Ultra-sensitive Gas Chromatographic Analysis of PAHs with a Temperature-controlled APLI-source

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Introduction

Atmospheric pressure laser ionization (APLI) coupled to a mass spectrometer is a very selective and particularly ultra-sensitive method to ionize and analyze PAHs via liquid or gas chromatography (LC resp. GC)[1-3]. It also has the advantage that non-aromatic analytes become efficiently ionizable after derivatization with an APLI marker, i.e., an efficiently ionizable PAH-group[4].

The sensitivity exceeds all known ionization techniques for PAHs such as atmospheric pressure photoionization (APPI), chemical ion-ization (CI) or medium pressure laser ion-ization (MPLI)[3].

Our enhanced home-built multi purpose ion source (MPIS) gives the opportunity to switch swiftly between GC and LC coupling stages to the same MS equipped with various ionization methods including APLI, APCI, and APPI.

Depending on the separation performance some HPLC applications use an eluent with high water content and/or apply high flow rates [5]. To prevent solvent condensation it is necessary to heat the source enclosure in a controlled fashion. Elevating the temperature of the ion source prevents deposition of non-ionized compounds thus significantly decreasing the background signal.

As an ultra-sensitive method GC-APLI is susceptible to a number of critical operational parameters (e.g., sheath gas or dry gas flows), to the mass spectrometer inlet design (spray shield and capillary cap geometries) and, in particular, to electrical field gradients. Even modest contaminations in the upstream GC injector system cause strong background signals in APLI. A helpful feature to prevent contamination in the injector system is an activated carbon filter mounted upstream in the carrier gas line.

Methods

Experimental Setup

MS:	oaTOF MS (micrOTOF, Bruker Daltonics, Bremen, Germany)
Ion Source:	home-built temperature-controlled multipurpose ion source (TC-MPIS)
Transferline:	home-built temperature-controlled GC-transfer line
Laser System	excimer-laser (KrF, 248 nm) (ATLEX 300 SI, ATL, Wermelskirchen, Germany)
Analyte Delivery:	HPLC-pump (L-6200 A, Merck-Hitachi, Tokyo, Japan) or gas chromatograph (GC 7890 A Agilent Technologies Inc., Shanghai, China)

Temperature-controlled multi purpose ion-source (TC-MPIS)

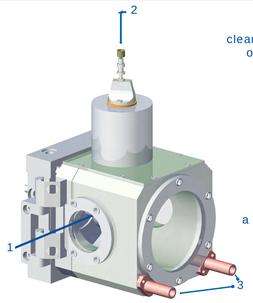


Figure 1) Schematic drawing of the TC-MPIS in LC-APLI-mode
1 - laser beam,
2 - PEEK™- connector to LC,
3 - heating cartridges

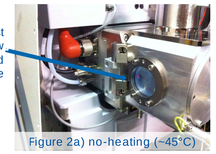


Figure 2a) no-heating (~45°C)

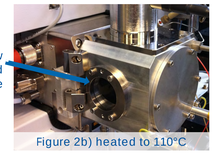


Figure 2b) heated to 110°C

Figures 2a / 2b) TC-MPIS in LC-mode running a 90% water-content eluent at 0.75 mL/min flow rate

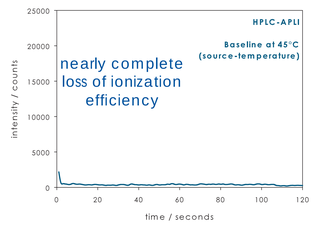


Figure 3a) HPLC-APLI-(TOF)MS baseline (TIC *m/z* 50-300) with condensed water inside the source enclosure

Chromatographic conditions:
source temperature 45°C,
H_2O/MeOH 90/10, flow rate 0.75 mL/min,
KrF excimer laser, rep.rate 100 Hz / 5mJ

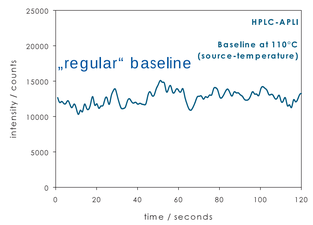


Figure 3b) HPLC-APLI-(TOF)MS baseline (TIC *m/z* 50-300) without any visible condensation inside the source enclosure

Chromatographic conditions:
source temperature 110°C,
H_2O/MeOH 90/10, flow rate 0.75 mL/min,
KrF excimer laser, rep.rate 100 Hz / 5mJ

Running HPLC-APLI with a high water-content eluent (>30%) or at high flow rates (>1 mL/min with 10% water-content) causes condensation inside the cold source enclosure (see figure 2a) and leads to water droplet formation and thus to absorption and diffraction of the laser beam. As a consequence, the available laser energy is considerably lowered. Even background signals are virtually absent; analytes are practically non-detectable. A baseline chromatogram with condensation of water is shown in figure 3a.
To prevent unwanted condensation the TC-MPIS is heated up to 150°C. Figure 2b shows the source running at 110°C, experimental conditions are the same as in 2a. Condensation ceases already at 80 °C, even with 0.75 mL/min (90/10 H_2O/MeOH). Figure 3b shows the baseline chromatogram without any visible condensation at 110°C source temperature.

GC-APLI-(TOF)MS with TC-MPIS

GC-APLI-(TOF)MS is an outstandingly sensitive method to determine polycyclic aromatic compounds. To demonstrate this sensitivity the limit of detection for 16 PAHs was determined (see table 1 and figure 5). The analyzed substances are both, part of the US-EPA-PAH-mixture, and part of the EU-PAH-priority [6] mixture.

To reduce contaminations of the injector unit an activated carbon filter was inserted into the carrier gas line as well as an Siltek™ deactivated quartz glass liner and the Merlin MicroSeal® septa were used.

peak number	compound name	m/z Da	amount on column amol	limit of detection ng/L
1	naphthalene-d_8	136	74	10
2	acenaphthylene-d_8	160	156	25
3	acenaphthene-d_{10}	164	1220	200
4	fluorene-d_{10}	176	142	25
5	phenanthrene-d_{10}	188	n. d.	
6	anthracene-d_{10}	188	13	2,5
7	fluoranthene-d_{10}	212	24	5
8	pyrene-d_{10}	212	9	2
9	benzo[c]fluorene	216	46	10
10	benzo[a]anthracene	228	439	100
11	chrysene-d_{12}	240	2	0,5
12	5-methylchrysene	242	41	10
13	benzo[b]fluoranthene	264	n. d.	
13	benzo[k]fluoranthene	264	n. d.	
14	benzo[a]pyrene-d_{12}	264	57	15
15	indeno[*1,2,3-cd*]pyrene	276	725	200
16	benzo[*ghi*]perylene	276	109	30
17	dibenzo[*a,h*]anthracene	278	180	50
18	dibenzo[*a,l*]pyrene	302	66	20
19	dibenzo[*a,e*]pyrene	302	n. d.	
20	dibenzo[*a,i*]pyrene	302	n. d.	
21	dibenzo[*a,h*]pyrene	302	n. d.	

Table 1) Detection limits and amounts on column determined with GC-APLI-(TOF)MS via 3s-concept (n=2)
n. d. = not determined

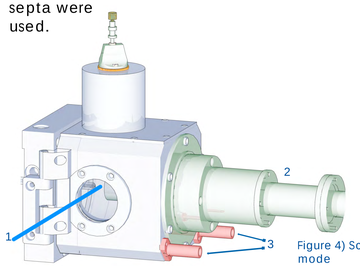


Figure 4) Schematic drawing of the TC-MPIS in GC-APLI-mode
1 - laser beam
2 - temperature controlled GC-transferline
3 – heating cartridges

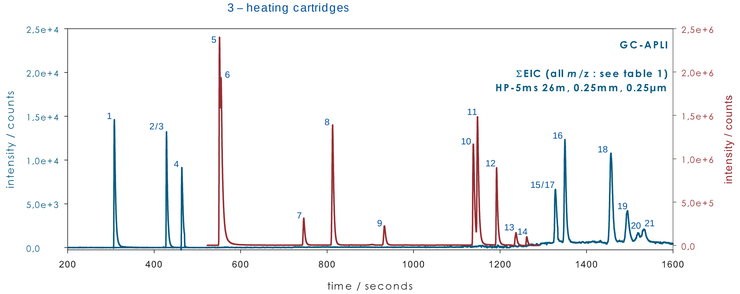


Figure 5) GC-APLI-(TOF)MS analysis of a complex PAH mixture (1 µg/L, inj.vol. 1µL) separated on a 26 m HP-5ms column (0.25 mm, 0.25 µm) with sections of optimized ion transmission parameters. Note: the sum of the EICs for different sections give different TICs as highlighted by the different y-axes scales.

Dry gas and MS inlet design impact

The use of dry gas in liquid chromatography/mass spectrometry (for example in ESI-MS or APLI-MS) is required to prevent water drops entering the first vacuum stage of the mass spectrometer. The impact of dry gas and other critical parameters (electrical fields, geometrical arrangement) of the mass spectrometer inlet design is still under investigation for the MPIS geometry [7].

A coupling of gas chromatography/mass spectrometry, particularly with APLI, is also susceptible to these critical parameters. In particular electrical field gradients in close vicinity of the inlet are critical, as well as the dry gas flow.

A simulation of ion trajectories is given in figure 6 for the standard spray shield arrangement (SSSA) (figure 7). To validate the simulations the impact of the dry gas flow was determined experimentally with one component present (chrysene, 100ng/L, 1µL inj.vol.) in GC-APLI (figure 8a).

For some applications such as GC-APCI the MS inlet geometry is modified, e.g. with a nanoLC end cap (figure 9). The dry gas flow impact was also studied for this arrangement (figures 8b and 10).

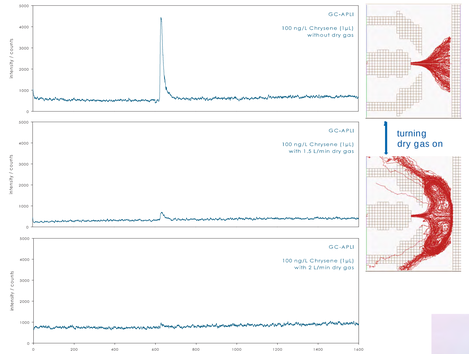
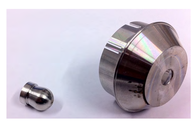


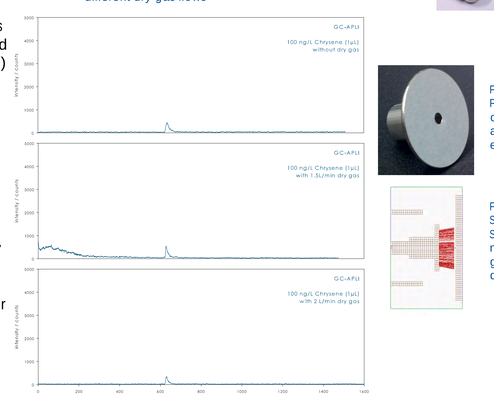
Figure 6 (left)
Simulated SIMION/SDS tracings for a standard spray shield arrangement without (top) and with dry gas (bottom)

For details on the simulation procedure, see poster TP070

Figure 7 (below)
Photograph of a commercially available standard spray shield (right) and capillary cap of type “pacifier” (left)



8a) GC-APLI-(TOF)MS (EIC 228 *m/z*) with standard spray shield arrangement and different dry gas flows



8b) GC-APLI-(TOF)MS (EIC 228 *m/z*) with nanoLC end cap geometry and different dry gas flows

Figure 9)
Photograph of a commercially available nanoLC end cap, D = 22 mm

Figure 10)
Simulated SIMION / SDS tracings for nanoLC end cap geometry without dry gas

Conclusions

A temperature-controlled atmospheric pressure ion source is essential for a stable LC-analysis with high water-content eluents or high eluent flow rates. The temperature-elevated TC-MPIS prevents condensation of water and can be used for both liquid chromatography and gas chromatography.

Gas chromatography in combination with APLI is a very powerful method to analyze PAHs present at extremely low concentrations. It is shown that GC-APLI-(TOF)MS is capable of analyzing PAH mixtures with an outstanding sensitivity and a linearity covering 2 to 3 orders of magnitude.

The sensitivity of GC-APLI is significantly decreased by application of a dry gas flow and/or the nanoLC end cap but shows narrower peaks. The electrical field generated by the nanoLC end cap (figure 10) deflects most of the ions from the MS-inlet. The dry gas flow has no significant effect in combination with the nanoLC end cap arrangement, however, the effect in SSSA is considerable.

Literature

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