Novel Laminar Flow Ion Sources for LC- and GC-API MS

Physical &Theoretical Chemistry Wuppertal, Germany [1]

RWTH AACHEN UNIVERSITY [2]

Ian Barnes[1]; Hendrik Kersten[1]; Walter Wissdorf[1]; Thorsten Pöhler[2]; Herwart Hönen[2]; Sonja Klee[1]; Klaus J. Brockmann[1]; Thorsten Benter[1]

Introduction

- ***Challenge*:**
  Turbulent flow, always present in classical API sources

  → Numerical simulations and experimental Particle Image Velocimetry (PIV)data show complex fluid dynamics
  s.a. Session WP28; Poster #606
  → Pronounced memory effects
  → Many unstable, hardly controllable source parameters impacting on flow dynamics
  → Adverse effects on reproducibility
  → Significant limitation of Dynamical Ionization Volumes (DIAV) in Atmospheric Pressure Laser Ionization (API)
  s.a. Session WP28; Poster #610

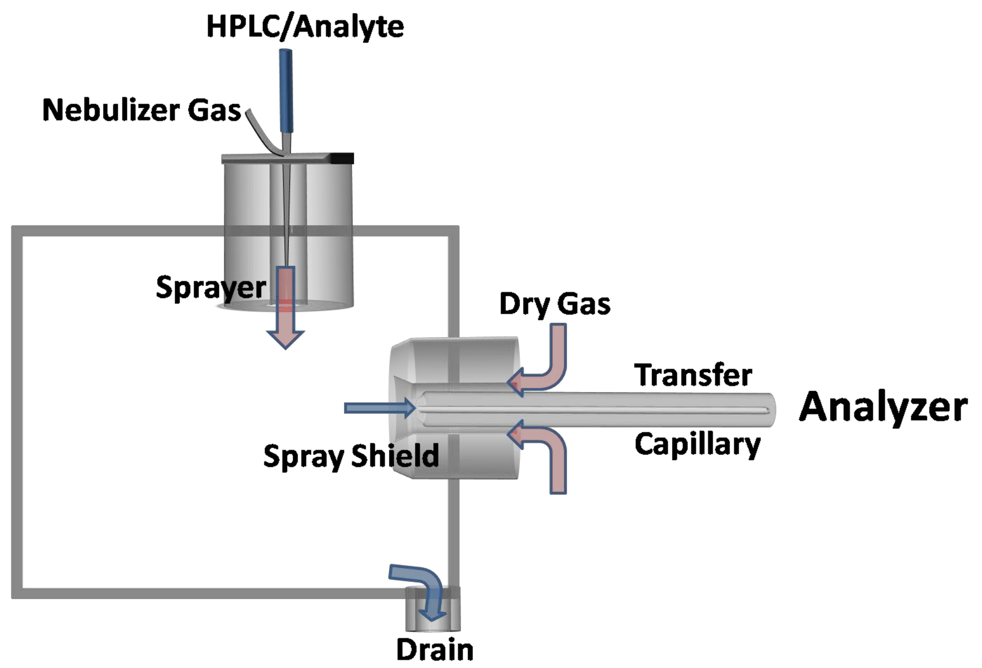
- ***Alternative approach*:**
  Laminar flow API sources

  → Experiments demonstrate efficient ion transmission
  → Simulation show typical Hagen-Poiseuille flow
  → Flow is determined by the MS
  → Analyte gas phase flow is introduced in an angle of 10°
  → For APLI, laser beam is coaxially positioned
  → For APPI, radiation source is mounted perpendicularly on the tube
  → For APCI, one or two needles, are positioned in sidearms at angles of 10° to the main axis

Methods

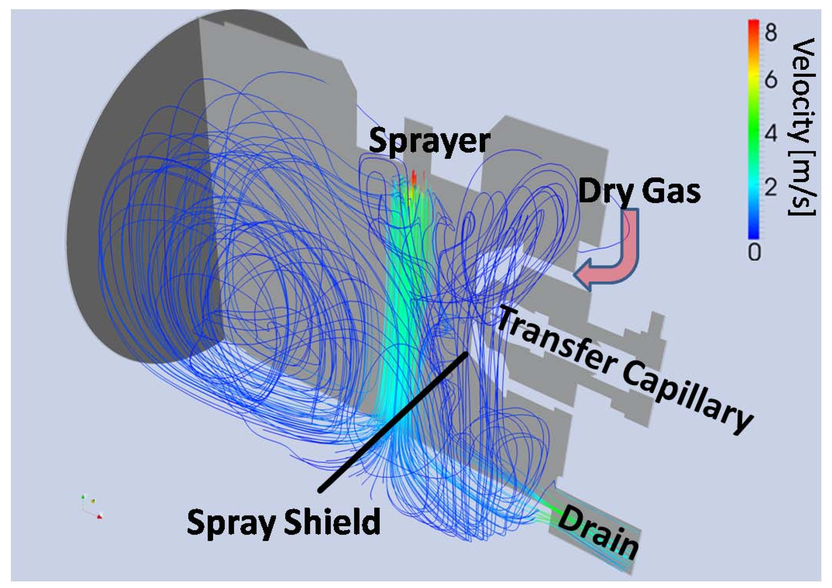
MS	Bruker esquire6000
Radiation source	homebuilt argon spark discharge lamps; Diode pumped solid state laser- *DPSS*- (CrylLas); KrF* excimer laser (Optex)
Gas phase samples	Photoreactor for gas phase degradation studies
Chemicals	p-xylene, pyrene, anthracene
Simulations	Ansys CFX-11

Fluid dynamic simulations of common API sources



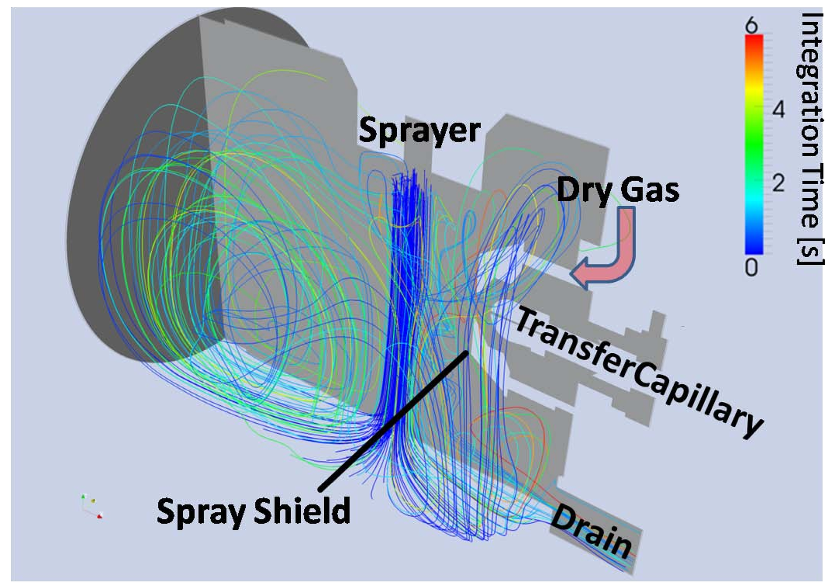
Typical API source design

→ Nebulizer Gas: + 0.5 – 2.0 L/min
→ Dry Gas: + 0.0 – 10.0 L/min
→ Transfer Capillary: - 0.8 – 1.5 L/min
→ Drain: setup dependent



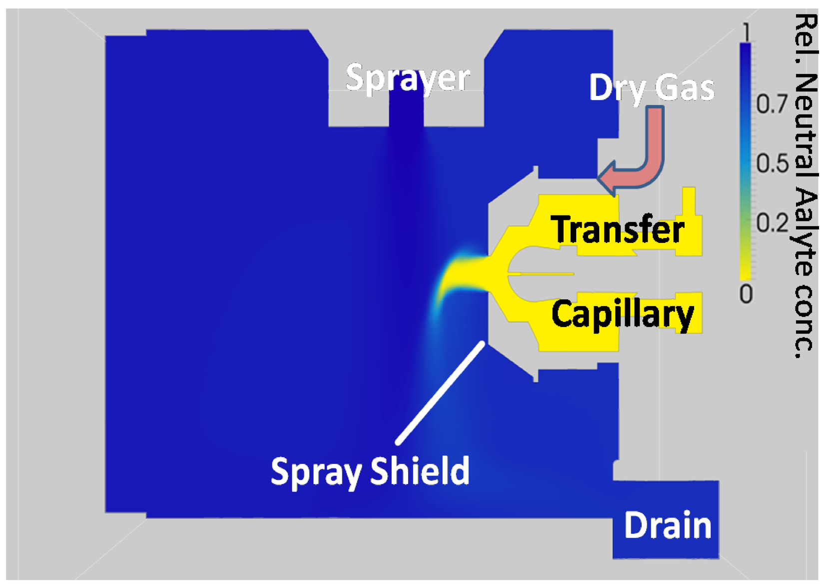
Velocity distribution

→ Trajectories demonstrate the complex flow characteristic.
→ Most stream lines "slow down" to less than 1 m/s.



Time integrated trajectories

→ Analyte dwell times of the order of seconds
→ Feasible explanation for observed memory effects

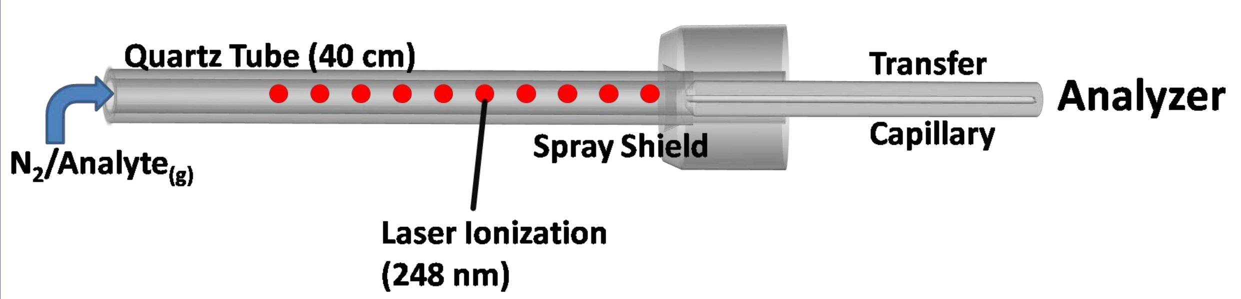


Neutral analyte distribution

→ Nearly Isotropic distribution in the entire ion source
→ Feasible explanation for elevated background signals

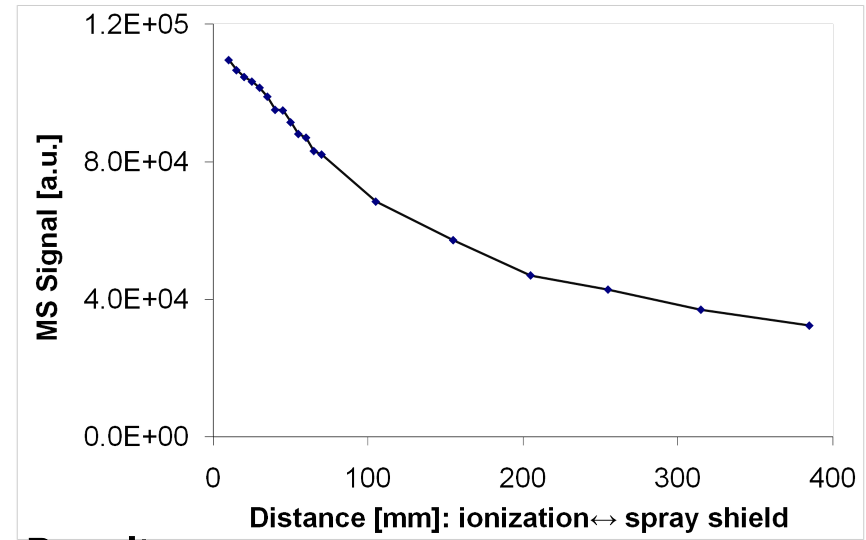
Investigation of ion transport efficiencies in laminar flow tubes

Experiment



Experimental setup:

→ 40 cm quartz tube, directly mounted on the transfer capillary
→ Scan of ionization positions with a 248 nm excimer laser (beam collimated to 1.5 mm cross section)



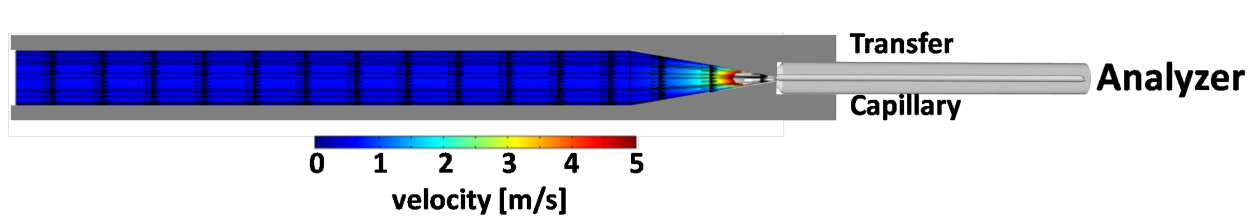
Results:

→ 36 % of signal intensity remains after 40 cm of transport
→ Investigations with metal tubes revealed comparable behavior

Simulation

Boundary conditions:

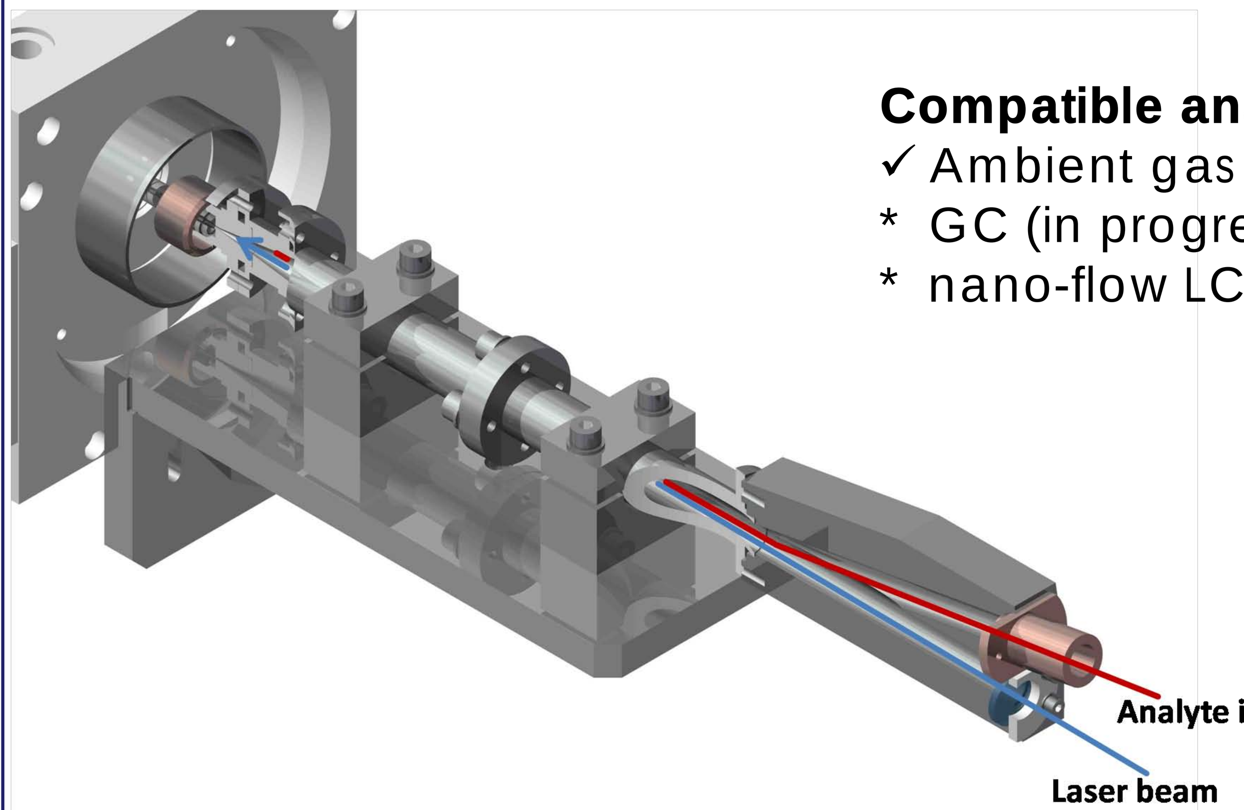
→ Gas flow of 1.4 L/min, determined by the MS
→ Tube i.d. of 9 mm, conically shaped end with 0.8 mm orifice



Results:

→ Typical Hagen-Poiseuille flow profile upstream of the capillary entrance region
→ Loss of ions occurs mainly by diffusion, as expected

Designs of Laminar Flow Ion Sources



Compatible analyte inlets:

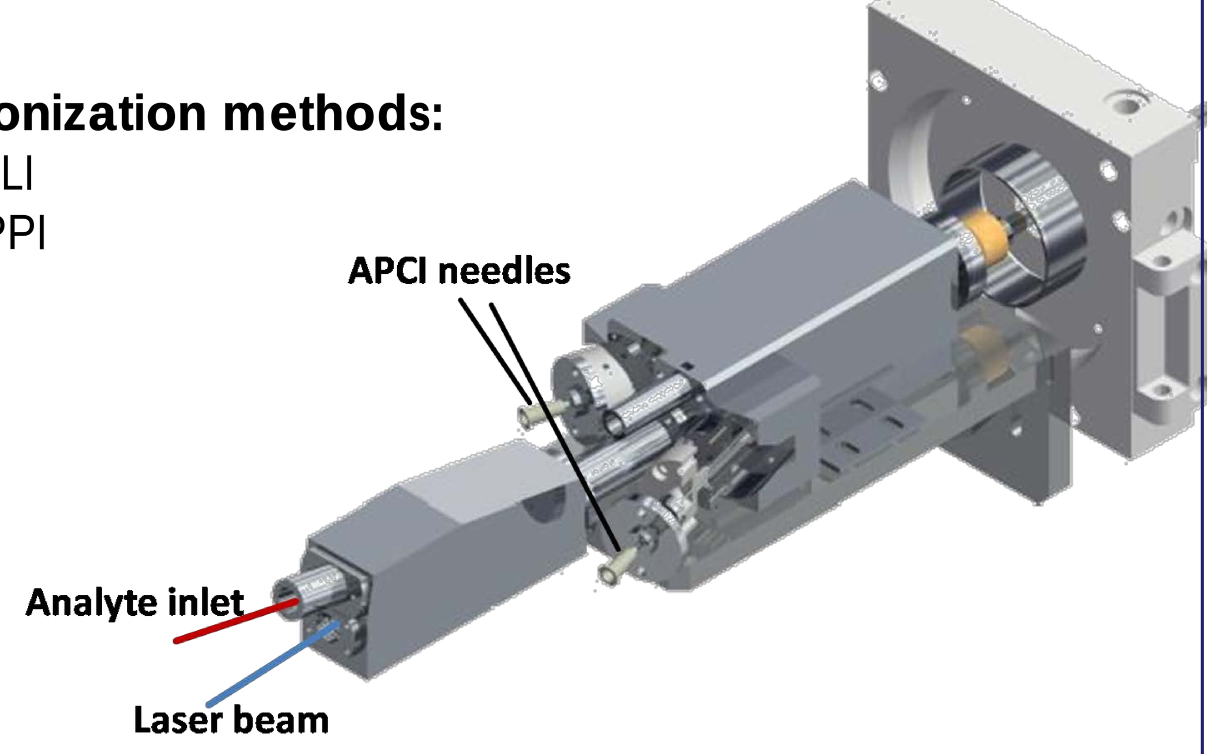
✓ Ambient gas phase samples
* GC (in progress)
* nano-flow LC (in progress)

Compatible ionization methods:

✓APLI; DA-APLI
✓APPI; DA-APPI
✓APCI

Results so far:

✓ High sensitivity in APPI and APLI
s.a. Session WP28; Poster# 608
✓ High sensitivity in APPI
s.a. Session TP27; Poster# 610
✓ effective DA-APLI and DA-APPI



Conclusions

- ***Benefits* of Laminar Flow API sources:**

  → Controllable flow
  → High ion transmission efficiency into the MS
  → Signifcant increase of the DIAV for APLI
  → Efficient irradiation of the sample flow (APPI and APLI)
  → Efficient heating
  → Easy cleaning
  → Sidearm design allows for multiple inlets (e.g., gas phase reagents)

- **Fully compatible:**

  Ionization
  → APLI, DA-APLI
  → APPI, DA-APPI
  → APCI

  Analyte inlet
  → Gas phase sampling
  → GC (in progress)
  → LC (in progress)

Literature

1) Constapel, M.; Schellenträger, M.; Schmitz, O. J.; Gäb, S.; Brockmann, K. J.; Giese, R.; Benter, Th. *Rapid Commun. Mass Spectrom.* **2005**, *19*, 326-336.
2) Kersten, H.; Funcke, V.; Lorenz, M.; Brockmann, K.; Benter, T.; O´Brien, R., Evidence of Neutral Radical Induced Analyte Ion Trans-formations in APPI and Near-VUV APLI. *Journal of the American Society for Mass Spectrometry* **2009**, 20, (10), 1868-1880
3) Schiewek, R.; Schellenträger, M.; Mönnikes, R.; Lorenz, M.; Giese, R.; Brockmann, K. J.; Gäb, S.; Benter, Th.; Schmitz, O. J. Ultrasensitive determination of polycyclic aromatic compounds with atmospheric-pressure laser ionization as an interface for GC/MS. *Anal. Chem.* **2007**, 79, 4135-4140.
4) Benter, Th.; Schmitz, O. J. Atmospheric Pressure Laser Ionization. In *Advances in LC-MS instrumentation*, Journal of Chromatography Library 72, Cappiello, A. Ed.; 2007.
5) Benter, Th. Atmospheric Pressure Laser Ionization. In *The Encyclopedia of Mass Spectrometry*, Gross, M. L., Caprioli, R. N., Eds., 1st ed.; Elsevier: Oxford, U.K., 2007.
6) Lorenz, M.; Schiewek, R.; Brockmann, K. J.; Schmitz, O. J.; Gäb, S.; Benter, Th. The distribution of ion acceptance in atmospheric pressure ion sources: Spatially resolved APLI measurements. *J. Am. Soc. Mass Spectrom.* **2008**, 19, 400-410.
7) Schrader, W.; Panda, S. K.; Brockmann, K. J.; Benter, Th. Characterization of non-polar aromatic hydrocarbons in crude oil using atmospheric pressure laser ionization and Fourier transform ion cyclotron resonance mass spectrometry (APLI FT-ICR MS). *Analyst* **2008**, 133, 867-869.
8) Schiewek, R.; Lorenz, M.; Giese, R.; Brockmann, K.; Benter, T.; Gäb, S.; Schmitz, O. J. Development of a multipurpose ion source for LC-MS and GC-API MS. *Anal. Bioanal. Chem.* **2008**, 392, 87-96.
9) Schiewek, R.; Mönnikes, R.; Wulf, V.; Gäb, S.; Brockmann, K. J.; Benter, Th.; Schmitz, O. J. A Universal Ionization Label for the APLI-(TOF)MS Analysis of Small Molecules and Polymers. *Angew. Chemie-Int. Ed.* **2008**, 47, 9989-9992.

Acknowledgement

Financial support is gratefully acknowledged:

DFG BE2124/6-1 and BE2124/4-1and **Bruker Daltonics**.