conditions is:

$$\begin{aligned} \text{Area A: } d[P]/dt &= k' \cdot [O_2^-] \text{ with } k' = k_2 \cdot [3M2NP] \text{ and } [O_2^-] = k_{O_2} \cdot t_A \\ \text{Integrated: } [P]_{t_A} &= k' \cdot 0.5 \cdot k_{O_2} \cdot t_A^2 \\ \text{Area B: } d[P]/dt &= k' \cdot [O_2^-] \text{ with } k' = k_2 \cdot [3M2NP] \\ \text{Integrated: } [P]_{t_B} &= [O_2^-] \cdot [1 - \exp(-k' \cdot t_B)] \\ \text{Combined: } [P]_{t_B} &= k_{O_2} \cdot t_A \cdot [1 - (1 - k' \cdot 0.5 \cdot t_A) \exp(-k' \cdot t_B)] \quad (\text{eq. 1}) \\ &= k_{O_2} \cdot t_A \cdot [1 - (1 - k_2 \cdot [3M2NP]_0 \cdot 0.5 \cdot t_A) \exp(-[3M2NP]_0 \cdot t_B)] \end{aligned}$$

The transfer times, t_A and t_B , are known, therefore it is possible to obtain k_{O_2} and k_2 by plotting the product signal vs. the excess concentration of the analyte and fitting equation (1) (see Figure a).

Example: Reaction of O_2^- with 3-methyl-2-nitrophenol (3M2NP)

- Reaction: $O_2^- + 3M2NP \rightarrow P$ ($[M+O_2]^-$ (+CID) $\rightarrow [M-H]^-$)
- Mixing ratio analyte: 50-600 ppbV; mixing ratio O_2^- : approx. 10 pptV

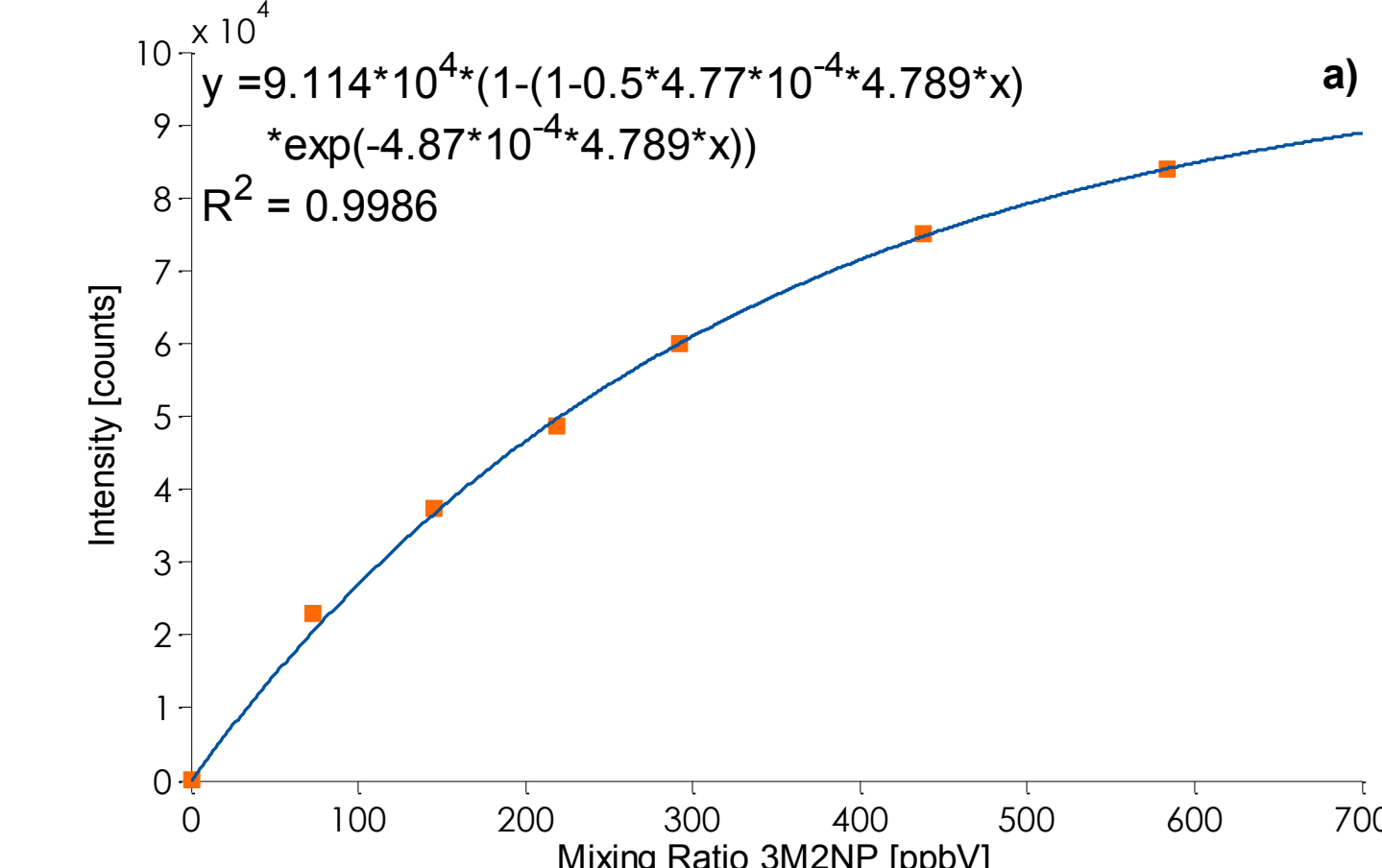
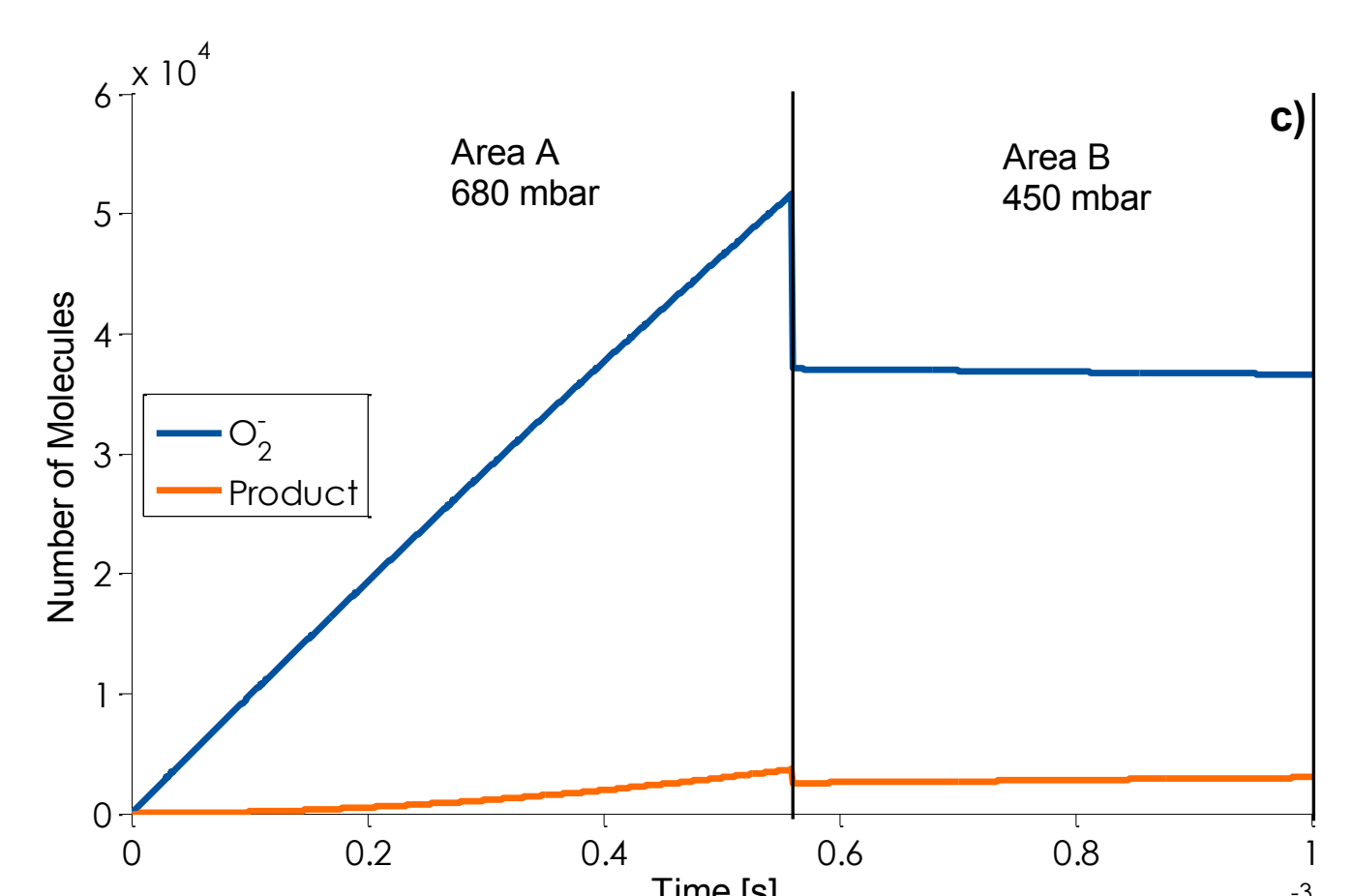
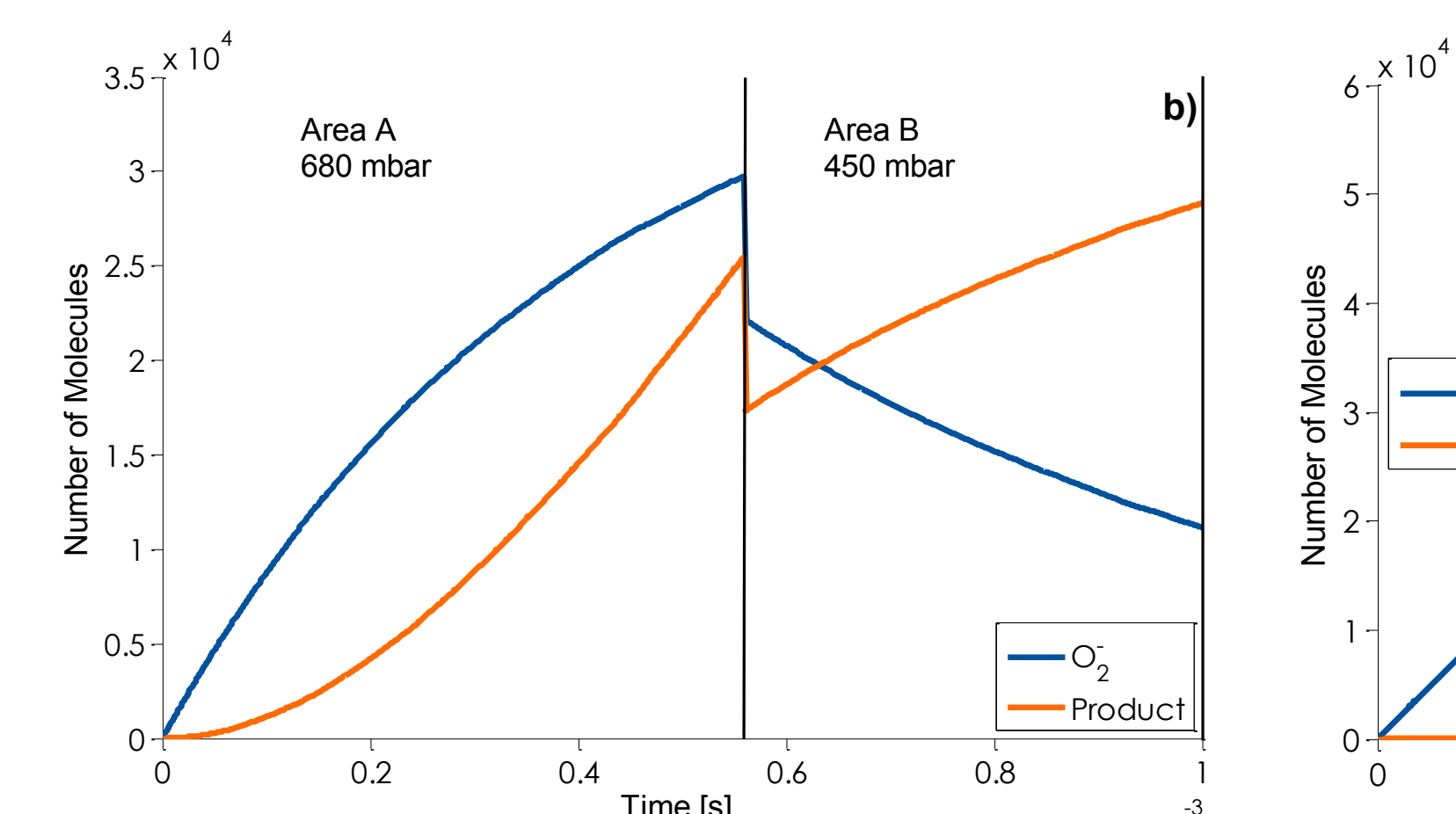


Figure a) shows the dependence of the signal intensity of $[M-H]^-$ on the mixing ratio of 3M2NP. The fitting function is identical with equation (1). For a pressure of 610 mbar (weighted average of the areas A and B) values for k_{O_2} and k_2 are determined as:

$$\begin{aligned} k_{O_2} &= 1.7 \cdot 10^8 \text{ molecule} \cdot \text{cm}^{-3} \cdot \text{s}^{-1} \\ k_2 &= 3.2 \cdot 10^{-10} \text{ cm}^3 \cdot \text{molecule}^{-1} \cdot \text{s}^{-1} \end{aligned}$$

Area	Reactions	Pressure [mbar] (weighted average)	Transfertime [μ s]
A	Formation of O_2^- Reaction with analyte	715	480
B	Reaction with analyte	485	490

Monte Carlo simulations show the concentration profiles of O_2^- and P, taking into account that the pressure changes inside the transfer capillary. The weighted average of the pressure in the particular area was used for the simulations.



Conclusions

- cAPECI is an emerging ionization method applicable for analytes with high electron affinity or gas phase basicity, such as
 - Oxygenated PAHs
 - Nitro containing explosives
 - Phenols
- Ionization within the transfer capillary strongly reduces ion transformation processes
- Selective ionization:
 - Excellent signal-to-noise ratios
 - Low limits of detection with short acquisition times
- The ion source has several advantages as compared to the previously used quartz capillary
 - Metal/window exchangeable
 - No sudden signal drops
 - Simultaneous use of other ionization methods/standard ion sources
- Determination of rate constants for reactions with O_2^- possible
 - Pseudo first order kinetics
 - Transfer times inside capillaries are known
 - Concentration distributions of reactant and product can be described by Monte Carlo simulations
- Charging effects were observed for cAPECI and other ionization methods. No charging effects are observed when:
 - a) unchanged standard glass capillaries are used
 - b) both ion polarities flow simultaneously through a modified capillary
 → The reason for this charging effect is under current investigation

Literature

- 1) A. Einstein; Über einen die Erzeugung und Verwandlung des Lichtes betreffenden heuristischen Gesichtspunkt, Ann. Phys. 1905, 322, 132-148.
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- 3) V. Derpmann, H. Kersten, T. Benter, K.J. Brockmann; Ionisationsquelle und Verfahren zur Erzeugung von Analytionen; DE 10 2011 104 355.5; Germany, 2011.
- 4) V. Derpmann, H. Sonderfeld, I. Bejan, H. Kersten, J. Kleffmann, R. Kogmann, T. Benter; Highly Efficient Ionization of Nitro-aromatic Compounds using Photoelectron Induced Atmospheric Pressure Ionization (PAPI) 59th ASMS Conference on Mass Spectrometry and Allied Topics Denver, CO, USA, 2011.
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