

## Improved sensitivity for PAH Analysis with GC/APLI-MS

I.Sanders<sup>1</sup>, T.Arthen-Engeland<sup>1</sup>, T.Zey<sup>1</sup>, A.Holle<sup>2</sup>, C.Baermann<sup>1</sup>, R.Schieweck<sup>2</sup>, O.J.Schmitt<sup>2</sup>, K.J.Brockmann<sup>2</sup>, T.Benter<sup>2</sup>  
<sup>1</sup>Bruker Daltonik GmbH, Bremen, Germany and  
<sup>2</sup>University of Wuppertal, Wuppertal, Germany

### Introduction

Recently Atmospheric Pressure Laser Ionisation (APLI) has been introduced to the existing atmospheric pressure ionisation techniques [1]. APLI is based on resonantly enhanced multi photon ionisation (REMPI) at atmospheric pressure and selectively ionises analytes with longer lifetimes in electronically excited states for the absorption of additional photons.

Differently to APPI (where high energy VUV photons ionise by single photons) the step-wise 2-photon absorption of APLI reduces the ionisation of solvent and matrix molecules and therefore increases analytical selectivity and sensitivity.

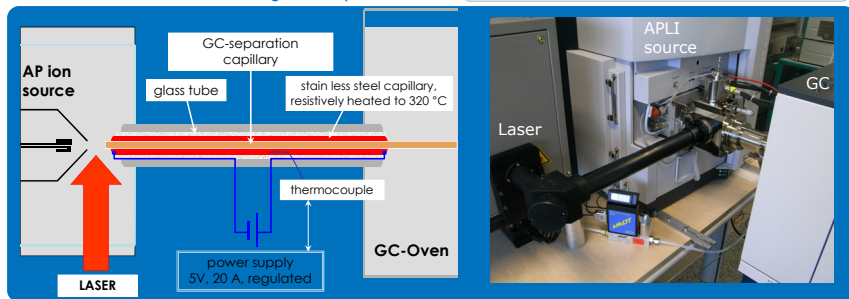
APLI is essentially useful for the trace analysis of polycyclic aromatic hydrocarbons (PAH) which are not easily accessible with standard API techniques, e.g. as ESI nor APCI. It has been demonstrated that GC/APLI-MS has the potential to become a very handy analytical method for the trace analysis of the US and EU priority pollutants PAH [2].

Here we present more data for the validation of the APLI procedure.

### Methods

GC/APLI-MS was performed with an Agilent GC 7890A with a manual split/splitless injector (injection volume always 1 µl). Temperature program for HP-5ms capillary column (30m, 0.25mm ID, 0.25µm) was 40°C(1min)-30°/min-150°-3°/min-238°-2°/min-272°-50°/min-300°C(6.5 min)=58 min, helium at 1 ml/min with constant flow. The GC capillary was directed via the transfer line controlled at 300°C into the APLI source and the effluence was guided by nitrogen sheath gas into the capillary transfer line of the MS. The laser beam was coupled into the free space between end of GC capillary and spray shield [2]. The KrF laser (ATLEX 300SI) was continuously operated at 248 nm, 100 Hz and 10 mJ. Spectra were recorded with a calibrated micrOTOF for hrMS. PAH calibration was performed with Bruker QuantAnalysis.

Fig. 1: Below: scheme and arrangement of APLI source and GC transfer line. Right: sample table



### Results

For the validation of the GC/APLI-MS method a series of analyses in the working range 1 pg/µl up to 500 pg/µl has been performed over several days. Blank runs were introduced to check the specificity of the method: careful cleaning of the syringe avoided memories in the low pg range. For the long term stability several GC/MS runs of a 100 pg/µl standard were compared, showing usual chromatographic resolution.

Run Name	Injection Volume (µl)	Injection Type	Split Ratio	Carrier Gas Flow (ml/min)	Carrier Gas Temp (°C)	Injection Temp (°C)	Transfer Line Temp (°C)	GC Oven Temp (°C)	GC Oven Time (min)	MS Ion Source Temp (°C)	MS Ion Source Time (min)	MS Ion Source Target
APLI20080001	1	Split	1:1	1.0	250	250	300	250	1.00	500	5.00	5000
APLI20080002	1	Split	1:1	1.0	250	250	300	250	1.00	500	5.00	5000
APLI20080003	1	Split	1:1	1.0	250	250	300	250	1.00	500	5.00	5000
APLI20080004	1	Split	1:1	1.0	250	250	300	250	1.00	500	5.00	5000
APLI20080005	1	Split	1:1	1.0	250	250	300	250	1.00	500	5.00	5000
APLI20080006	1	Split	1:1	1.0	250	250	300	250	1.00	500	5.00	5000
APLI20080007	1	Split	1:1	1.0	250	250	300	250	1.00	500	5.00	5000
APLI20080008	1	Split	1:1	1.0	250	250	300	250	1.00	500	5.00	5000
APLI20080009	1	Split	1:1	1.0	250	250	300	250	1.00	500	5.00	5000
APLI20080010	1	Split	1:1	1.0	250	250	300	250	1.00	500	5.00	5000
APLI20080011	1	Split	1:1	1.0	250	250	300	250	1.00	500	5.00	5000
APLI20080012	1	Split	1:1	1.0	250	250	300	250	1.00	500	5.00	5000
APLI20080013	1	Split	1:1	1.0	250	250	300	250	1.00	500	5.00	5000
APLI20080014	1	Split	1:1	1.0	250	250	300	250	1.00	500	5.00	5000
APLI20080015	1	Split	1:1	1.0	250	250	300	250	1.00	500	5.00	5000
APLI20080016	1	Split	1:1	1.0	250	250	300	250	1.00	500	5.00	5000
APLI20080017	1	Split	1:1	1.0	250	250	300	250	1.00	500	5.00	5000
APLI20080018	1	Split	1:1	1.0	250	250	300	250	1.00	500	5.00	5000
APLI20080019	1	Split	1:1	1.0	250	250	300	250	1.00	500	5.00	5000
APLI20080020	1	Split	1:1	1.0	250	250	300	250	1.00	500	5.00	5000
APLI20080021	1	Split	1:1	1.0	250	250	300	250	1.00	500	5.00	5000
APLI20080022	1	Split	1:1	1.0	250	250	300	250	1.00	500	5.00	5000
APLI20080023	1	Split	1:1	1.0	250	250	300	250	1.00	500	5.00	5000
APLI20080024	1	Split	1:1	1.0	250	250	300	250	1.00	500	5.00	5000
APLI20080025	1	Split	1:1	1.0	250	250	300	250	1.00	500	5.00	5000
APLI20080026	1	Split	1:1	1.0	250	250	300	250	1.00	500	5.00	5000
APLI20080027	1	Split	1:1	1.0	250	250	300	250	1.00	500	5.00	5000
APLI20080028	1	Split	1:1	1.0	250	250	300	250	1.00	500	5.00	5000
APLI20080029	1	Split	1:1	1.0	250	250	300	250	1.00	500	5.00	5000
APLI20080030	1	Split	1:1	1.0	250	250	300	250	1.00	500	5.00	5000

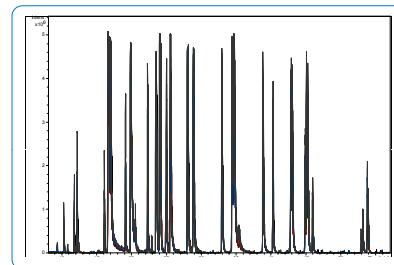


Fig. 3 Reproducibility of five GC/MS runs of the same 100 pg/µl PAH Mix acquired at different days over a period of 1 month (April-May 2008), sample from EA UK containing also alkylated PAH

The working range for the smaller PAH was 1 to 250 pg/µl, for the heavier PAH this was from 1 to 500 pg/µl.

This quantification procedure has also been applied to extracts of fish liver, sea water and wood paint samples.

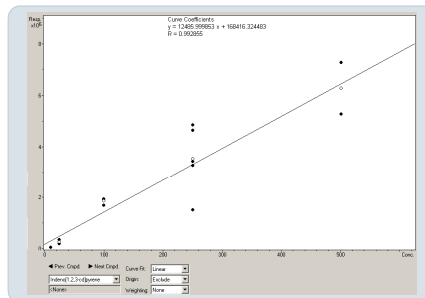


Fig. 4 Calibration Indeno[1,2,3-cd]pyrene in pg/µl

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### Summary

GC/APLI-MS has been evaluated on for its potential as a routine analytical procedure. The KrF laser was working reliably during this one-week sequence of analyses with more than 1.7e+7 shots.

The LOQs were found in the low pg (per µl) range but lower values may be achieved by reducing the background signals and applying an auto-sampler for routine analysis.

APLI-MS has also been coupled to LC for PAH analysis. First results indicate lower chromatographic resolution and a working range at slightly higher concentrations.

### Conclusions

GC/APLI-MS has the potential to become a reliable technique for ultra-trace analysis of PAH:

- working range up to ca. 0.5 ng/µl
- quantification limit down to pg/µl
- specific and reproducible
- standard GC resolution

[1] Constapel et al., Rap. Commun. MS 19 (2005) 326  
 [2] Schiewek et al., Anal. Chem. 79 (2007) 4135