GC-MS Performance of a Laminar Flow API Source Including APCI/PAPI, APLI and CAPI for Multi-Mode

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Introduction

State of the art: Laminar Flow Atmospheric Pressure Ion Sources (LFIS) [1]:

- Efficient ion transmission was demonstrated by numerical simulations and experiments (continuous gas phase sampling)
- Mass spectrometer sampling inlet determined flow results in laminar velocity profile
- Compared with classical API sources, significant increase of the dynamic ion acceptance volume (DIAV) for APLI is observed (**See also Session TP04; Poster #068)**
  - Efficient irradiation of the sample flow
- Controlled heating of the gas flow
- Easy cleaning of the source enclosure
- Controlled operation conditions
  - gas flows, gas temperature, primary ionization region, ion-molecule reaction region

Challenge:

All previous experiments were realized with continuous gas phase sampling.

- Determination of the analytical performance of an LFIS coupled to a gas chromatographic (GC) stage using a variety of ionization methods (APLI, APCI, Capillary Photoionization-CAPI)

Workflow:

- **Realization of GC-LFIS hyphenation**
- **Investigation on the chromatographic separation performance**
- **Investigations on the performance of different ionization methods in a true multi-mode operating system**

Methods

Experimental Setup

MS: Bruker micrOTOF

Ion Source: Home built Multi Mode Laminar Flow Ion Source

Work Function Determination

Radiation Sources:
1. ATL ATLEX 300 SI, KrF*;
   λ= 248 nm
   5 mJ/pulse
   4 … 8 ns pulse duration
   100 Hz pulse frequency
2. Home built spark discharge lamp

Reactant gas Source: Home built tubular APCI Source

Numerical Calculations

Software: Comsol Multiphysics v4.0a / v4.1

Ionization Stages

Tubular APCI

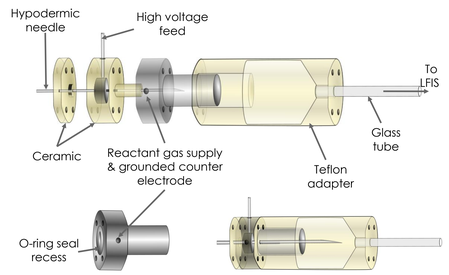

Figure 1) Schematic of the novel tubular APCI

- High yields of primary ions with an experimentally optimized geometry
  - → The electrical field and laminar gas flow are optimized for the introduction of primary ions into the reaction area for secondary ionization of the analyte **(cf. Figure 2)**
- Minimized perturbation of electrical fields at the inlet to the MS
- Optimized discharge conditions
  - → Separation of the corona region from the analyte flow
  - → Temperature and flow control
  - → Addition of water (ppmV final mixing ratios) in a controlled fashion
- Possible addition of reactant gases (e.g. He) into corona-discharge region through the hypodermic needle

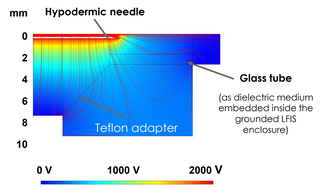

Figure 2) Electrical field inside the optimized LFIS geometry

Experimental Setup

GC-LFIS-Coupling to the MS equipped with APLI, APCI and CAPI

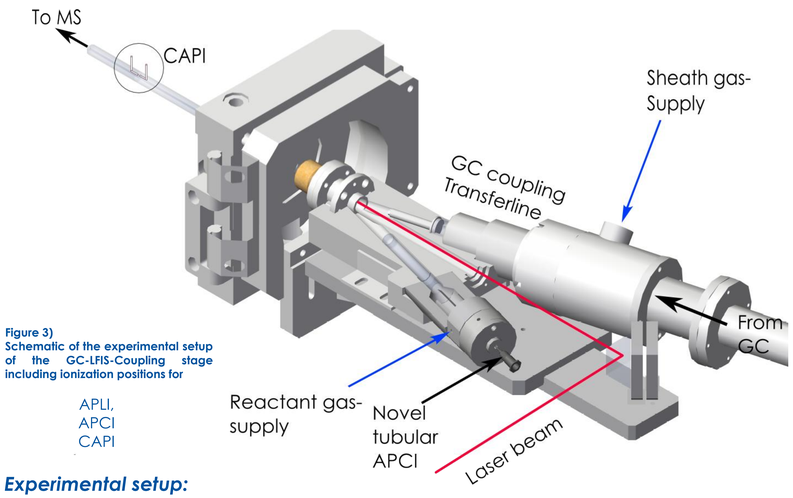

Figure 3) Schematic of the experimental setup of the GC-LFIS-Coupling stage including ionization positions for

APLI,
APCI
CAPI

Experimental setup:

LFIS:

- Temperature controlled metal block including three tubular feeds
  - Left feed: coupling of tubular APCI/ PAPI
  - Center feed: coaxial guidance of the laser beam
  - Right feed: introduction of analyte (coupling of the transferline (TFL) coming from GC)
- Intersection of the feeds at 10° angle
- Each feed can be used for flow control
- Overall flow is determined by the MS inlet port pumping speed

GC-Coupling:

- Redesign of the commercially available transferline (TFL)[4] for the Bruker Multi Purpose Atmospheric Pressure Ion Source (MPIS) [2]
- Extension of the heated GC column enclosure close to the intersection of the LFIS feeds prevents analyte loss at the walls and peak broadening
- The laminar sheath gas flow is accelerated by constricting the gas transfer region
- Depending on the individual flow settings the analyte dwell time in the gas transfer region is on the order of 200 - 300 ms

Ionization Stages

Operational

APLI [3]

- Selective photoionization for polyaromatic hydrocarbons (PAHs)
- More efficient irradiation of the sample flow with APLI in the LFIS as compared to classical API Sources with orthogonal laser beam delivery:
  1. The irradiated volume per laser pulse is at least four times larger as compared to the classical orthogonal geometry
  2. Within the travel time of ~ 200 ms from the TFL exit to the MS sampling orifice analyte molecules are at least irradiated with 15 laser pulses (@ 100 Hz rep. rate; 0.9 L/min flow rate)

CAPI[1] **(See also Session MP01; Poster #020)**

- Spark discharge lamp embedded windowless in the transfer capillary
- High photon flux on a small illuminated area
- Strongly reduced dwell time of ions in the collision region reduces the extent of ion transformation processes in favor of a kinetically controlled ion distribution
- High temporal and spatial discharge stability characteristics stabilize the analytical performance

Work in Progress:

PAPI **(See also Session MP01; Poster #004, 006)**

APPI/ DA-APPI

DA-APLI

Conclusions

GC-coupling

→ Optimized TFL ensures the transfer of the analytes into the LFIS without significant loss of separation performance

Analytical performance of the LFIS

→ The results presented demonstrate that the analyte dwell time in the LFIS does not lead to noticeable GC peak broadening

→ No noticeable memory effects

→ MS-determined flow
  - Upstream gas flow control is essential

Tubular APCI

→ Separation of the discharge area and the analyte flow leads to:
  - Controlled, selective, and efficient ionization
  - Stable discharge conditions

→ Perturbing electrical fields at the inlet to the MS are virtually absent; the operational parameters of the corona discharge do thus not impact on the ion sampling efficiency

Future aspects

- Optimization of operational conditions and hardware components of the GC-coupling
- Optimization of the APCI conditions:
  - Water concentration
  - Reactant gas species
  - Gas flows
  - Corona needle material

Results

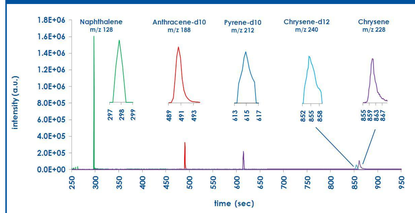

Figure 4) Gas chromatogram of five polyaromatic hydrocarbons (PAHs) as observed in a GC-LFIS-APLI-TOF MS experiment

Table 1) List of analytes in the PAH-mixture (cf Fig. 4)

analyte	concentration [µg/L]	m/z
naphthalene	1000	128
anthracene-d10	10	188
pyrene-d10	5	212
chrysene	2.5	228
chrysene-d12	2.5	240

Experimental results:

- The intention of the present work is to provide basic information on the LFIS-GC coupling, AP-GC performance and the performance of the different ionization methods, including the novel tubular APCI
- The results reported here are preliminary. A thorough in-depth investigation of the overall performance is underway

Analytical performance of the LFIS

- Recorded chromatograms show **high separation performance.** Baseline separation of chrysene and its deuterated analogue is readily achieved
- Peak shapes are essentially **symmetric** with a **width of a few seconds**
- The chromatograms determined with the LFIS show **no significant peak broadening or tailing**
  - Nearly identical peak shapes were obtained in experiments by direct injection from the GC into the transfer capillary

CAPI coupled with the GC-LFIS-system

- No adverse effect on GC separation observed
- Mainly $[M+H]^+$ formation was observed (> 88 %); $[M-H]^+$ (11 %); $[M]^+$ (0,03 %)
  - The formation of $[M-H]^+$ using CAPI is under investigation and may result from fragmentation of excited states of $[M]^+$

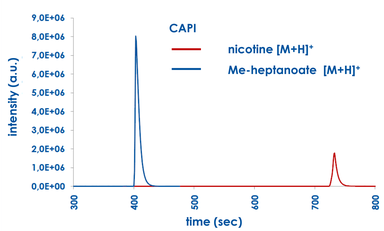

Figure 5) Separation of methyl-heptanoate and nicotine in a GC-LFIS-CAPI-TOF MS experiment

Tubular APCI in the LFIS

- No adverse effect on GC separation performance observed
- **ONLY $[M+H]^+$ is observed**
  - Spatial separation of discharge and analyte flow minimizes transformation of the analyte within the primary discharge area, e.g. oxidation.
  - Analyte ions are formed by chemical ionization , i.e. proton transfer, only
  - Selectivity for analytes with appropriate gas phase basicity

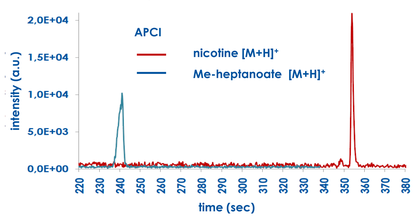

Figure 6) Separation of methyl-heptanoate and nicotine in a GC-LFIS-APCI-TOF MS experiment

Literature

1) Kersten, H. *Development of an Atmospheric Pressure Ionization source for in situ monitoring of degradation products of atmospherically relevant volatile organic compounds*, Dissertation, Bergische Universität Wuppertal, Wuppertal, **2011**; urn:nbn:de:hbz:468-20110418-092806-6
2) Schiewek, R.; Lorenz, M.; Giese, R.; Brockmann, K.; Benter, T.; Gäb, S.; Schmitz, O. J. *Development of a multi-purpose ionsource for LC-MS and GC-API MS*, Anal. Bioanal. Chem. **2008, 392, 87-96.**
3) Constapel, M.; Schellenträger, M.; Schmitz, O. J.; Gäb, S.; Brockmann, K. J.; Giese, R.; Benter, Th. Rapid Commun. Mass Spectrom.**2005, 19, 326-336.**
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