Progress in the development of a GC-APPI source with femto-gram sensitivity

Hendrik Kersten; Kirsten Haberer; Kai Kroll; Faezeh Dousty; Thorsten Benter

Physical & Theoretical Chemistry
Wuppertal, Germany
Institute for Pure and Applied Mass Spectrometry

Introduction

ASMS 2013:
At the *ASMS conference 2013* we introduced a new approach for a GC-APPI interface attached to a high resolution Exactive™ Orbitrap mass spectrometer [1]. The principal idea of the source design was rather simple: A tightly sealed ionization volume and a chemically and photo-physically inert matrix. In combination with the well defined sample injection via the GC this concept is in full accord with the necessary prerequisites for pure and efficient direct photoionization.

ASMS 2014:
Details of a significantly improved GC-APPI interface are presented.

Methods

mass spectrometer

Exactive™ Orbitrap, Thermo Scientific

- sampling rate: 10 Hz
- resolution: 10 000
- scan range: 50 – 1000 *m/z*

custom ion source

nitrogen with low ppbV impurity level

- flat gasket sealing (Sigraflex®, A.W. Schultze, Geesthacht, Germany)
- 400 W heater and power supply
- ion source material Invar36
- cone coating: electrochemical gold layer or PVD double layer of Al and MgF_2
- Syagen Kr RF lamp with power supply
- Omega® CC High Temperature Cement
- inorganic coating: Ipseal Khaki (Indestructible Paint, Ltd.)

gas supply

nitrogen with low ppbV impurity level

- compressed gas cylinder
- Vici Metronics N_2 purifier
- mass flow controller (Bronkhorst)

gas chromatograph

GC 450 series, Thermo Scientific

- column: TR-Dioxin 5MS (30 m x 0.25 mm ID x 0.1 µ)
- GC transfer line: 325°C
- Helium (99.999 %) with 1.5 ml/min

samples

EPA 8270 LCS Mix 1, Supelco

- dilutions: 50 fg/µl – 1 ng/µl

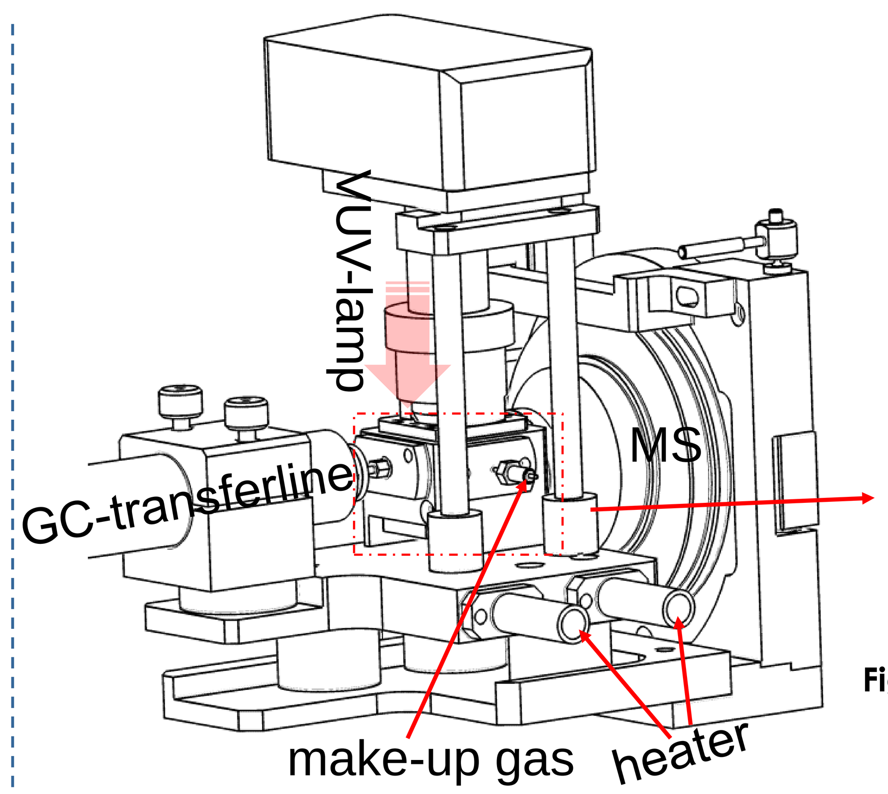
CFD simulations

Autodesk Simulation CFD

Current Research Setup

central design aspects

- gas-tight ionization volume
- non-outgassing materials
- electrical isolation (DC capillary)
- operation up to 350°C
- no cold spots
- injection of the GC flow into the major make-up gas flow
- photon flux and analyte density overlap
- balance between irradiation time and peak width



ion source enclosure

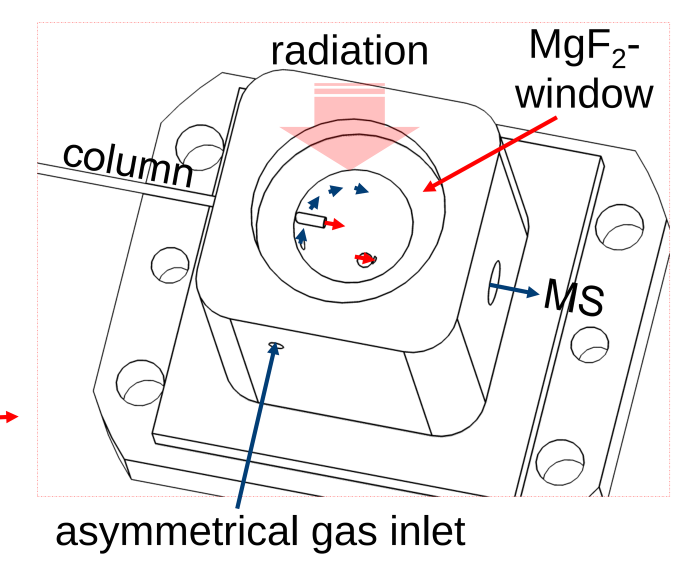


Figure 1: Schematic of the entire GC-API interface (left) and close up of the ion source enclosure with gas flows and radiation entrance as indicated (top).

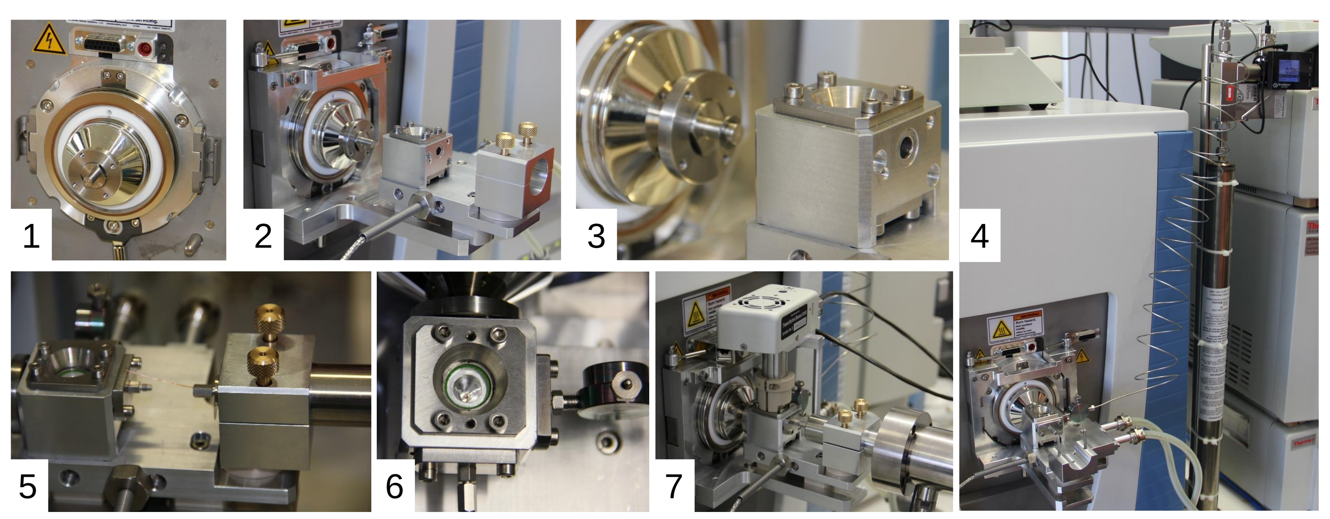
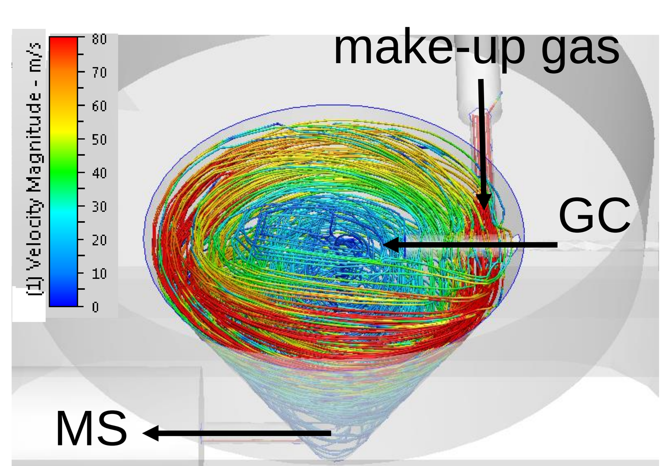


Figure 2: Step-by-step source setup
1) **custom stainless steel capillary modified with a gas-tight connector to the ion source**
2) **mounting of the electrically isolated heater table, incl. ion source and GC-transferline mount**
3) **custom Sigraflex® flat gaskets for each connection**
4) **N_2 purifier and mass flow controller**
5) **insertion of GC transfer line with mica insulator to the ion source; column adjusted and sealed with standard ferrule**
6) **Invar36 ion source, cone polished and coated (Au or Al/MgF_2); optical access through MgF_2 window, sealed with cement and a protective inorganic coating (green ring)**
7) **commercial APPI lamp modified with a custom lamp holder, placed on top of the ion source**

Currently three setups are in use (**University of Wuppertal**, **ThermoScientific Bremen**, **University of Essen-Duisburg**).

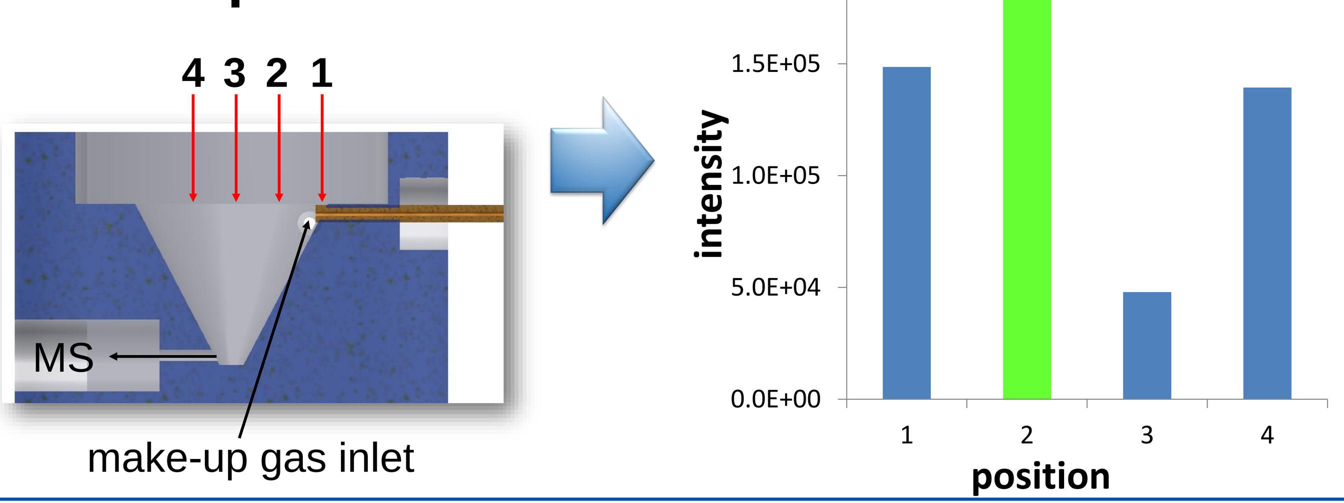
Flow Dynamics



- conical ionization volume
- asymmetrical make-up gas inlet
- **vortex** inside ionization volume
- anisotropic velocity flow
- GC-flow into the vortex
- ~ 20 ms residence time
- no dead volume
- no GC peak broadening

Figure 3: CFD calculation for 850 ml/min make-up gas, 1.5 ml/min GC-column flow and 1050 mbar outlet pressure.

column position



- sensitive to the vortex flow
- sensitive to optimal irradiation

Figure 4: (Far left) Investigation of four different column positions in the ionization volume. (Left) Intensity distribution for naphthalene as a function of the column position.

First Idea of an Ion Max Compatible Version

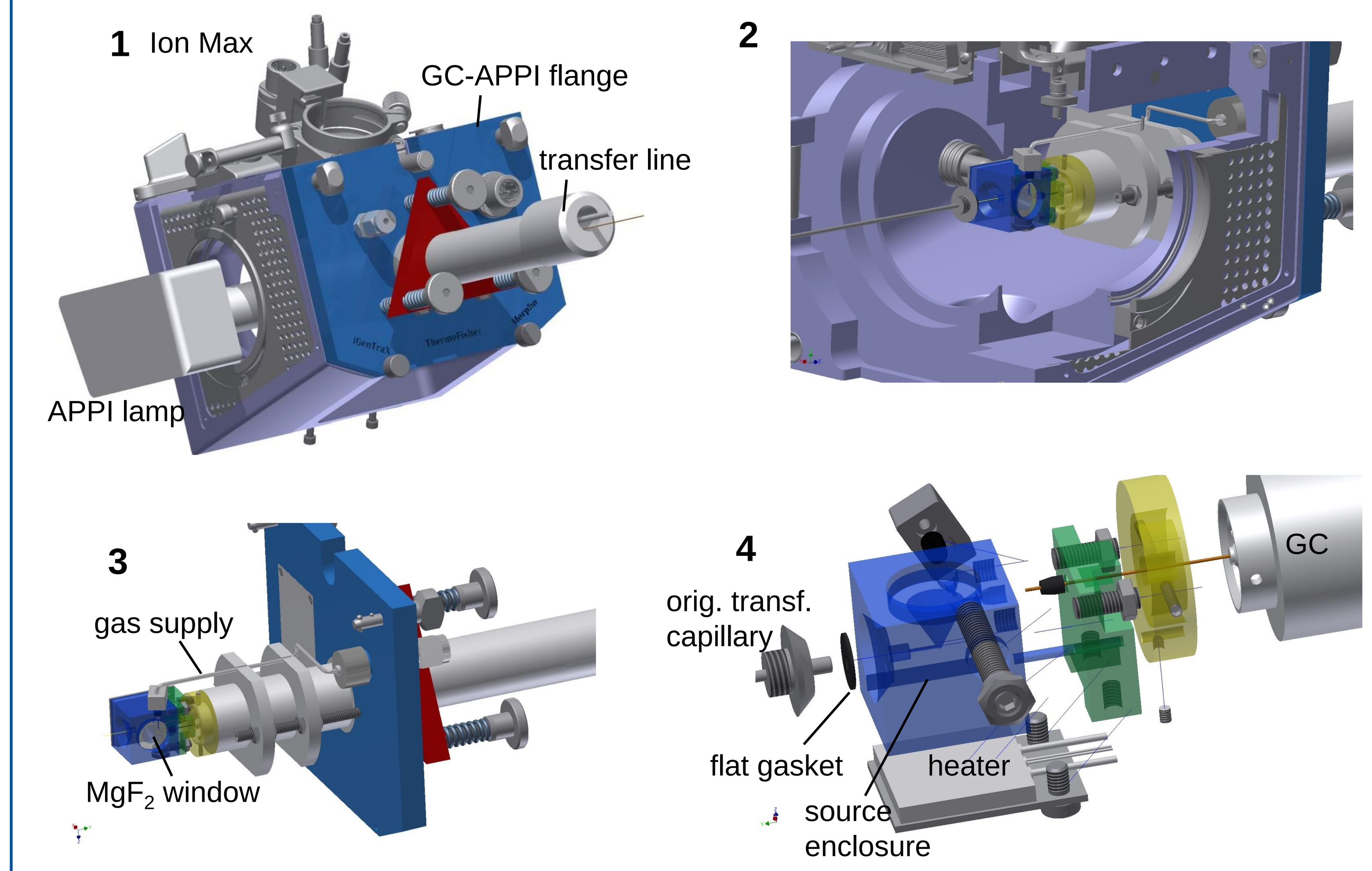


Figure 6: (1) GC-APPI installed within the Ion Max housing, (2) section view of the Ion Max housing with original transfer capillary, (3) GC-APPI flange and (4) explosive drawing of the ion source.

Sample Irradiation

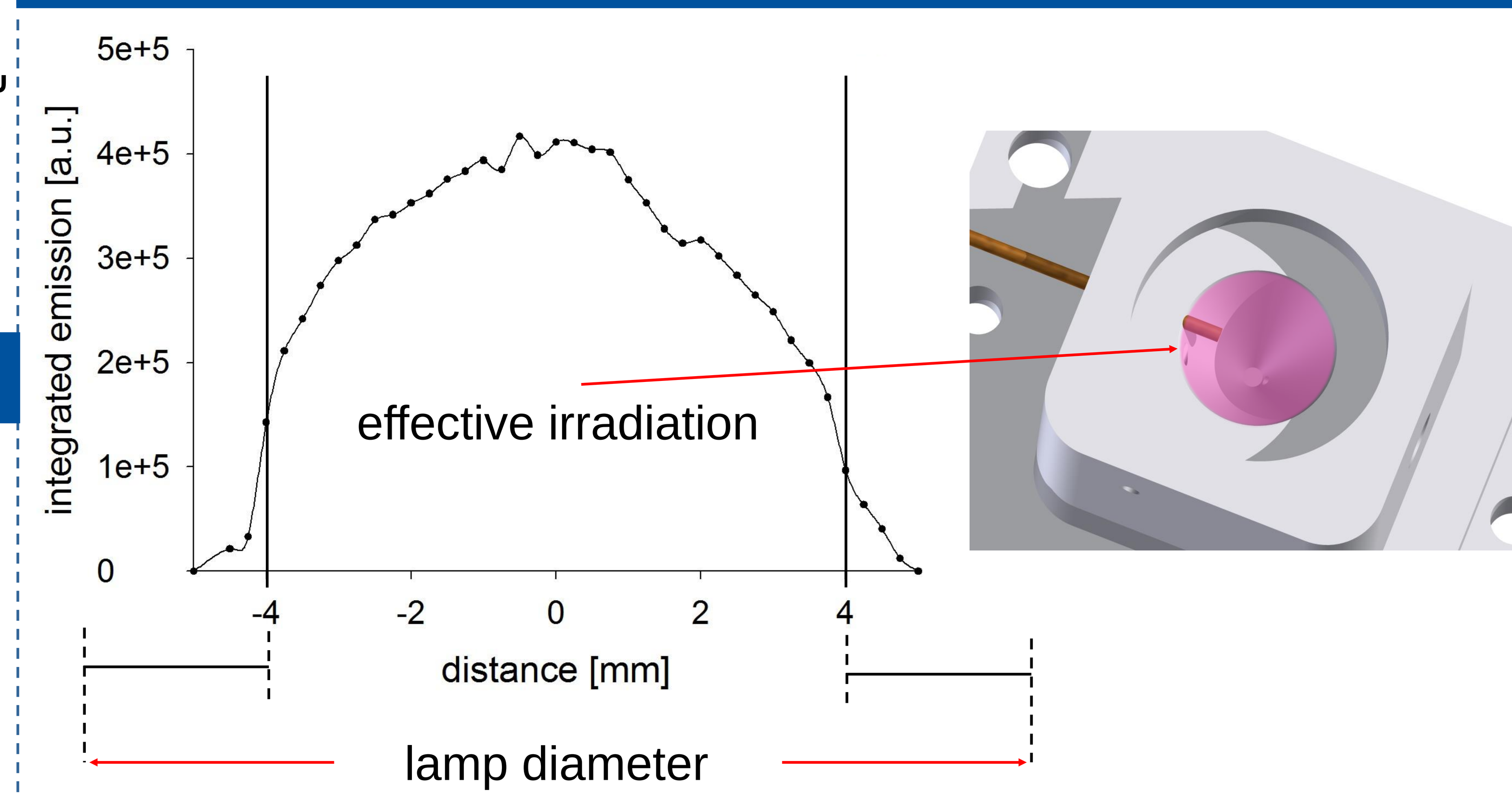


Figure 5: (top) Plot of the total integrated intensity of 10.0 and 10.6 eV photons emitted by the Kr RF lamp as a function of the lamp window position [2]. (top right) Schematic of the optimized cone geometry matching the effective irradiated area.

- optimized overlap between photon flux and analyte density
- high-gloss polished cone
- electrochemically gold coated (*version at Thermo facility, Bremen*)

or

- PVD double coating of Aluminum and MgF_2, with up to 80% reflectivity at 120 nm wavelength [3]
(*version recently installed at the University of Essen-Duisburg*)

Conclusions

improvements:

- O-rings replaced by Sigraflex® flat gaskets
- cemented MgF_2 window
- ion source enclosure made of Invar36
- conical ionization volume and asymmetrical make-up gas inlet maintain a vortex flow pattern
- GC-flow injection into vortex core
- carefully balanced system of irradiation time, convectional and diffusive peak broadening, and radiation overlap with the eluent
- careful surface finish of the ion source cone

current performance:

- 24/7 heating of the entire setup at 325°C for several weeks
- no background except from column bleeding starting at around 280°C
- peak width down to 0.6 s (FWHM)
- lower limit of detection in the fg range

see also:

A.C. Peterson et al. 62nd ASMS Conf., Baltimore, MD, 2014, MOD pm 4:10.

T. Benter et al., 62nd ASMS Conf., Baltimore, MD, 2014, MP 315.

T. Kauppila et al., 62nd ASMS Conf., Baltimore, MD, 2014, MP 299.

Literature

[1] H. Kersten, K. Kroll, K. Haberer, T. Benter, GC- and the Exactive – Development of an API Interface *Proceedings of the 61st ASMS Conference on Mass Spectrometry and Allied Topics, Minneapolis, MN, USA (**June 2013**)*

[2] Vaikkinen, A.; Haapala, M.; Kersten, H.; Benter, T.; Kostiainen, R.; Kauppila, T. J.: Comparison of Direct and Alternating Current Vacuum Ultraviolet Lamps in Atmospheric Pressure Photoionization. *Analytical Chemistry.* **84**, 1408-1415

[3] Hass, G.; Tousey, R.: Reflecting Coatings for the Extreme Ultraviolet. *Journal of the Optical Society of America.* **49**, 593-601 (1959).

Acknowledgement

Thermo Scientific is acknowledged for supplying the Exactive, the GC and the GC column.