Development of a dual-mode laminar flow ion source for APPI- and APLI-GC-MS

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Introduction

At the annual ASMS meeting in 2010, we introduced a novel laminar flow ion source (LFIS) for API-MS [1]. In the following years, we presented the capabilities of the LFIS with the analysis of in-situ samples from atmospheric smog chamber experiments [2]. Based on the original LFIS, we designed a novel interface for GC-API-MS.

Challenges:

- Design of a novel GC-MS interface, suitable for atmospheric pressure photoionization (APPI) and atmospheric pressure laser ionization (APLI)
- Design with sustained chromatographic fidelity
  - → Prevention of cold spots
  - → Prevention of dead volumes
- Swift change between APPI and APLI operation
- Variable ionization chamber volume (length and inner diameter) to optimize for the ionization efficiency and ion transport in APPI and APLI
- Controllable via MS-software

Experimental Setup

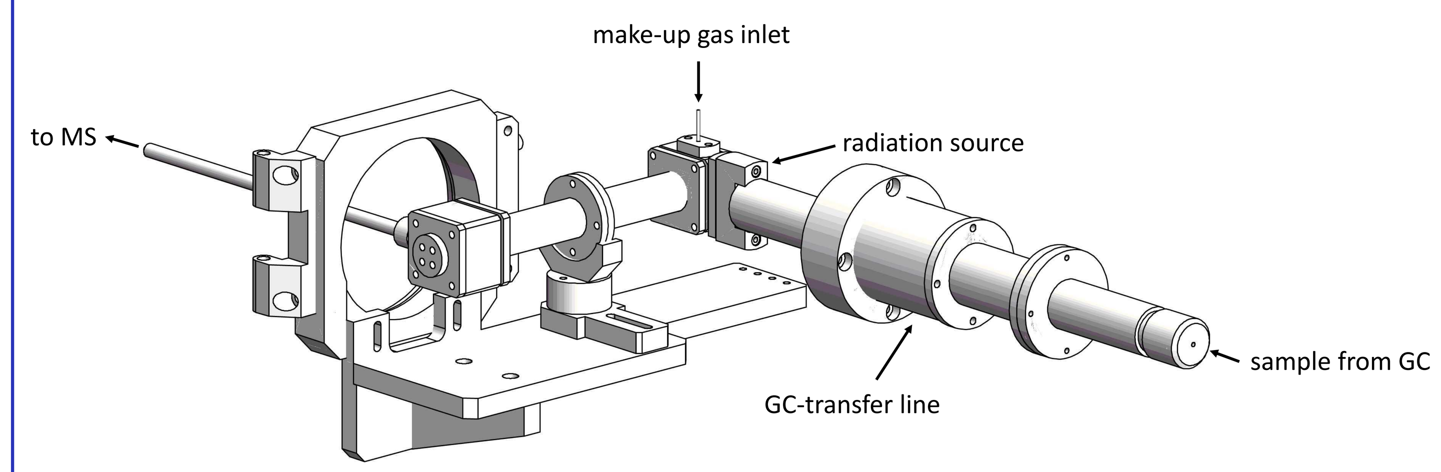

Figure 1a: The custom dual-mode laminar flow ion source setup

Setup	Length [mm]	Inner diameter [mm]	Ion dwell time [ms]
1	150	5	240
2	85	5	140
3	150	2.5	70
4	85	2.5	50

Table 1: Overview of the different setup modifications; ion dwell times calculated from make-up gas volume flow

Crucial design aspects

- Tightly sealed ionization volume
- Chemically and photo-physically inert matrix gas
- Conical ionization volume inlet
- Asymmetrical make-up gas inlet
  - ➢ Vortex inside ionization volume for higher ionization efficiency
- Injection of the GC flow into the major make-up gas flow

  (The concept of the ionization volume inlet is based on the GC-APPI source presented by Kersten et al. in 2014 [3])
- Use of non outgassing materials
- Controlled operation temperature up to 300 °C

CFD Simulations

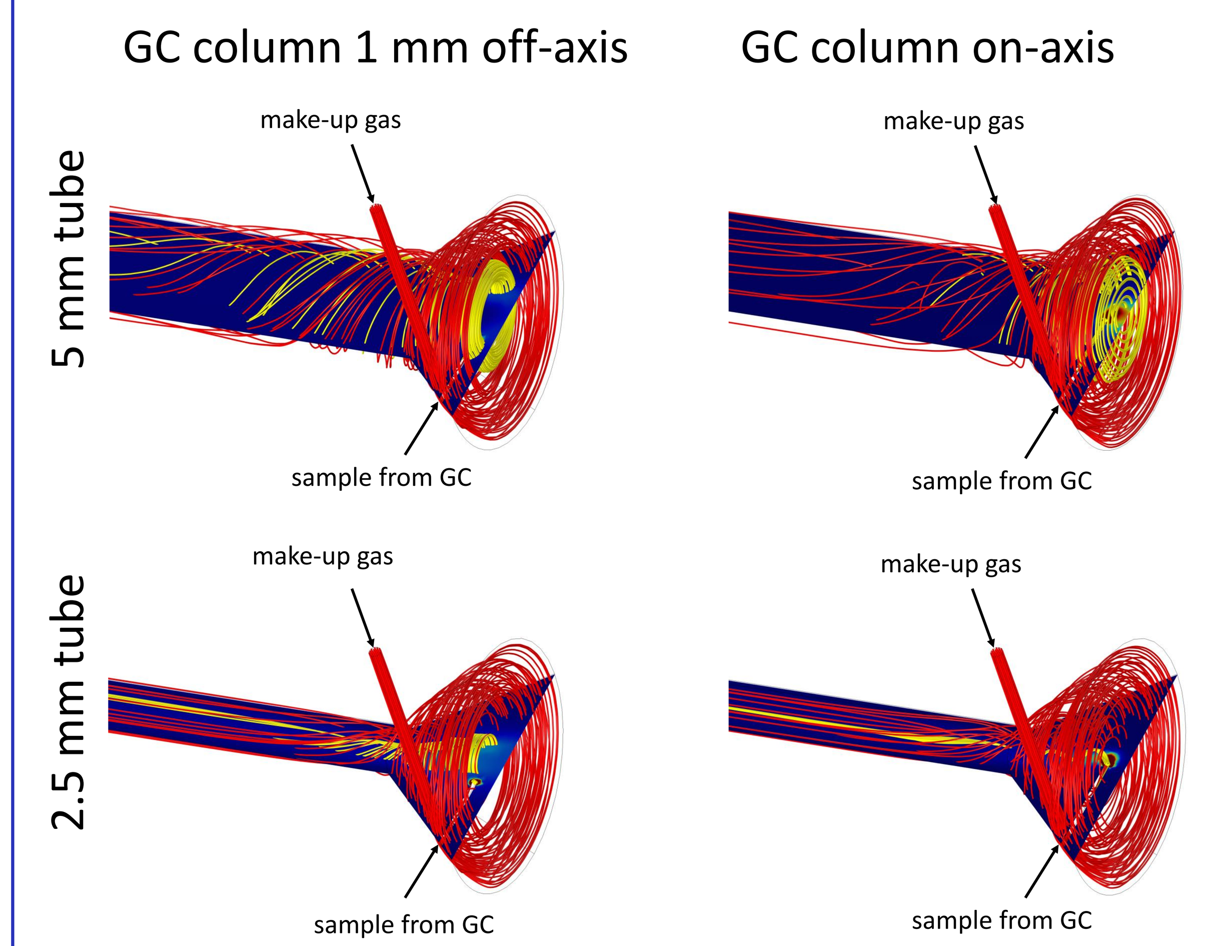

Figure 2a: CFD simulation of the ionization volume inlet. Make-up gas flow 760 mL/min; GC column flow 2 mL/min. The red flow lines indicate the make up gas flow, the yellow flow lines indicate the GC column effluent

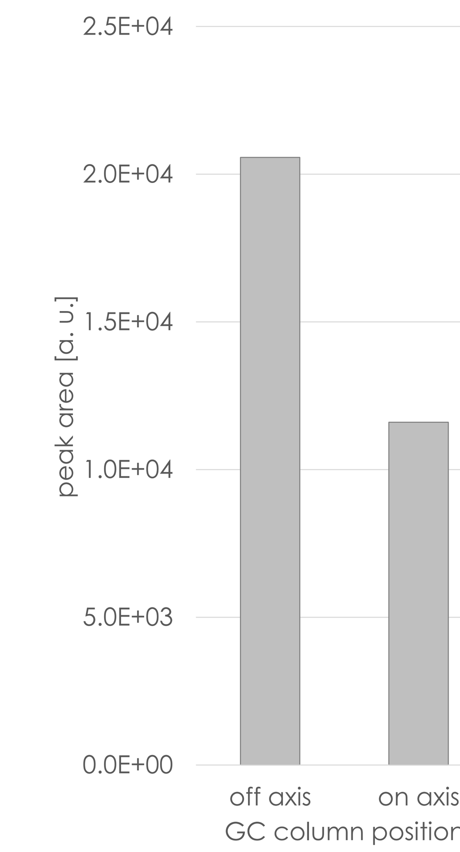

Figure 2b: Variation of GC column position for setup 1, APPI. 100 pg/µL naphthalene

Conclusions

- 24/7 heating of all setups at 300 °C for several weeks without loss of performance
- GC measurements reveal a high level of linearity in the pg on-column range
- Transfer of the analytes into the MS without significant loss of separation performance
  - ➢ Peak widths down to 0.7 s (FWHM)
- Simple variation of geometric parameters
- Ion source is interfaced to MS control software

APLI Mode:

- As expected, a larger inner diameter and a longer dwell time leads to a better ionization efficiency and gain in sensitivity
- Limit of detection for PAHs down to the fg range

APPI Mode:

- Setup 1 shows a significant decrease in sensitivity compared to setup 2. The longer tube length presumably leads to more pronounced ion-wall losses
- Gain of sensitivity with longer dwell times in the conical ionization inlet (vortex)
- The simulations show a longer residence time in the cone with 5 mm tube diameter. These results are in accordance with the measurements
- A GC column position slightly off axis leads to an increased ionization efficiency

Methods

MS	amaZon speed ETD, Bruker Daltonik GmbH
Ion Source	Custom-made dual-mode laminar flow ion source
Radiation Source	APPI: VUV Kr discharge RF lamp emitting 10.0 and 10.6 eV photons (Syagen, Morfo) APLI: ATL Atlex KrF*-excimer laser (248 nm, 5 mJ, 50 Hz)
GC	GC 7890 A, Agilent Technologies Inc.
Transfer Line	Custom temperature-controlled GC-transfer line
Samples	EPA 8270 LCS Mix 1, Supelco 78 compounds Dilutions: 1 fg/µL – 100 pg/µL Naphthalene diluted in n-hexane Dilutions: 10 fg/µL – 1 ng/µL
GC injection	Split ratio 1/100 (already included in the concentration values) Injection volume 1 µL
Make-up gas	Nitrogen 5.0, Messer Industriegase GmbH Flow rate: 760 mL/min
CFD simulations	Comsol Multiphysics 4.4

Performance

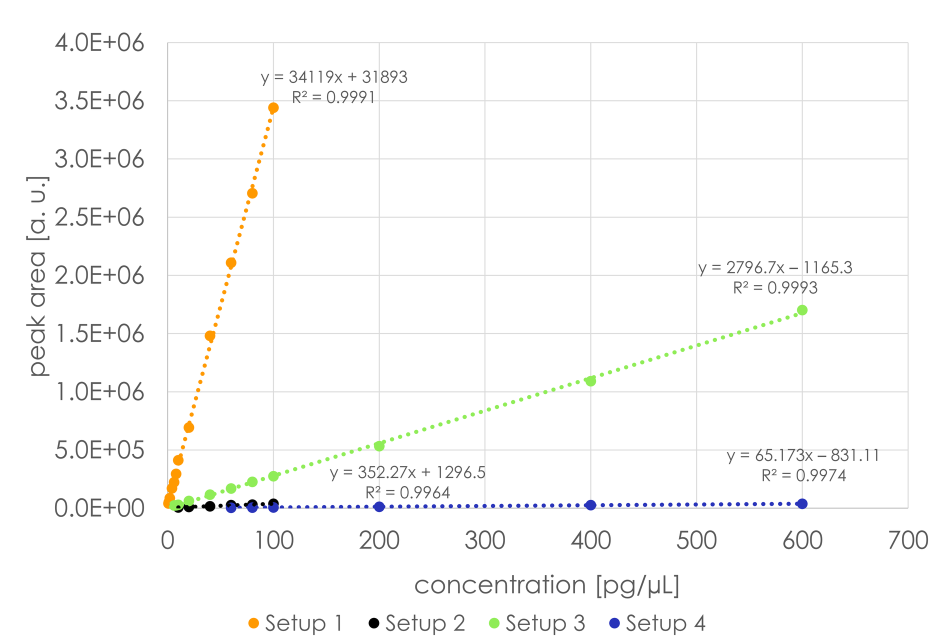

Figure 3a: Linear ranges for the four modifications of the laminar flow ion source setup in APLI mode for naphthalene (m/z 128).

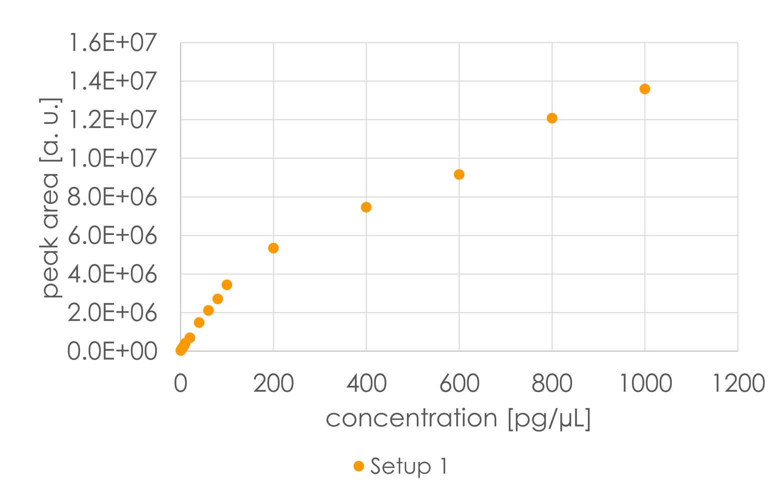

Figure 3b: Dilution series of naphthalene 0.8 – 1000 pg/µL (m/z 128). Setup 1, APLI

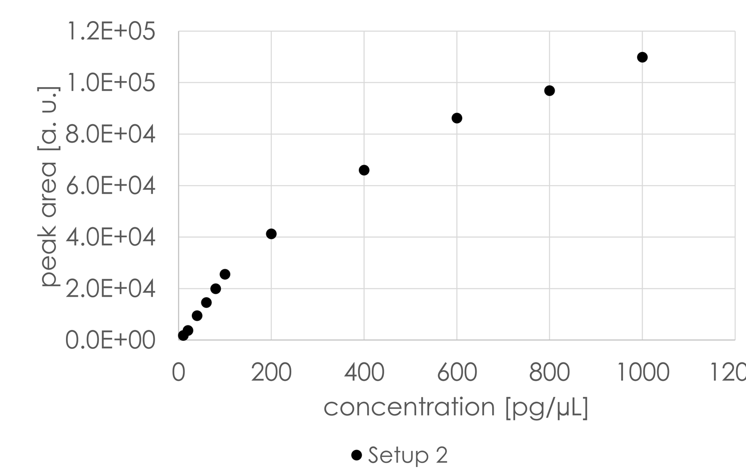

Figure 3d: Dilution series of naphthalene 0.8 – 1000 pg/µL (m/z 128). Setup 1, APPI

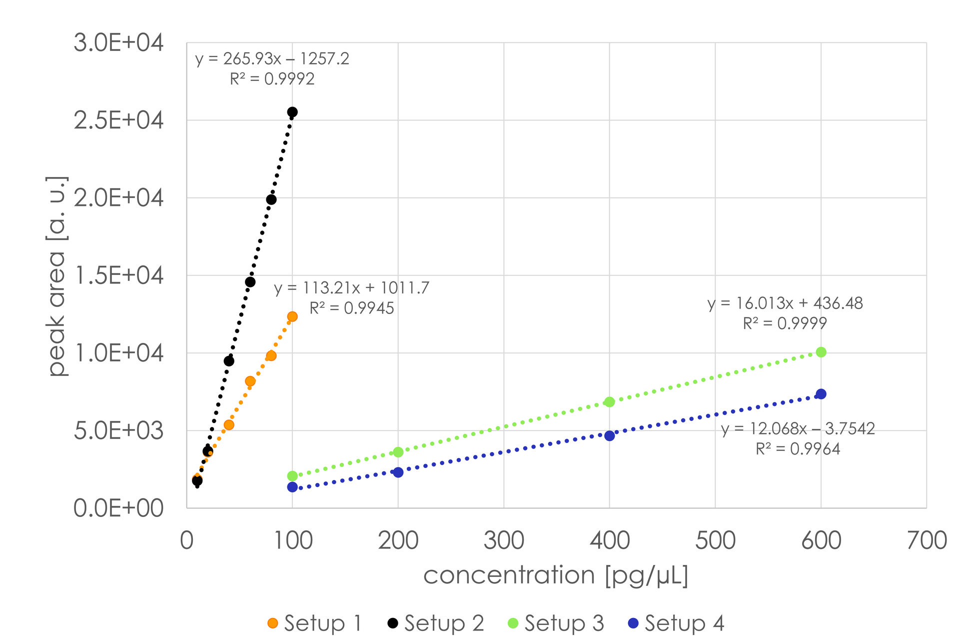

Figure 3e: Determination of the linear ranges of the four versions of the laminar flow ion source setup, APPI, for naphthalene (m/z 128)

Note: The pronounced signal deviation around 200 pg/µL is observed in all four setups and for both ionization methods. The reasons for this behavior are yet unknown and subject to current investigations.

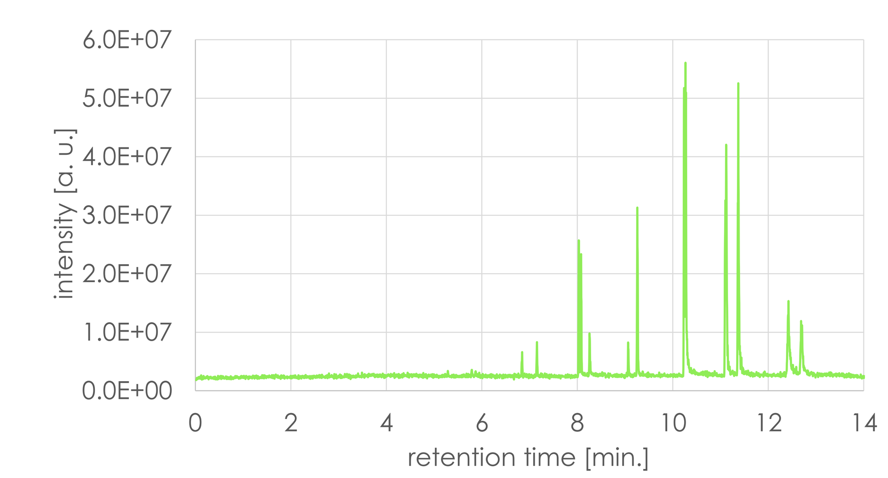

Figure 3c: Chromatogram of the EPA 8270 LCS Mix 1 (100 pg/µL). Ion source setup 3, APLI mode.

APLI					APPI			
Peak width (FWHM) [s]	Limit of Detection* [pg/µL]	Slope	Linear range** [pg/µL]	Setup	Linear range** [pg/µL]	Slope	Limit of Detection* [pg/µL]	Peak width (FWHM) [s]
0.8 – 1	0.6	34119	0.8 – 100	1	10 – 100	113	8	1 – 1.3
0.7 – 1.1	6	35	10 – 100	2	10 – 100	265	6	0.8 – 1.1
0.8 – 1.3	3	2797	6 – 600	3	100 – 600	16	60	0.8 – 1.3
0.8 – 1.3	40	65	60 – 600	4	100 – 600	12	80	0.7 – 1.3

* S/N = 3 ** for a dilution series of Naphthalene in n-hexane

Table 2: Analytical performance of the four laminar flow ion source versions for APLI- and APPI-GC-MS.

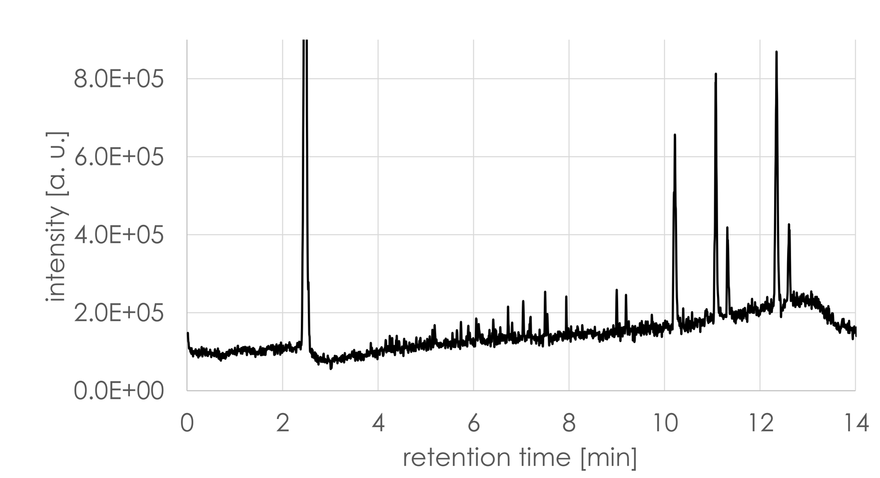

Figure 3f: Chromatogram of the EPA 8270 LCS Mix 1 (100 pg/µL). Setup 1, APPI mode.

Literature

[1] Barnes, I.; Kersten, H.; Wissdorf, W.; Pöhler, T.; Hönen, H.; Klee, S.; Brockmann, K. J.; Benter, T., Novel laminar flow ion sources for LC- and GC-API MS, *58th ASMS Conference on Mass Spectrometry and allied topics*, Salt Lake City, UT, USA (**2010**)

[2] Barnes, I.; Kersten, H.; Bejan, J.; Benter, T., In- situ MS monitoring of atmospheric degradation product studies of aromatic hydrocarbons with APPI and APLI, *59th ASMS Conference on Mass Spectrometry and allied topics*, Denver, CO, USA (**2011**)

[3] Kersten, H.; Haberer, K.; Kroll, K.; Benter, T., Progress in the development of a GC-APPI source with femto gram sensitivity, *62nd ASMS Conference on Mass Spectrometry and allied topics*, Baltimore MD, USA (**2014**)

Acknowledgement

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