Investigation of reactant ion transmission efficiency of a tubular APCI-configuration in Laminar Flow Ion Sources (LFIS)

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Introduction

Challenge

Maximization of available reactant ion concentration for Atmospheric Pressure Chemical Ionization (APCI)

Investigation of transfer conditions and impact on obtained mass spectra of different materials for the transfer region of a Laminar Flow Ion Source (LFIS)

State of Knowledge:

1. In APCI the formation of additional mass signals caused by interactions between analyte and highly reactive discharge species is often observed (e.g., oxidation)
2. Obviation of direct interaction between the analyte gas flow and the hot corona discharge region is essential for the reduction of unwanted analyte transformation processes
3. In Laminar Flow Ion Sources the APCI reactant ions ($[H(H_2O)_n]^+$) are generated separately and merge with the analyte containing gas flow further downstream
4. In general the concentration of available reactant ions is increased by the use of a tubular APCI design
5. For maximization of available reactant ion concentrations the transfer of the ions within the LFIS has to be optimized
6. At atmospheric pressure (AP) the transfer of ions is dominated by gas flows
7. **At atmospheric pressure ions strongly interact with the walls causing loss of reactant ions and "charging effects" that adversely affect the performance of ion guiding constructions**

Question:

Is it possible to affect the degree of the interaction between the ions and the walls by variation of set-up parameters such as gas flows, voltages, materials, etc.?

Methods

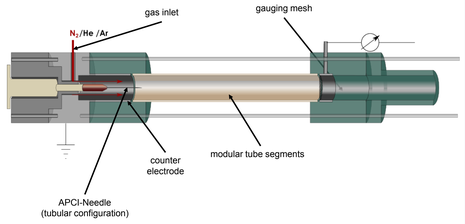
Experimental Setup

Electrometer:	KEITHLEY 6430 SUB-FEMTOAMP REMOTE SourceMeter®
MS:	Bruker esquire3000 quadrupole ion trap
Ion Source:	Custom build tubular APCI including a commercially available APCI-needle device
Discharge Gases:	Nitrogen (5.0), Helium (5.0) and Argon (5.0)

Experimental Setups

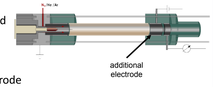
Setup 1:

- **Tubular APCI source** including a commercially available APCI-needle device generally also used in LFIS (current control by *Esquire-Control*-Software, 1 - 4 µA).
- Coupling to **modular tube segments** (mimics the AP transfer-region of the LFIS); simple variation of length and material (tube segments are insulated)
- **Total ion current** measured with a directly coupled gauging mesh (insulation to the tube segments possible)
- Controlled gas inlet



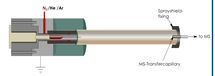
Setup 2:

- Modification of setup 1 with an **additional electrode** located between tube segment and gauging mesh
- **Total ion current** measurement
- Variation of potential at the additional electrode



Setup 3:

- Direct coupling of the AP transfer region to the transfer capillary of the MS
- No contact with the walls
  → **only gas phase sampling**
- Surplus of carrier gas avoids contamination with external gas



Tube Configurations

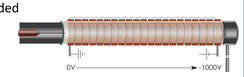
Materials:

- Borsilicate glass
- Teflon®
- PVC
- Anodized aluminum
- Borsilicate glass surrounded by Electrode array

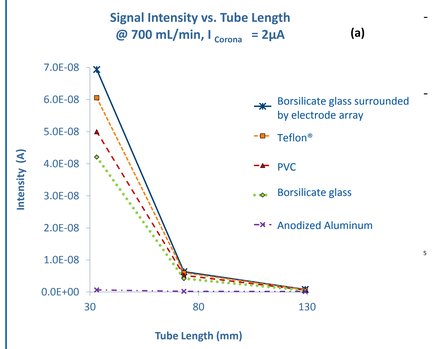
(Potential gradient along the glass tube; see right hand)

Length:

- 33,1 mm (short tube)
- 73,24 mm (medium tube)
- 129,1 mm (long tube)



Material Comparison



Tube Length Variation (setup 1, (a)):

- All materials (except anodized aluminum) show **similar final signal intensities** (up to nA using the short tubes)
  → **Similar wall loss** for all materials (except anodized aluminum)
- Large **differences in the response times** required to reach the final intensity

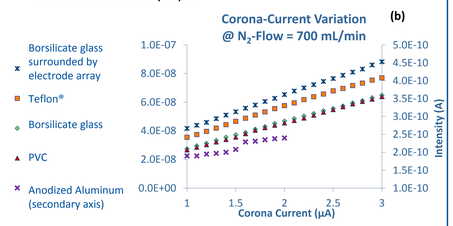
Material	Response time (s)
Electrode arrayed Glass	< 1
Glass	< 10
Anodized Aluminum	~ 20
Teflon	~ 150
PVC	~ 450

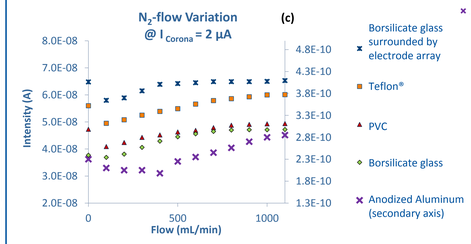
→ **final signal intensity independent** of the wall material
Build-up of a **comparable surface layer**?

→ Material dependent response time for attainment of an **equilibrium state** of the boundary layer?

Corona Current Variation (setup 1, (b)):

- **Comparable response** to the variation of corona current for all materials
- A corona current higher than 2 µA is not possible with anodized aluminum
  → Change of corona discharge characteristics



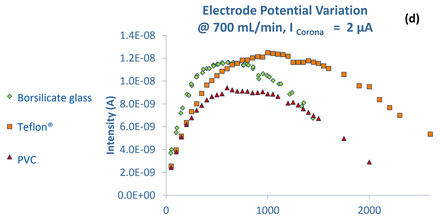


Flow Variation (setup 1, (c)):

- All materials show **low response** to variation of the N_2-flow
- At non-flow conditions no significant change in final intensity
  → Signal is almost independent of the flow
  → **Space charge driven** transfer

Electrode Potential Variation (setup 2, (d)):

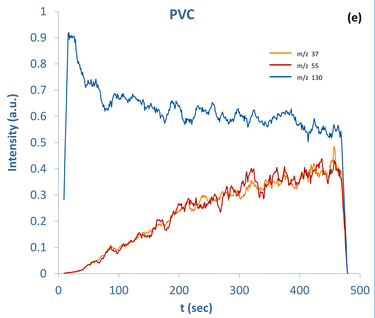
- Potential variation at the additional electrode results in a significant **increase of the signal** (maximum at a few hundred volts)
  → Focusing effect at AP?
- **Comparable slopes** for different tube lengths
- **Shift of the maximum** of the slope for different materials
- Maximum signal reached with floating electrode



Mass Spectrometric Measurements

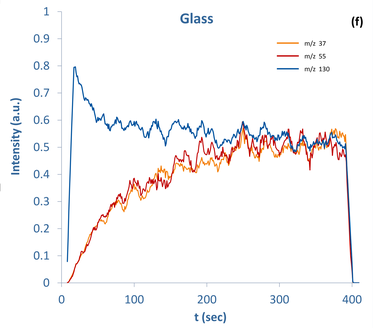
Influence of the Tube Material on the Mass Spectrum:

- Measurements with setup 3 including PVC (e) and glass (f) as the transfer region
  - This kind of sampling reflects only the effect on the gas phase
- Figures (e) and (f) show the time dependent behavior of two reactant ions (m/z 37 $[H(H_2O)_2]^+$ and m/z 55 $[H(H_2O)_3]^+$) and a background signal (m/z 130 $[M+H]^+$) after ignition of the discharge
- Distinct difference between the behavior of reactant ions and background ions
  - Immediate appearance of the background signals
  - Delayed response of the reactant ion signals ("accumulation")
- Change of material results in different response times



General picture of the processes of reactant ions in APCI

- Reactant ions ($[H(H_2O)_n]^+$) are produced in the generally accepted reaction path ($N_2^+ \rightarrow N_4^+ \rightarrow H_2O^+ \rightarrow H_3O^+ \rightarrow H(H_2O)_n^+$) close to the corona discharge area [1]
- Due to the high water concentrations and large rate constants at AP conditions the equilibrium distribution of the protonated water clusters is reached after a few microseconds (n = 2 - 7; n_{max} = 4 at AP and 10 ppm H_2O)[2], [3]
  → After perturbation the cluster distribution is reestablished within in a few microseconds
- Within a $[H(H_2O)_n]^+$ cluster the positive charge is distributed over the entire cluster, i.e., there is no "central" proton
- The entire cluster system undergoes continuous "ligand switching" processes [4]
- The ligand switching is a fast process [4]
  → Proton bound water clusters never retain a fixed size (fast dynamic process)[5]



Model of „fast moving" protons

- Fig. (a), (e) and (f) indicate loss of ions to the walls
  - Increasing the surface area results in increasing signal losses (Fig. (a))
  - Reduction of the ion retention time in the transfer region impacts the signal (see electrode arrayed glass)
- Different wall loss behavior of reactant ions and background ions
- Fig (e) and (f) indicate that the loss of reactant ions establishes an equilibrium (behavior will be an admixture of wall and reactive loss)
- **Adsorption processes** in a boundary layer comprised of water (and other components) should be similar for the considered ions
  - In the transfer region even background ions may exist as water clusters $[M+H+(H_2O)_n]^+$ (further CID processes inside the MS lead to $[M+H]^+$ signal) [5]
- Loss due to an **electrical field effect** is unlikely (the behavior of all ions would be affected similarly)
- **Diffusion** should be on the same order of magnitude for the investigated range
- HOWEVER the **$[H(H_2O)_n]^+$ system is a fast interacting system**
  → Protons can be transferred from cluster to cluster without the need of motion of the entire cluster (cf. conductance of water)
  → The "diffusion of H^+" to the walls may thus become orders of magnitude faster as compared to background ions

Conclusions

- Downstream ion signal intensity independent of the wall material (except metal)
  → Build-up of a chemically comparable surface layer possible
- Material dependent response time for attaining an "equilibrium" state
- Space charge driven transfer within the transfer region
- Surface layer is affected by an externally applied potential
- The fast passing of charge inside the transfer region by proton propagation within the $[H(H_2O)_n]^+$ cluster system may generate a higher interaction between the reactant ions and the walls **(Model of "fast moving" protons)**

Further investigations are required for a better understanding of the impact of such boundary layers on the transfer efficiency for reactant ions in LFIS sources

Literature

[1] Dzidic, I.; Carrol, D.I.; Stillwell, R.N.; Horning, E.C., *Comparison of Positive Ions Formed in Nickel-63 and Corona Discharge Ion Sources Using Nitrogen, Argon, Isobutane, Ammonia and Nitric Oxide as reagents in Atmospheric Pressure Ionization Mass Spectrometry;*, Anal. Chem., **1976**, Vol. 48, No. 12, p. 1763-1776,

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[3] Benter, Th.;@ all ASMS 2012 MOG Talk: *On the pivotal role of ion bound clusters in atmospheric pressure ionization mass spectrometry;*

[4] Midey, A.J., *Reactions of H3O+(H2O)n with Formaldehyde and Acetraldehyde*, J. Phys. Chem. A, **2000**, 104, p. 2706 – 2709

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