

Distribution of Ion Acceptance in a Fluid-dynamically Optimized Multi-purpose Ion Source



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Introduction

Data on the distribution of ion acceptance (DIA) as gathered from spatially resolved atmospheric pressure laser ionization (APLI, (1-3)) measurements have previously been reported (5-7). In particular the combination with temporally resolved photo-ionization experiments have provided deep insight into the analytical limitations due to fluid-dynamical drawbacks of current atmospheric pressure (AP) ion source designs (6-8). A pronounced analyte dwell time in the ion source and a broad distribution of ion storage times foster memory effects and chromatographic peak broadening, particularly in LC hyphenation.

The analytical limitations result from unfavorable transport conditions within the ion source. Long analyte dwell times and thus long trajectories for ionic (6,7) and molecular species cause the "buffering nature" of the ion source. One approach toward a fluid-dynamical optimization is to design the ion source as a true "flow system" with orthogonal MS sampling, i.e. with up- and downstream flow control. Such an "Active Elevated Floor" (AEF) unit is capable of preventing a large-volume analyte distribution and a broad distribution of transfer times – important origins of memory effects and broad chromatographic peaks.

Methods

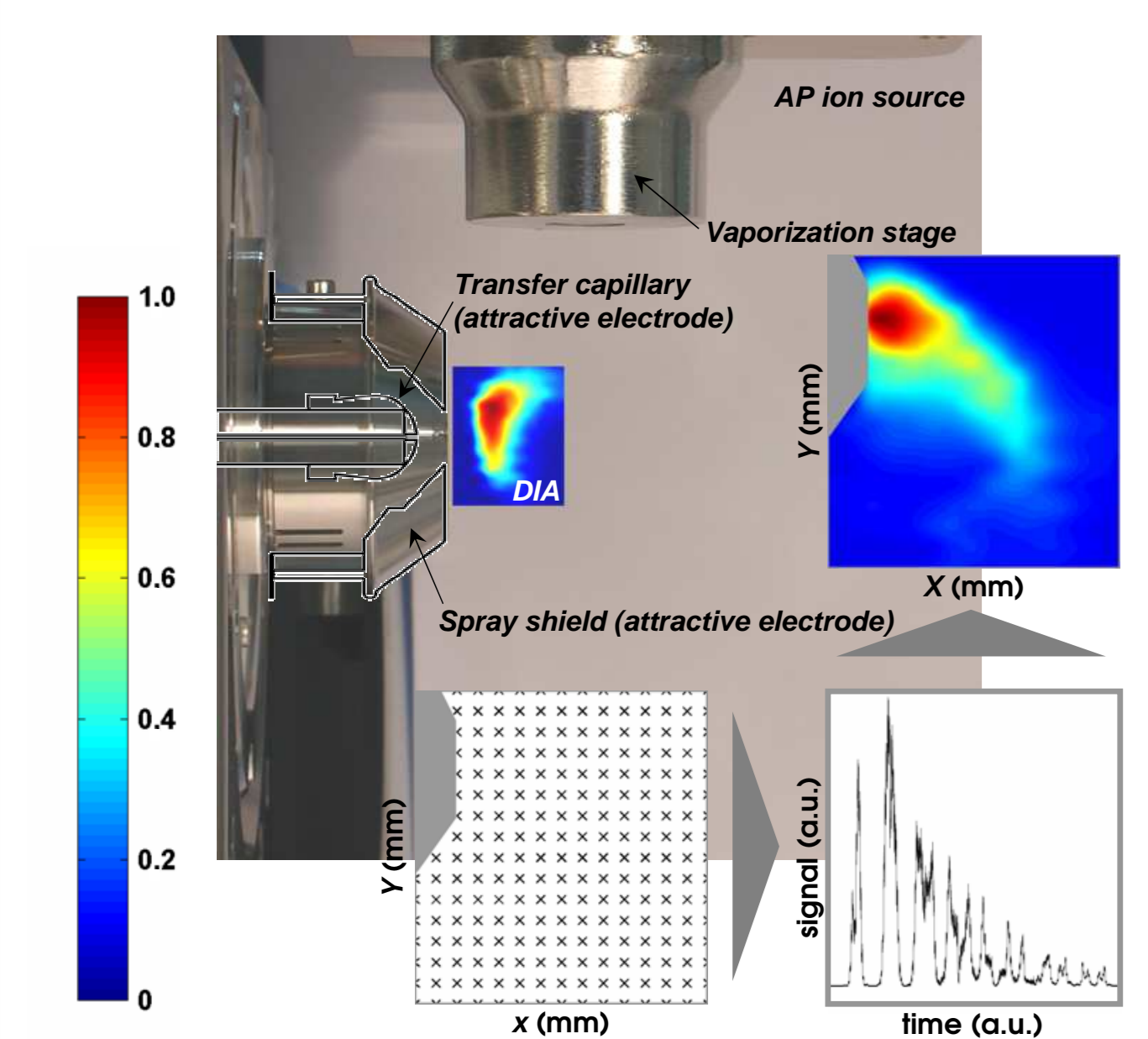
Experimental setup

MS: Bruker micrOTOF
Ion source: Multi-purpose ion source (MPIS) (4), optionally with AEF unit (cf. Fig. 6)
Light source: ATL ATLex 300 KrF* laser ($\lambda = 248$ nm), CryLas DPSS ($\lambda = 266$ nm)
HPLC: Halo C18, 4.6 x 30 mm, 2.7 μ m, MeOH/H₂O (90/10), 1 mL/min, 20 μ L 1 μ mol/L pyrene in MeOH/H₂O (95/5)

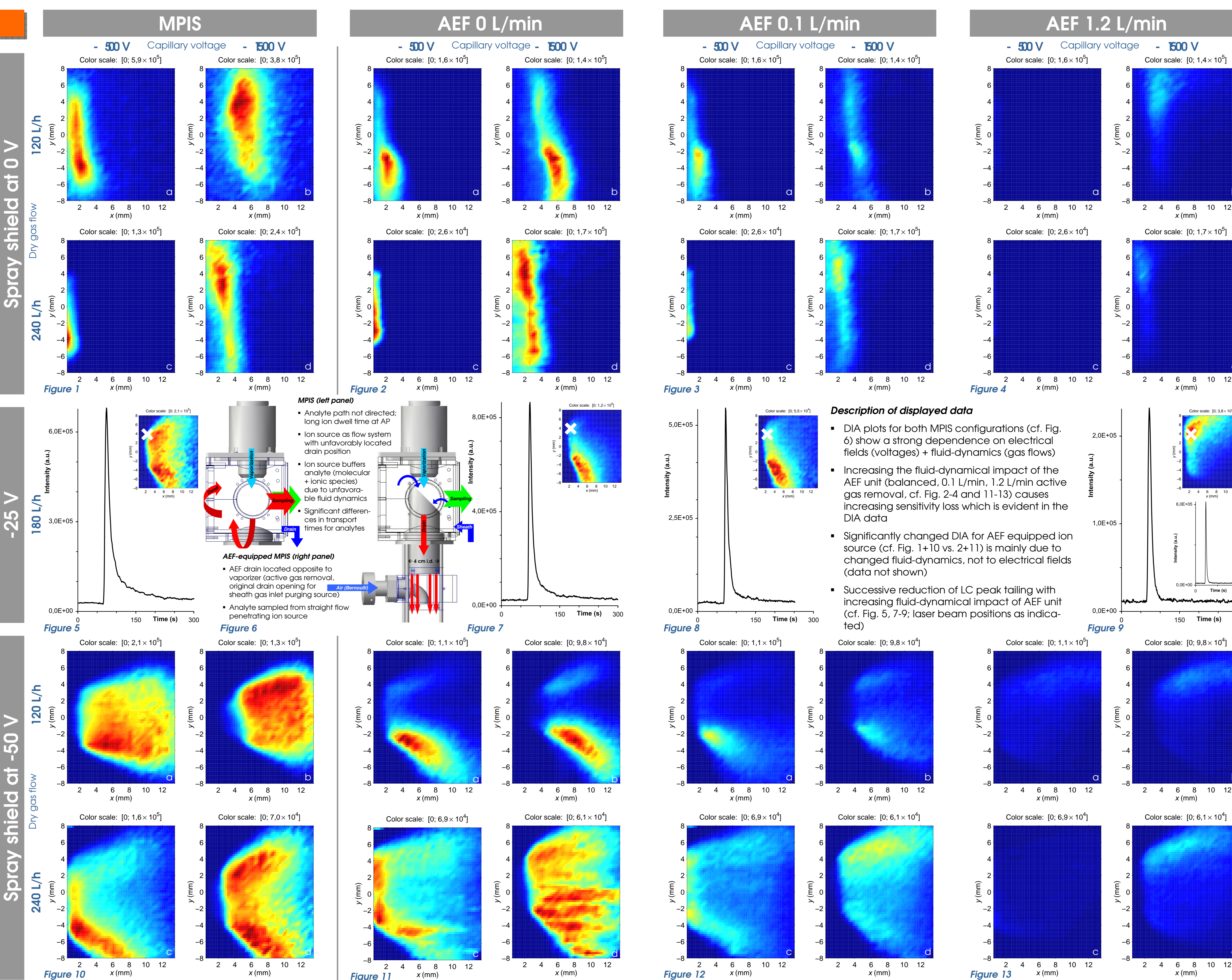
DIA measurements

Light source: ATL ATLex 300 KrF* laser, 50 Hz, 5 mJ
Analyte: 0.1 μ mol/L pyrene in MeOH, 100 μ L/min liquid flow introduction
Gas flows: 120...240 L/h dry gas @ 200°C, 3 bar nebulizer pressure @ 320°C, Dry nitrogen (gas cylinders)

DIA: Principle and spatial arrangement



Results



Conclusions

Distribution of ion acceptance

- Significant changes of sensitivity distribution in MPIS with altered fluid-dynamical conditions (cf. Fig. 1, 10 vs. 2...4, 11...13)
- Significant reduction of absolute sensitivity due to the removal of any analyte not directly sampled (as expected)

LC application of AEF

- LC peak width reduction already for passive operation / changed position of drain opening (data not shown)
- Stable operation of AEF-equipped ion source with active exhaust (set-up shown in Fig. 6) for a wide range of gas + liquid flows
- Moderate sensitivity reduction in temporally resolved LC data (cf. Fig. 5, 7-9) as compared to significant drop in intensity for integral data on sensitivity distribution (cf. Fig. 1...4, 10...13)

Interpretation

- AEF equipped MPIS reduces the signal contribution of analyte species with long dwell times within the AP ion source reservoir; the effect increases up to a considerable gas removal from the ion source (ion source purged with additional sheath gas, cf. Fig. 6)
- Temporal variability of analyte (ions + molecules) transport mechanisms is avoided, stable conditions are indicated by narrow (also for equally sized, cf. inlay in Fig. 9) LC peaks
- MPIS geometry equipped with AEF represents flow system with orthogonal MS sampling
- AEF equipped ion source prevents analyte buffering and enables fast online analysis

Outlook

- Since reduced sensitivity is due to incomplete analyte ionization and ion sampling processes within the ion source, further research will be focused on these aspects

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