A comparison of the performance of diode pumped solid state lasers and excimer lasers in LC-APLI MS

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Introduction

Experimental as well as computational studies suggest:

Small cross-section laser beams should be suitable for use in LC-APLI MS.

- The quality and magnitude of the detected APLI MS signals mainly depend on:
  - **Ionization cross section** of the neutral analytes
  - **Spatial overlap** of the neutral analyte distribution with the laser irradiated volume
  - **Ion detection efficiency,** i.e. the spatial overlap of the laser irradiated volume with the dynamic ion acceptance volume (DIAV) of the MS
- DIA (distribution of ion acceptance) plots show the impact of sum of the above parameters on the MS signal
- Typical DIAVs are of the order of 0.40 cm^2.
- Beam cross sections of common excimer laser systems for APLI-MS are ~1.0 cm^2
- Diode pumped UV solid state lasers (DPSS) with smaller-than-a-shoe-box dimensions exhibit beam cross sections of ~2 x 10^{-3} cm^2

Are DPSS lasers suitable for APLI?

Methods

Laser systems:	ATL ATLEX 300 SI, KrF* (s. Tab. 1) CryLas FQSS 266-50 Nd:YAG (s. Tab. 1)
Mass analyzer:	Bruker micrOTOF with a multi-purpose ion source (MPIS)
Solution:	10 nM pyrene in methanol
Parameters:	Direct syringe injection via HPLC pump
MS settings:	Nebulizer gas 3000 mbar; 320 °C Dry gas 3.0 L/min; 200 °C Spray shield 0 V Capillary -1000 V Solvent flow 350 µL/min

Background Information

Table 1: Comparison of laser system parameters

	ATLEX 300 (Excimer Laser)	FQSS 266-50 (DPSS Laser)
Wavelength	248 nm	266 nm
Pulse energy	8 mJ	60 µJ
Repetition rate	200 Hz	200 Hz
Pulse width (FWHM)	5 ns	1 ns
Beam profile	rectangular	circular
Beam area	0.7 x 0.7 cm^2	(2.0± 0.8) x 10^{-3} cm^2
Calc. power density	3.3 x 10^6 W · cm^{-2}	3.0 x 10^7 W · cm^{-2}

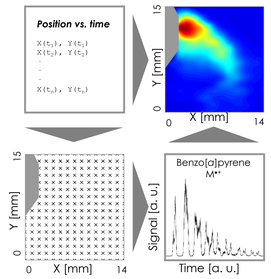


Figure 1: DIA data investigation

Experimental Setup

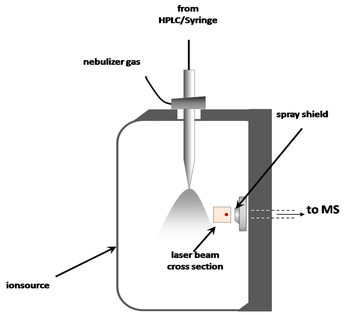


Figure 2: Experimental Overview

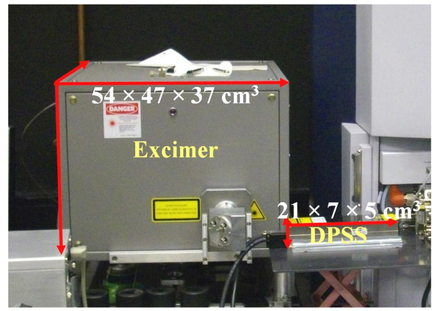


Figure 3: Comparative picture of the two laser systems

Results

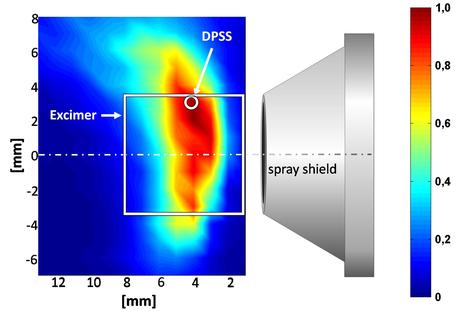


Figure 4: Individual laser positions for maximum signal intensity mapped on a DIA measurement with common ion source parameter settings for LC-APLI MS.

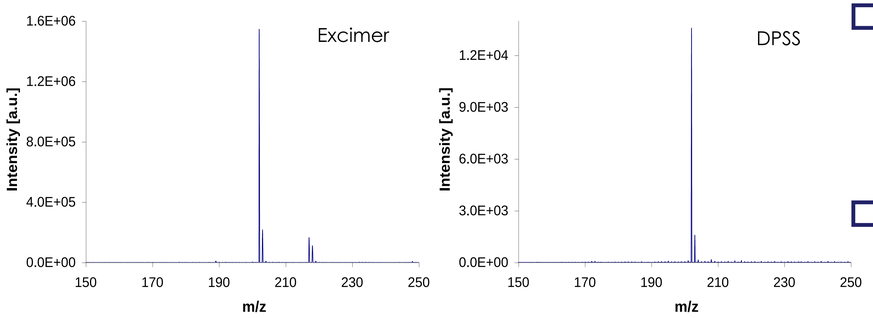


Figure 5: Mass spectra recorded upon irradiating a 0.01 µM pyrene solution in MeOH with the excimer laser (left), and the DPSS laser (right), positioned as shown in Figure 4. The S/N ratio with the DPSS laser is a factor of 70 lower than with the excimer laser, resulting in a 70 times higher detection limit.

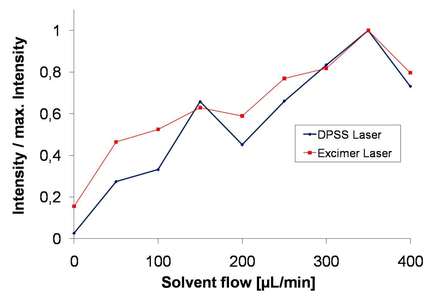
Calculations using DIA data suggest:

Integrated signal intensity of the DPSS irradiated area accounts for **0.65 %** of the integrated area covered by the excimer laser

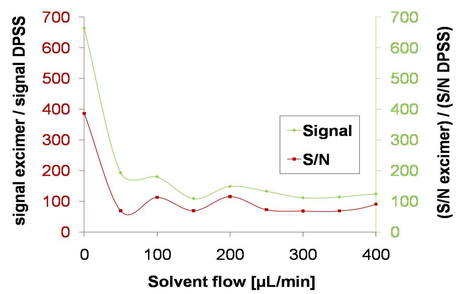
Experiment shows:

1. Maxima of DIA and manual scan coincide
2. DPSS signal intensity: **0.88 %** of the signal obtained with the excimer laser

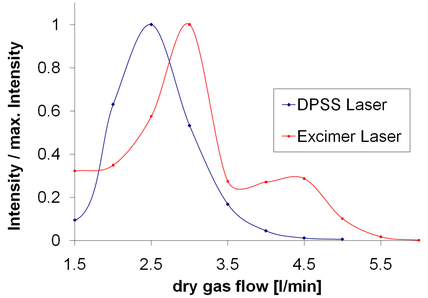
Dependencies of the Signal Intensity: Impact of flow parameters (fixed beam positions and settings according to Fig. 4)



- Comparable response with both laser systems
- Non-linear behavior suggests complex flow characteristics (cf. Poster WP 607)



- Factor ~ 120 between recorded signal with excimer and DPSS
- Significant performance increase of excimer below ~150 µL/min due to higher sensitivity to background analyte (s.a.: Poster TP 610)



Excimer laser leads to enhanced tolerance for MS settings:

Shifts in the DIAV are well buffered by the large beam area/irradiated volume.

Conclusions

The results demonstrate:

The use of the DPSS laser leads to a loss in signal intensity (120x), S/N ratio, and detection limit (70x, respectively).

Excimer laser

Pro:
- **High performance** in terms of detection limit
- **Broader tolerance** range towards shifts of the DIAV

Con:
- Large **size**
- Comparably **expensive** (~ 35 k€)
- **Maintenance cost**
- **Noise** intensity
- More vulnerable **towards ion source memory effects**

DPSS laser

Pro:
- **Small**
- Comparable low **cost** (~10 k€)
- Virtually **no noise**
- Easy **handling**
- Simple system **integration /installation**
- Less vulnerable towards **ion source memory effects**

Con:
- **Performance lowered** by factor 120 in terms of signal intensity, by a factor 70 in terms of S/N ratio and detection limit
- **Small tolerance** range to parameters that cause shifts in the DIA maximum

Comparison measurements regarding GC-APLI MS are currently underway

Literature

1) Constapel, M.; Schellenträger, M.; Schmitz, O. J.; Gäb, S.; Brockmann, K. J.; Giese, R.; Benter, Th. *Rapid Commun. Mass Spectrom.* **2005**, *19*, 326-336.
2) Benter, Th.; Schmitz, O. J. Atmospheric Pressure Laser Ionization. In *Advances in LC-MS instrumentation*, Journal of Chromatography Library 72, Cappiello, A. Ed.; 2007.
3) Benter, Th. Atmospheric Pressure Laser Ionization. In *The Encyclopedia of Mass Spectrometry*, Gross, M. L., Caprioli, R. N., Eds., 1st ed.; Elsevier: Oxford, U.K., 2007.
4) Lorenz, M.; Schiewek, R.; Brockmann, K. J.; Schmitz, O. J.; Gäb, S.; Benter, Th. The distribution of ion acceptance in atmospheric pressure ion sources: Spatially resolved APLI measurements. *J. Am. Soc. Mass Spectrom.* **2008**, *19*, 400-410.
5) Schrader, W.; Panda, S. K.; Brockmann, K. J.; Benter, Th. Characterization of non-polar aromatic hydrocarbons in crude oil using atmospheric pressure laser ionization and Fourier transform ion cyclotron resonance mass spectrometry (APLI FT-ICR MS). *Analyst* **2008**, *133*, 867-869.
6) Schiewek, R.; Lorenz, M.; Giese, R.; Brockmann, K.; Benter, T.; Gäb, S.; Schmitz, O. J. Development of a multipurpose ion source for LC-MS and GC-API MS. *Anal. Bioanal. Chem.* **2008**, *392*, 87-96.

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