EUROfusion

SP X: Re-excitation of Laser-Induced Plasma for Depth Profile Quantitative Analysis of Real Reactor Wall Samples.

Pavel Veis, Sahithya Atikukke, Shweta Soni, Matej Veis, Sanath J. Shetty et al (CU)

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Outline

- LIBS experimental setups
  - VUV-NIR ps/ns LIBS
  - Resonant LIBS, LIBS-LIF, MW LIBS
- Towards Re-excitation of Laser-Induced Plasma
  - Standard CF LIBS & depth profile analysis by ns laser
  - ps versus. ns LIBS - comparison
  - Resonant LIBS for depth profile quantitative analysis (ns laser)
  - MW assisted LIBS for depth profile quantitative analysis
- Conclusions

REVIEW papers

- LIBS in nuclear fusion and plasma wall interactions:

Maurya, G.S., Marín-Roldán, A., Veis, P., Pathak, A.K., Sen, P.
Journal of Nuclear Materials, 541(2020) 152417

H. Van der Meiden et al.
Nucl. Fusion 61 (2021) 125001

Conf. talks:

Veis P., Marín Roldán A., Dwivedi V., Atikukke S., Veis M.: LIBS for the analysis of fuel retention and PFM characterization, **Invited talk, LIBS for Extreme Applications, Peking, Dec. 2022**

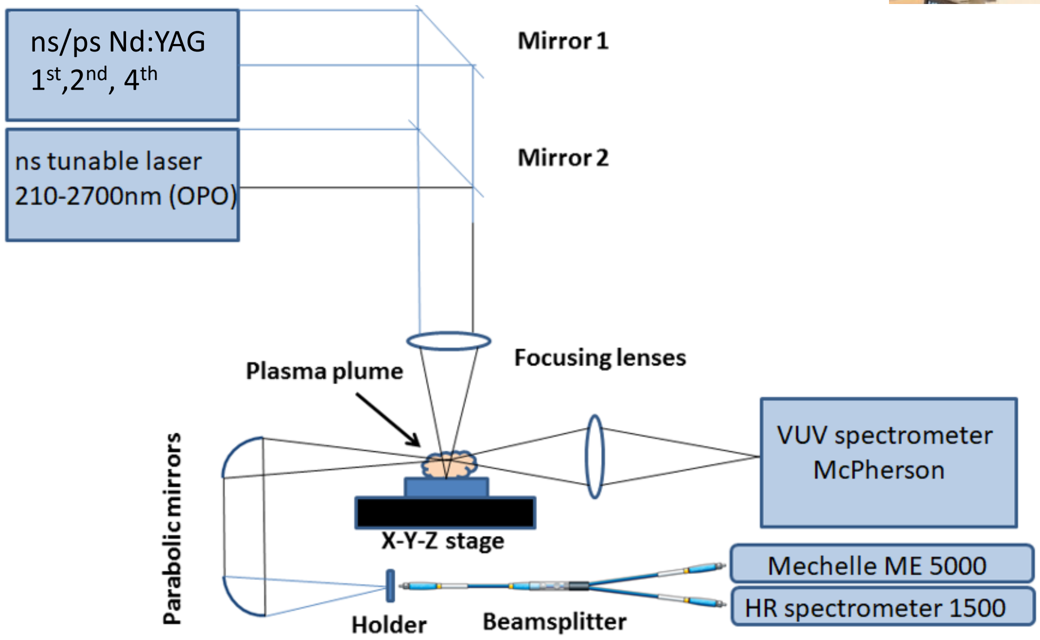
Marín Roldán A., Dwivedi V.,et al: LIBS of PFM: characterization and fuel retention studies, **talk, LIBS conf., Bari, Sep. 2022**

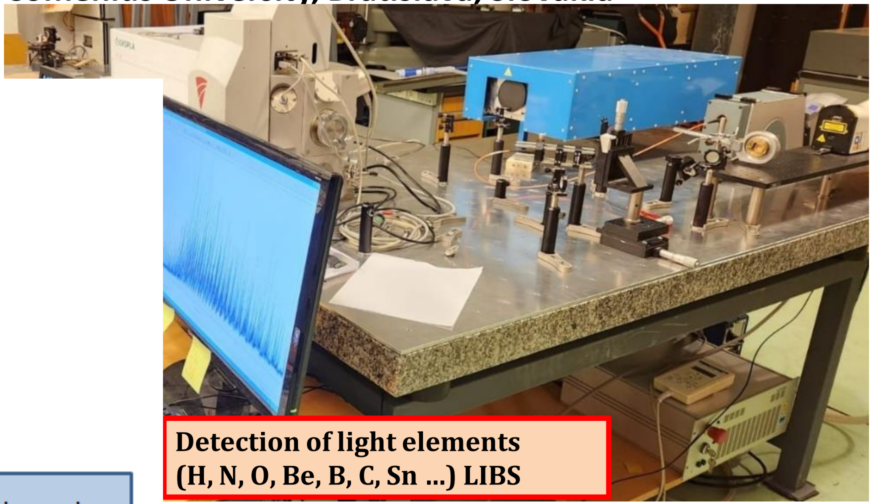
Veis P., et al, Calibration Free LIBS for Depth Profile Analysis of Impurities, Migrated Material and Retained Fuel in Fusion Relevant Materials, **Invited talk, NLIBS, Tampere, Mar. 2024**

LIBS experimental setups – LIBS VUV/NIR, R-LIBS, LIF

Comenius University, Bratislava, Slovakia

Nd:YAG ns laser (Quantel, Brilliant, CFR 200) ,Nd:YAG ps laser, tunable (210-2700 nm) OPO ns laser (EKSPLA NT342C-10-SH)





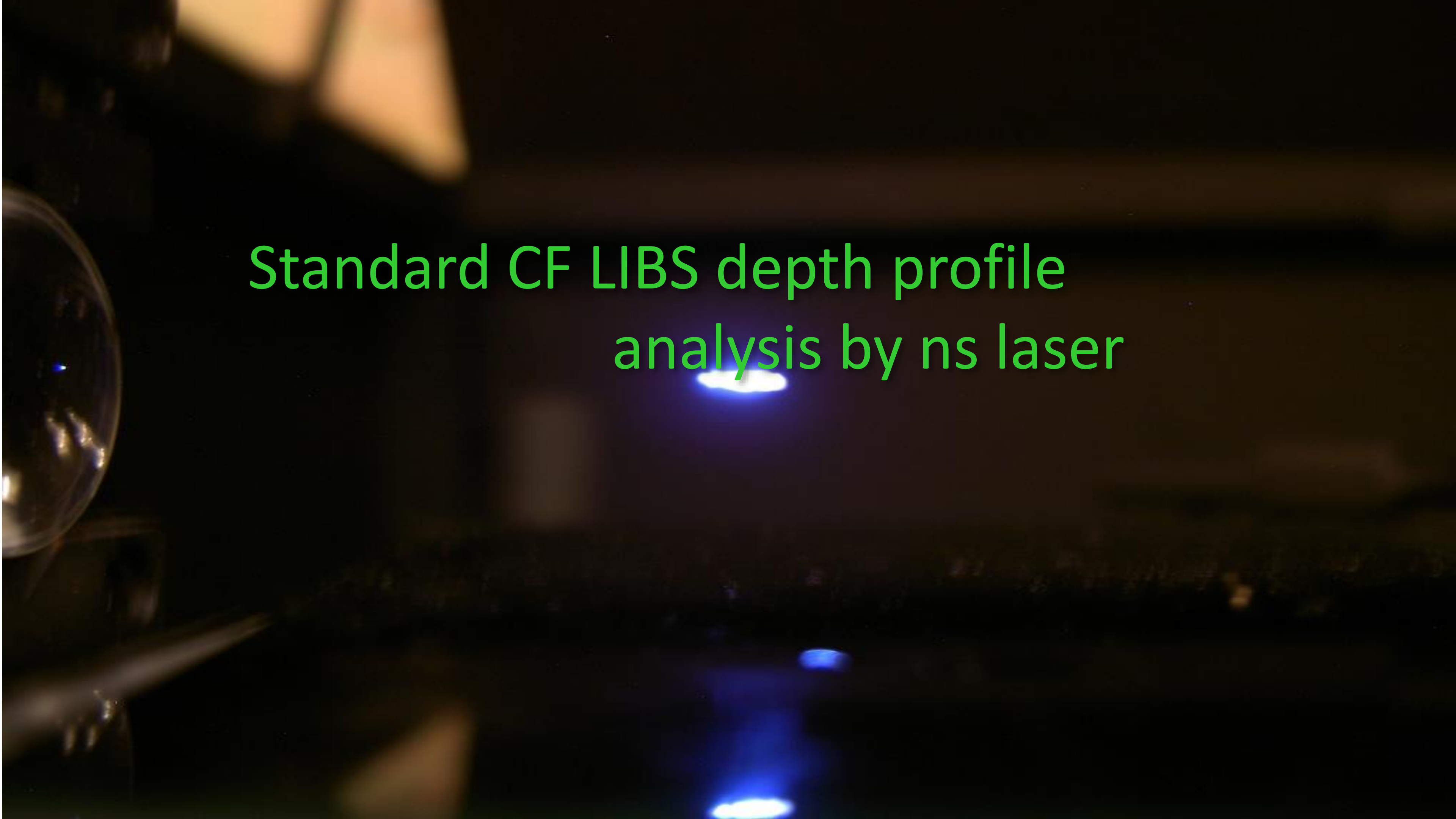
Detection of light elements (H, N, O, Be, B, C, Sn ...) LIBS

Broadband spectra
LIBS, CF LIBS

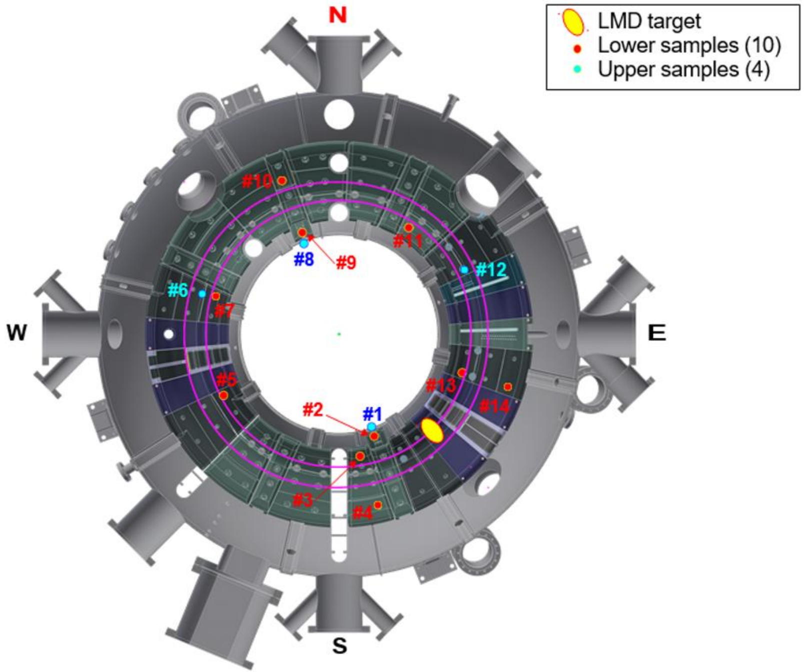
T_e, n_e
Molecular spectra
T_{rot}, T_{vib}

Echelle spectrometer (Andor ME500, 200-975 nm)
VUV spectrometer (McPherson, 115 -300 nm)
High resolution spectrometer (THR 1500 Jobin Yvon)
Equped with iCCD and EMCCD cameras (Andor)

1. **Trace element detection in complicated matrixes(Mo, W, Fe...)**
2. **Spectral lines profiles: Stark broadening => n_e**
   Stark and isotopic shifts, D/H ratio

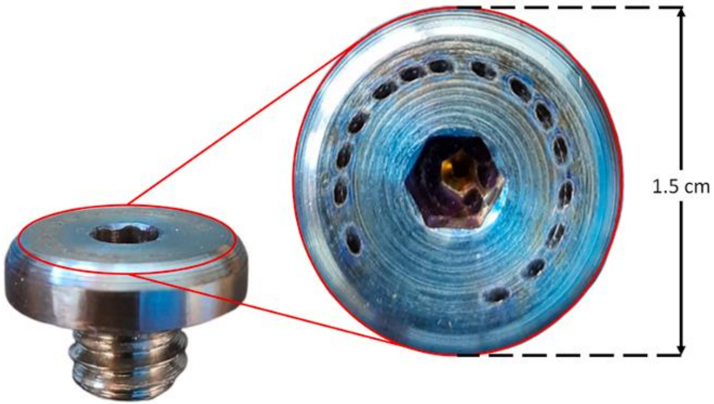

Standard CF LIBS depth profile
analysis by ns laser

Surface analysis - LM experiment - Li campaign



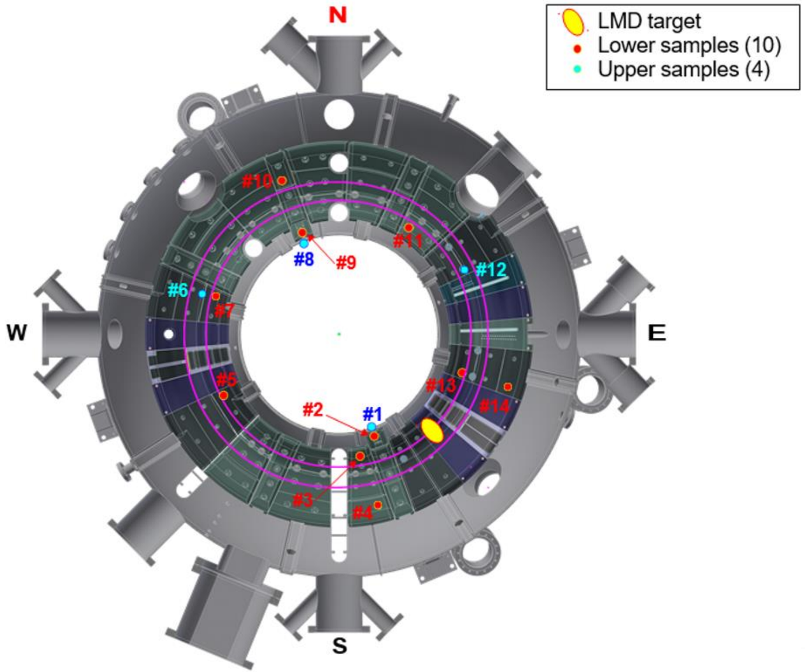
P. Veis, S. Atikukke *et al.*, NME, 25 (2020) 100809

Screws from COMPASS TOKAMAK
CF LIBS in air at atm. pressure

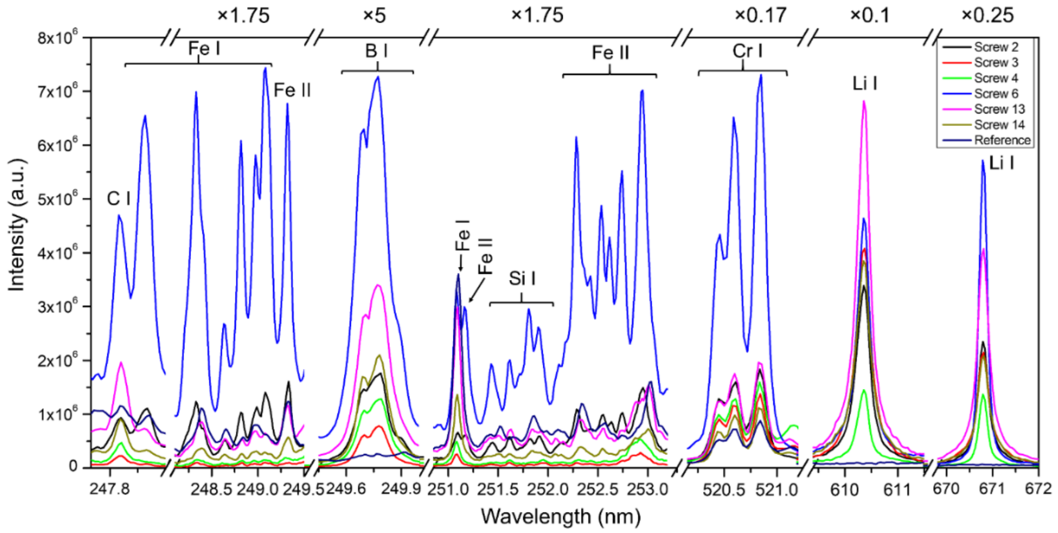


Nd:YAG ns laser @ 1064 nm, Quantel, 13.5 mJ,
ME5000, Andor, iCCD camera (iStar's DH743)
Delay and gate width and - 1.5 µs and 3 µs

Spectra Acquired



Screws from COMPASS TOKAMAK
CF LIBS in air at atm. pressure



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Nd:YAG ns laser @ 1064 nm, Quantel, 13.5 mJ,
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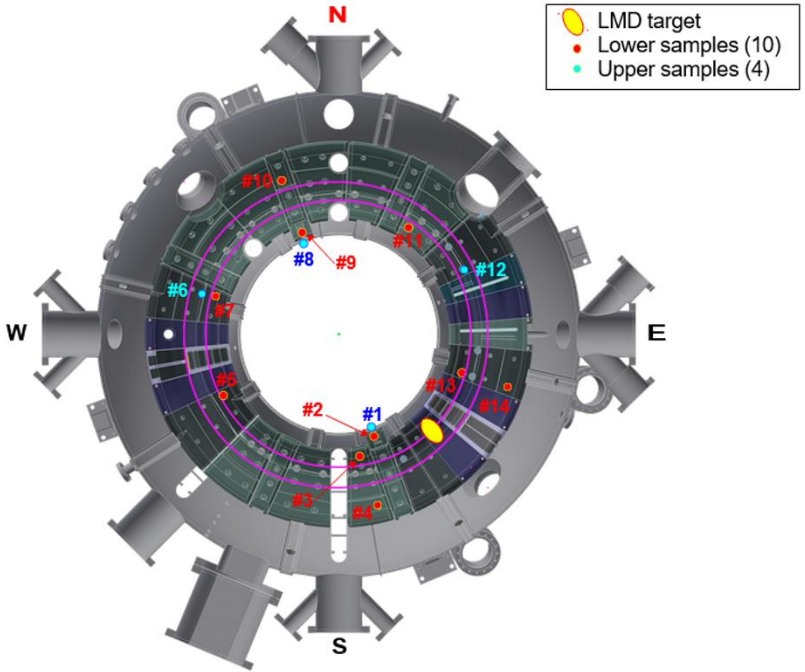
Delay and gate width and - 1.5 µs and 3 µs

Depth Profile



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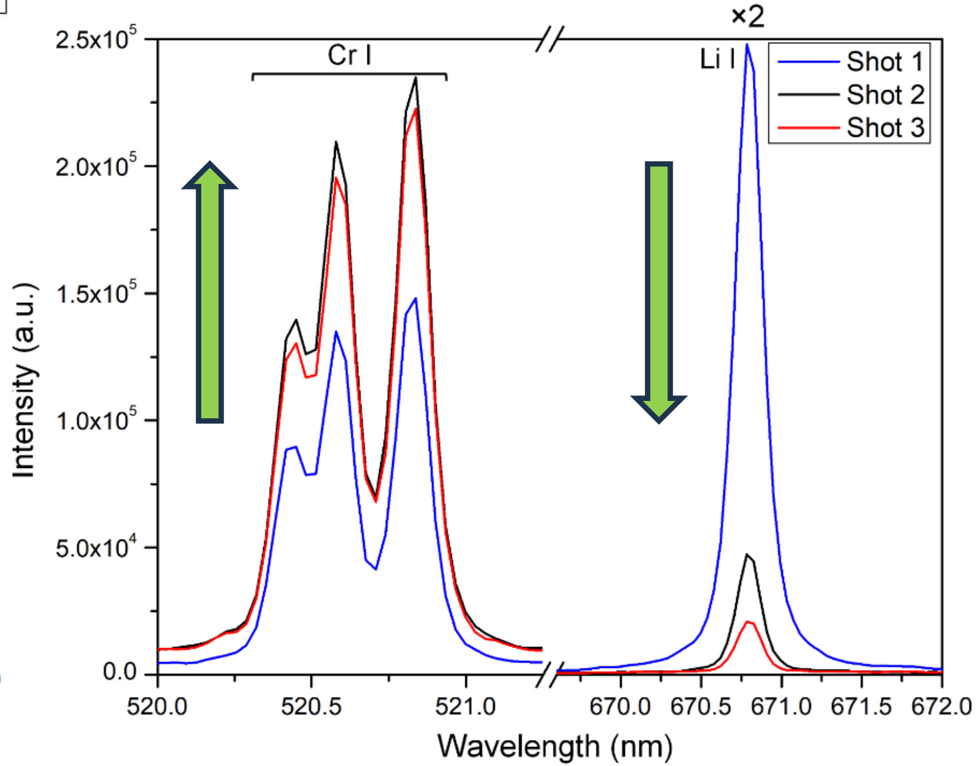
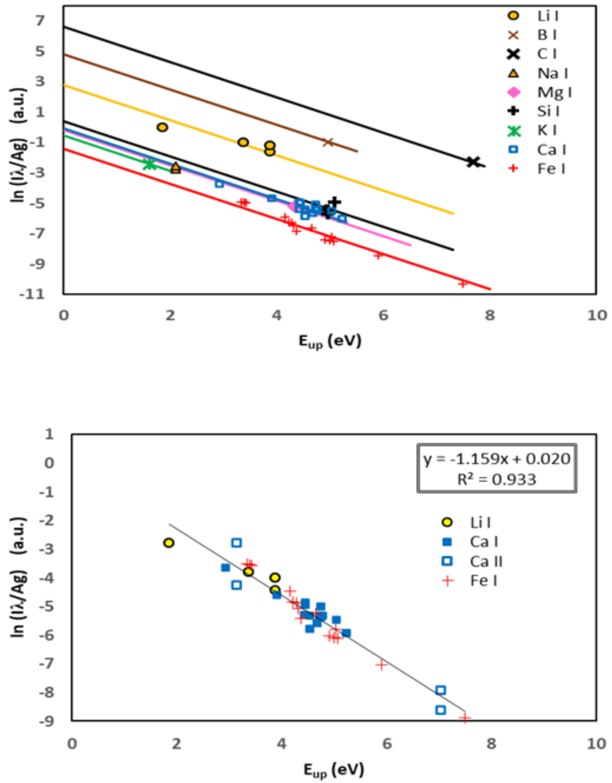
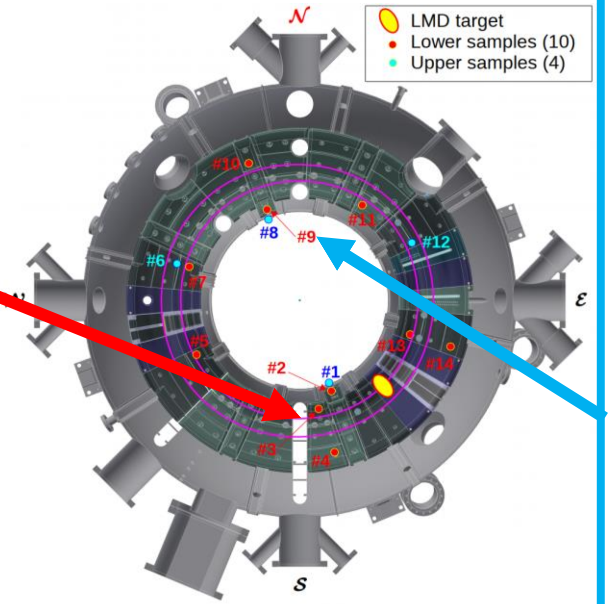
Screws from COMPASS TOKAMAK
CF LIBS in air at atm. pressure



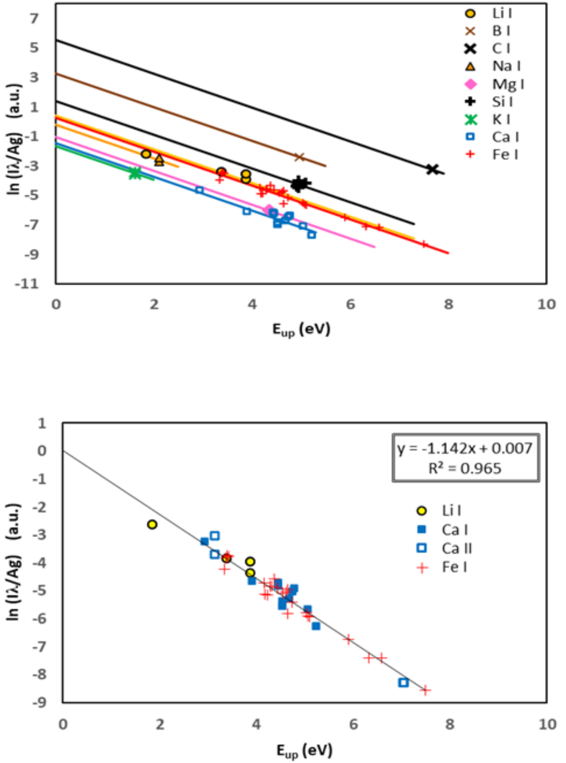
CF LIBS and depth profile analysis – Li campaign

Saha-Boltzmann plot for screw no. 3:



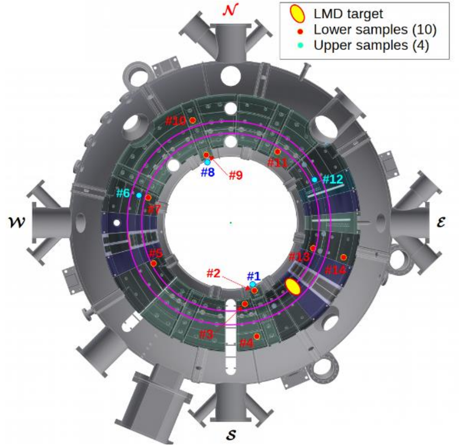


Saha-Boltzmann plot for screw no. 9:

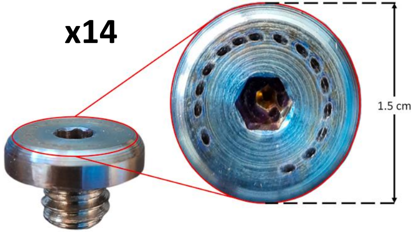


CF LIBS and depth profile analysis – Li campaign

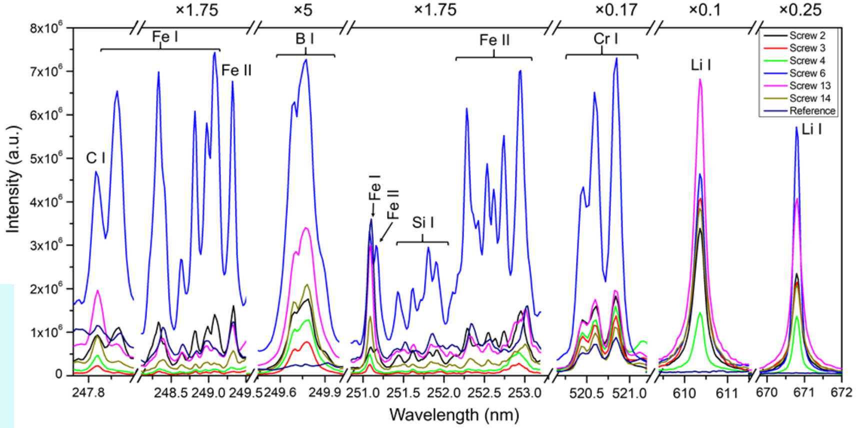
Analysis of wall impurities on Ni Cr screws



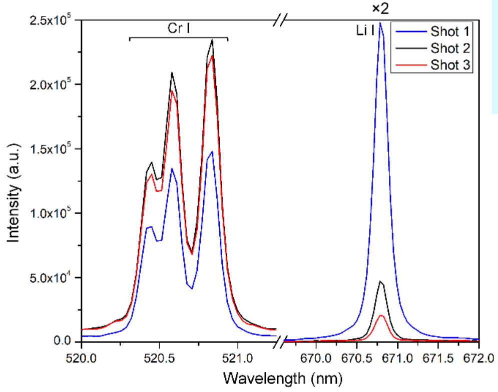
x14



- Screw 3, 12, 13 and 14 has highest Li (in %) content
- Screw 1,8 and 11 have lowest Li (in %) content
- Screws 3,13 and 14 – closest to LM divertor
- Screw 8 and 9 - farthest



Experimental LIBS spectra of Li I at gate width 3 μs, gate delay: 1.5 μs



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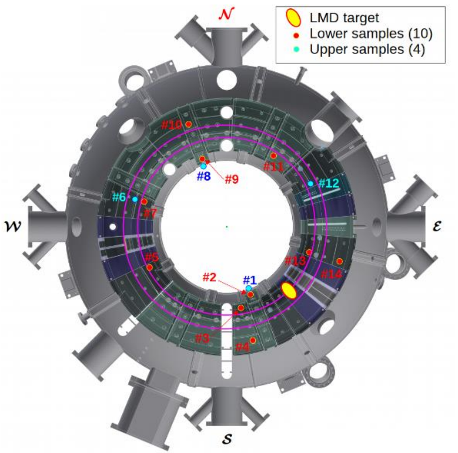
Atomic percentages for Li, B, C, and Fe. N denote the number of the screw.

N	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Li	0.4	2.3	7.3	1.2	1.1	1.0	2.4	0.3	1.9	2.1	0.3	10.6	8.6	5.2
C	89.3	89.3	82.9	88.4	89.3	90.5	87.5	94.2	91.3	89.3	93.2	73.3	77.3	83.4
B	10.3	8.4	9.8	10.3	9.6	8.6	10.1	5.5	6.8	8.6	6.5	16.0	14.1	11.4

Surface analysis - LM experiment - LiSn campaign



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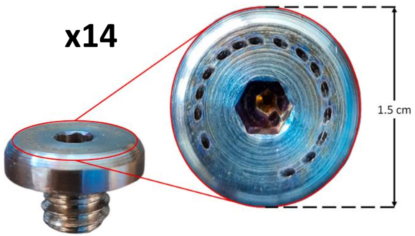
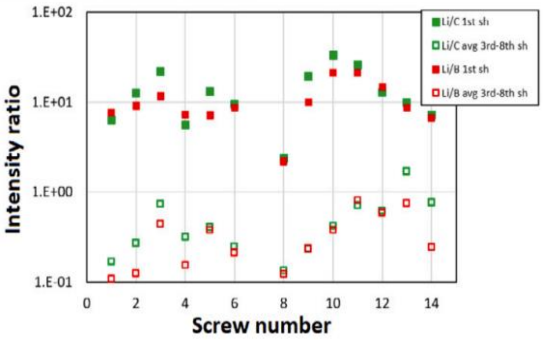
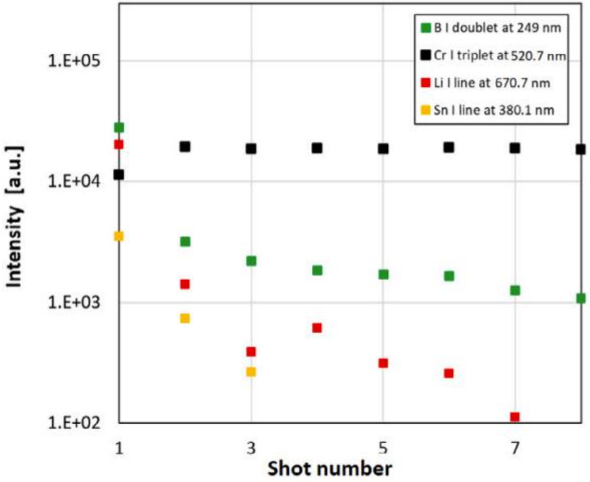
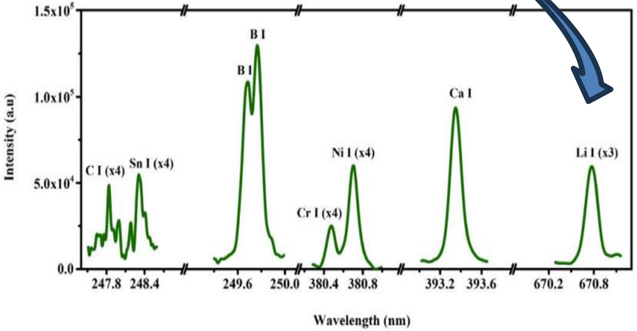


Screws from COMPASS TOKAMAK
CF LIBS in Ar 100 mbar pressure

- What is the Li/Sn quantity ratiom in the deposited layer?
- Ln is easy to detect.
- What is the minimal Sn quantity, which we will be able to be detected in complivated matrix of Cr-Ni-(Fe)?







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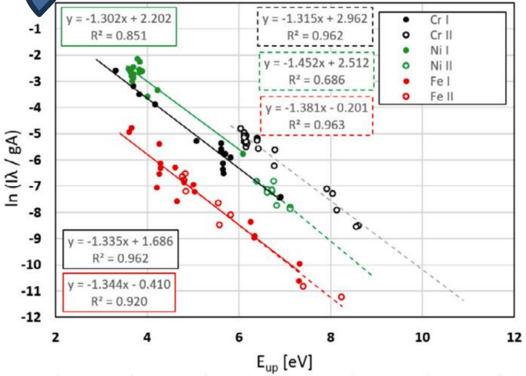
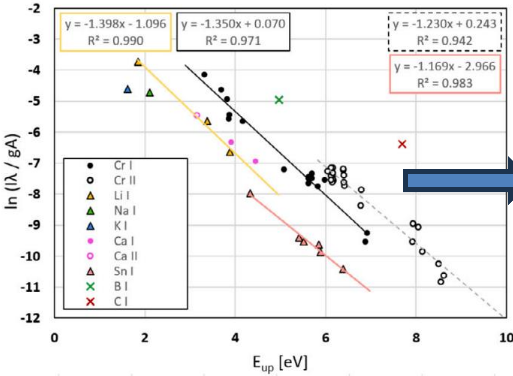
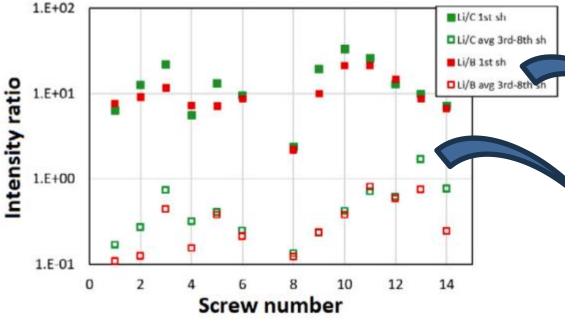
CF LIBS depth profile analysis – LiSn campaign

	T1	T2	T3	T4	MIN	MAX
Shot	3–8	3–8	3–8	3–8	1	1
T_e	0.75 ±0.02	0.71 ±0.02	0.76 ±0.03	0.77 ±0.02	0.77 ±0.02	0.77 ±0.01
n_e	2.01 ±0.49	1.10 ±0.81	1.74 ±0.57	1.34 ±0.55	1.54 ±0.22	3.00 ±0.20







el.	MIN [%]	MAX [%]	el.	MIN [%]	MAX [%]
Li	0.296 ±0.17	0.810 ±0.26	Ni	13.1 ±0.72	11.0 ±0.56
Sn	0.095 ±0.05	0.234 ±0.1	Fe	1.52 ±0.09	1.54 ±0.10
B	4.35 ±0.36	5.53 ±0.30	Na	0.273 ±0.14	0.473 ±0.16
C	66.6 ±4.64	69.1 ±4.17	K	0.703 ±0.36	0.671 ±0.19
Cr	12.9 ±1.21	10.3 ±0.89	Ca	0.255 ±0.02	0.362 ±0.03

- **CONCLUSION:**
- **Main components of the first layer are: C, B, Ni, Cr.**
- **Measured Sn quantity ranges from 0.1 to 0.23 at.%.**
- **Measured Li quantity ranges from 0.3 to 0.81 at.%.**
- **Minimal quantity of Sn to be able to detect is around 0.1 at.%.**
- **Observed Li/Sn quantity ratio is 3 to 3.5.**

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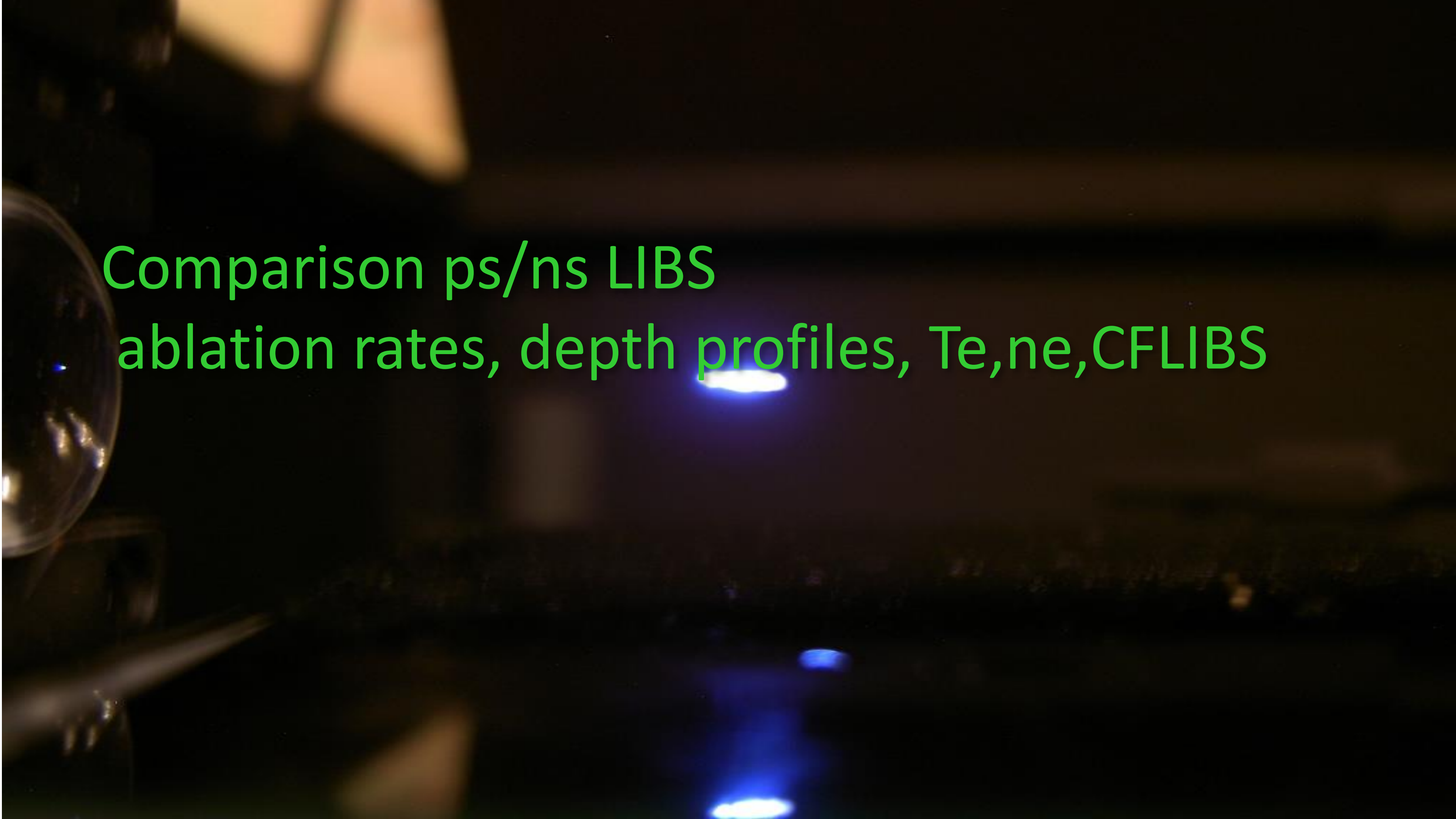
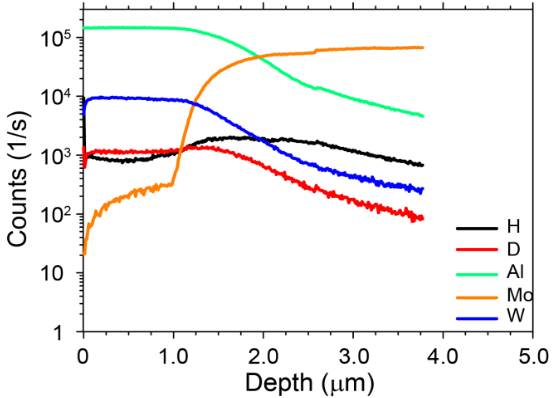
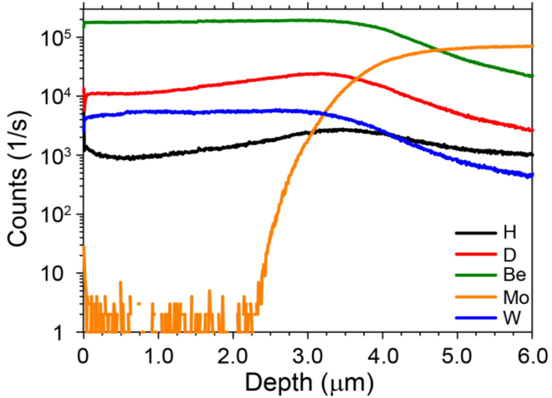
Comparison ps/ns LIBS

ablation rates, depth profiles, Te,ne,CFLIBS

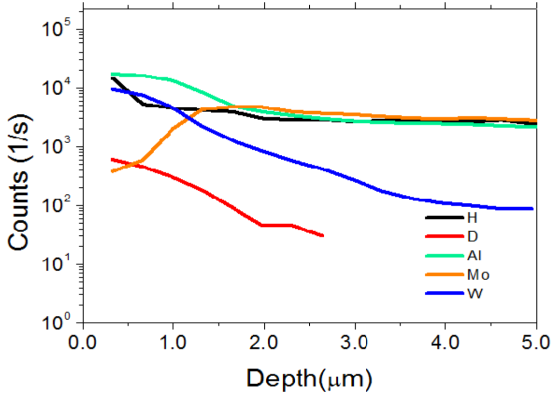


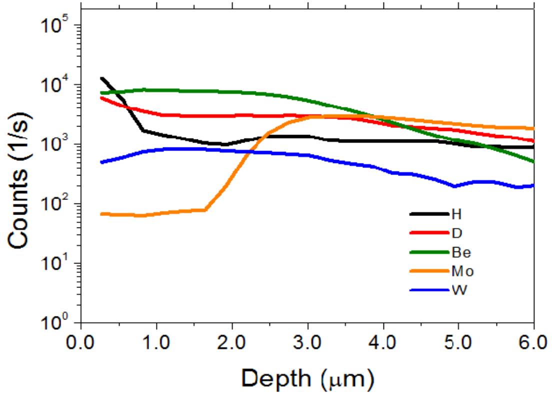
Depth profiling – comparison LIBS and SIMS – for fuel retention evaluation



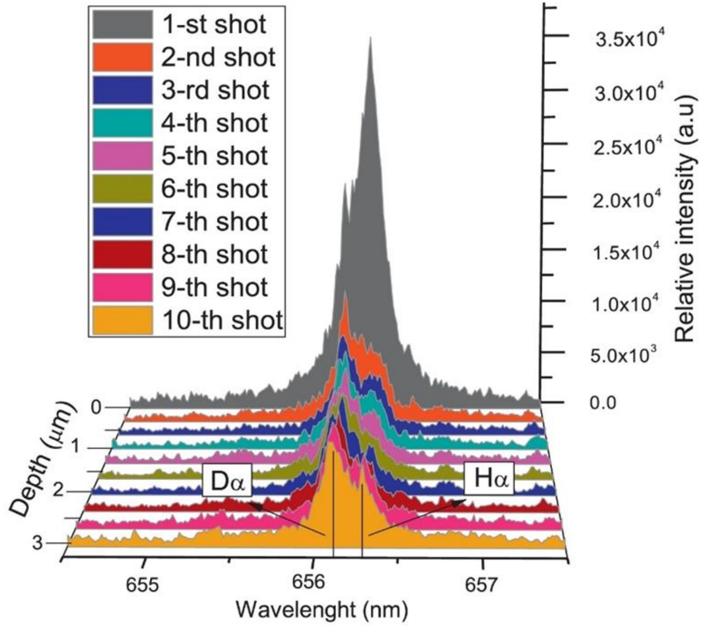


SIMS depth profiles of different elements in D-doped Al67W33 (left) and Be67W33 (right) coatings.





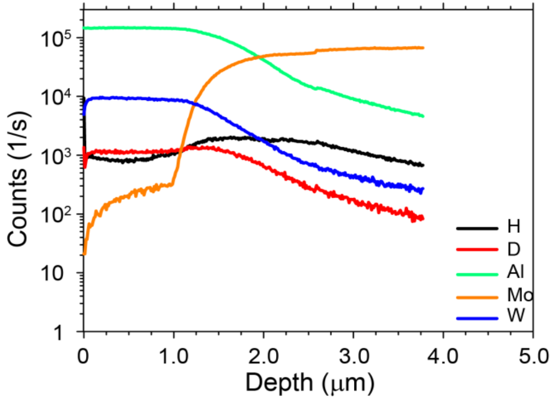
LIBS depth profiles of different elements in D-doped Al67W33 (left) and Be67W33 (right) coatings.

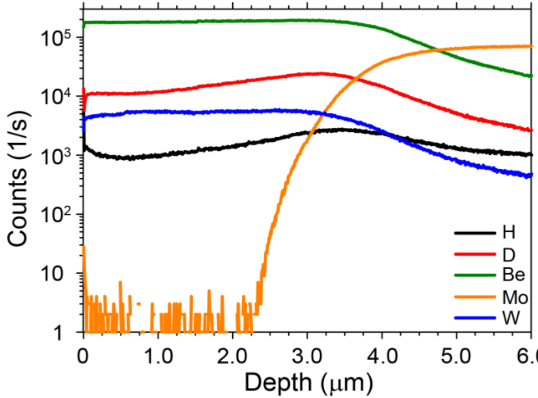


Evolution of Be67W33D LIBS spectra from 1st shot to 10th shot showing the decaying tendency of the Dα and Hα lines

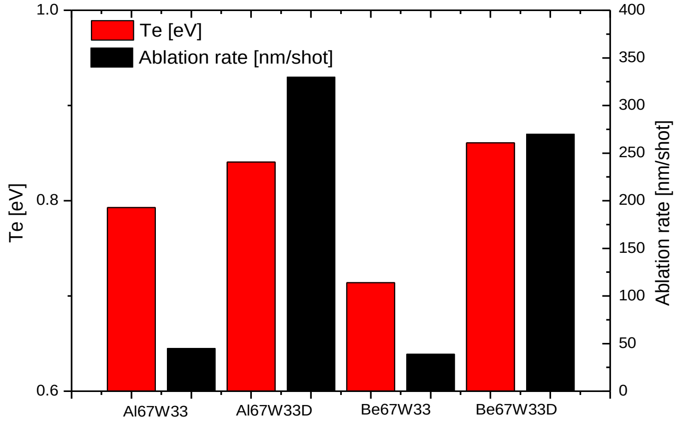
M. Suchoňová, P. Veis, et al. , Materials and Energy, 21 (2017) 611

Depth profiling – comparison LIBS and SIMS – for fuel retention evaluation



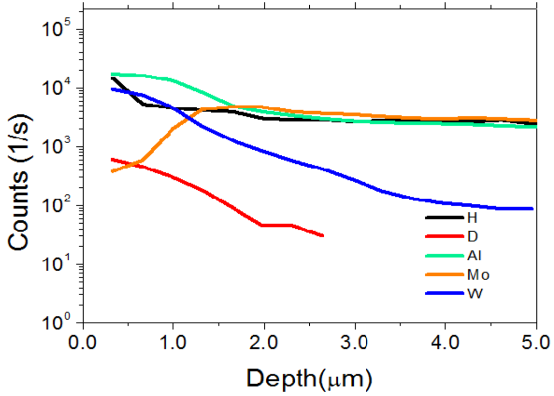


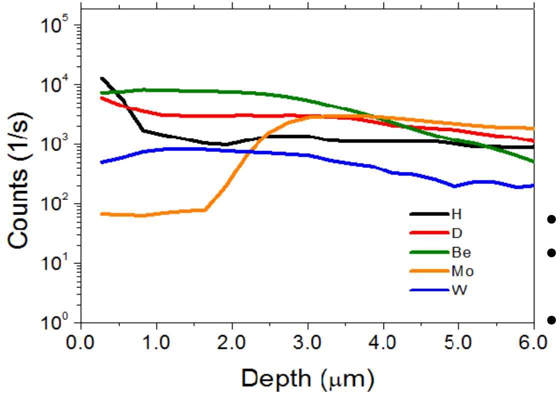
SIMS depth profiles of different elements in D-doped Al67W33 (left) and Be67W33 (right) coatings.



Ablation rates for the Al/ Be- W samples with/without D.

Ablation rate [nm/shot]	Al67W33	Be67W33
w/o D	45 ± 8	39 ± 10
with D	330 ± 80	275 ± 35





LIBS depth profiles of different elements in D-doped Al67W33 (left) and Be67W33 (right) coatings.

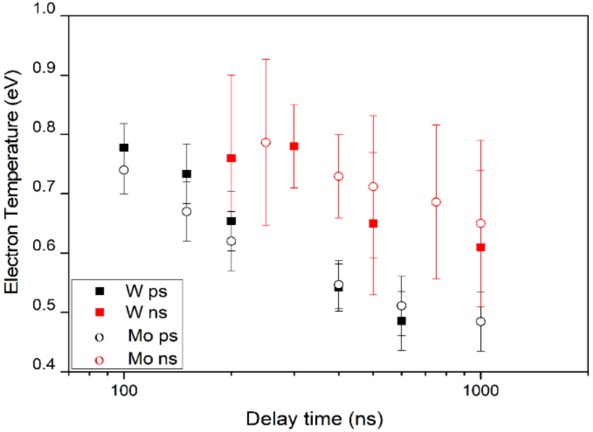
- **We achieved better resolution (nm/pul.) for samples w/o D**
- **Resolution depends on Te, Ne, sample phys./chem. properties**
- **LIBS plasma has higher Te for samples with D**

M. Suchoňová, P. Veis, et al. ,
Materials and Energy, 21 (2017) 611

Comparison ps/ns LIBS – pure W and Mo material

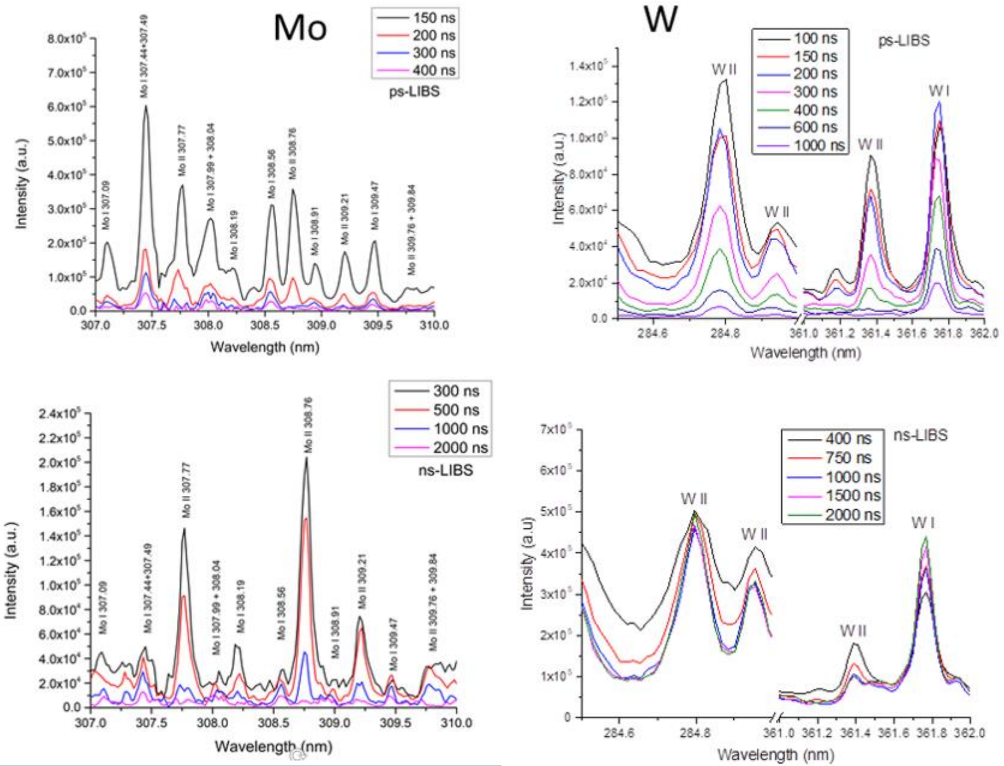
W and Mo as substrates

Regime	Mo	W
ps	85 ±13 nm/pulse	55 ±11 nm/pulse
ns	318 ±63 nm/pulse	207 ±42 nm/pulse



ps

ns



A. Marín Roldán, P. Veis *at al.*, Fusion Engineering and Design 172 (2021) 112898.

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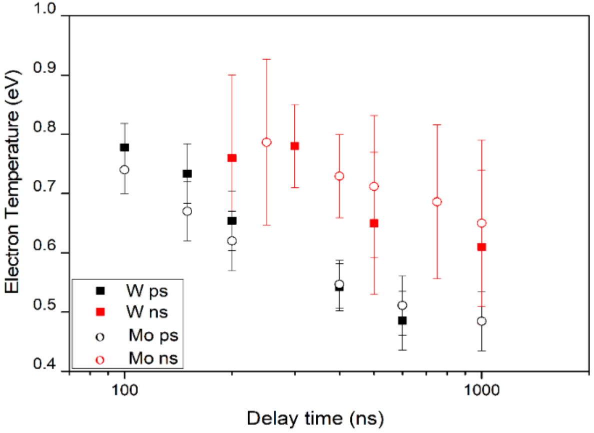
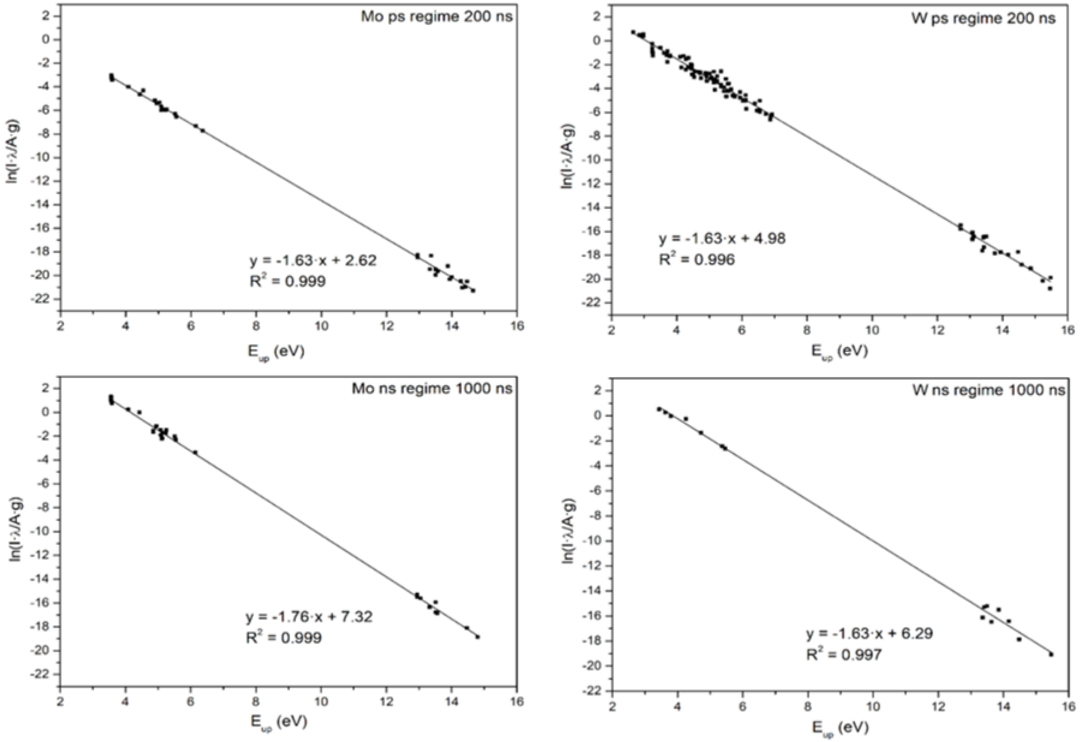


ps

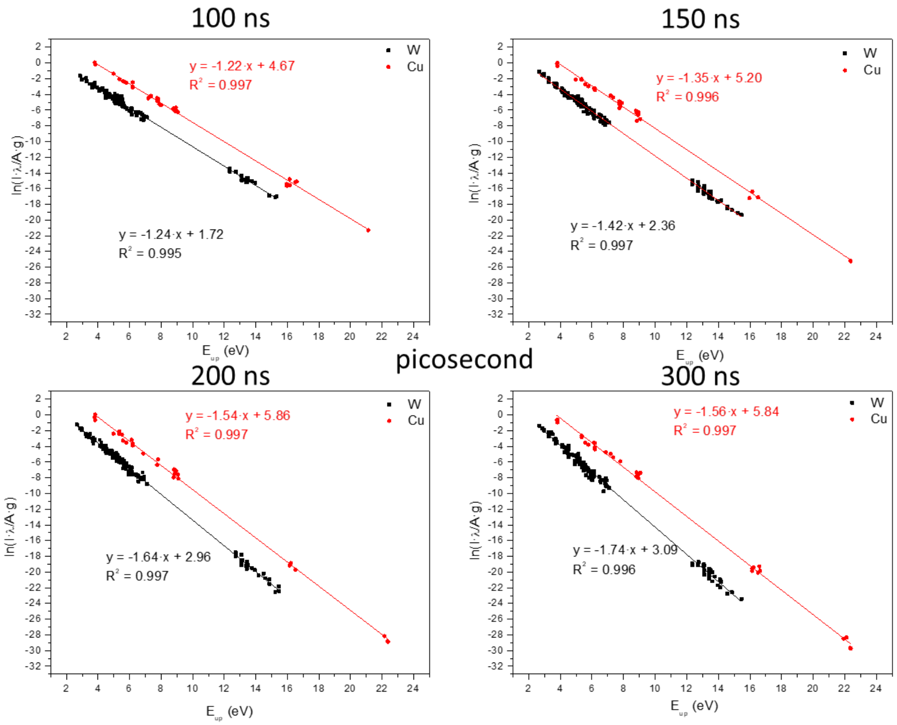
ns

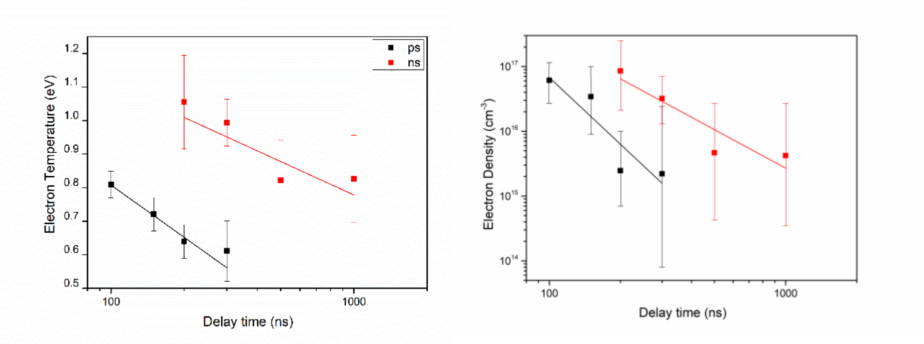


A. Marín Roldán, P. Veis *at al.*, Fusion Engineering and Design 172 (2021) 112898.

Comparison ps/ns LIBS – CF LIBS of W-based alloy

WCu as W-based alloy

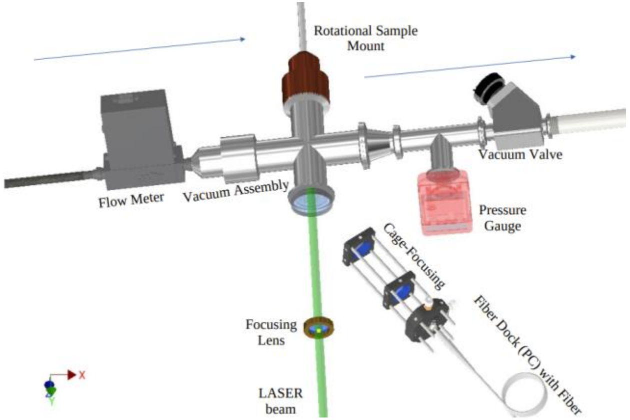




Regime	ps				ns			
Element	100 ns	150 ns	200 ns	300 ns	200 ns	300 ns	500 ns	1000 ns
W	72.3	70.2	70.0	70.7	73.5	69.5	69.6	70.5
Cu	27.7	29.8	30.0	29.3	26.5	30.5	30.4	29.5

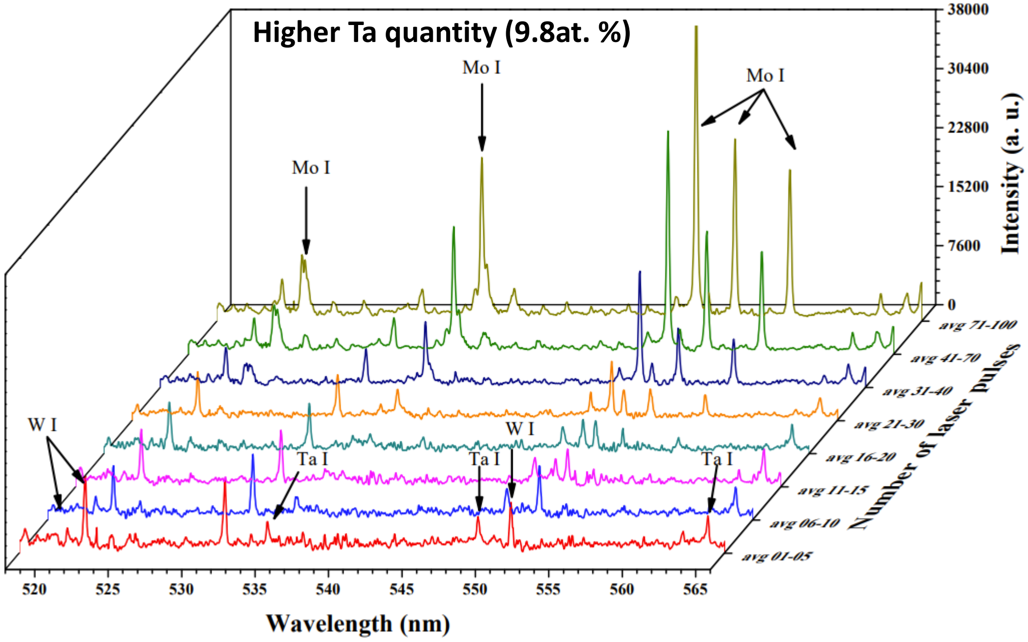
A. Marín Roldán, M. Pisarčík, M. Veis, M. Držík, P. Veis, Spectrochimica Acta Part B: Atomic Spectroscopy 177 (2021) 106055.

ps LIBS - depth profiling of WTa(D)/Mo



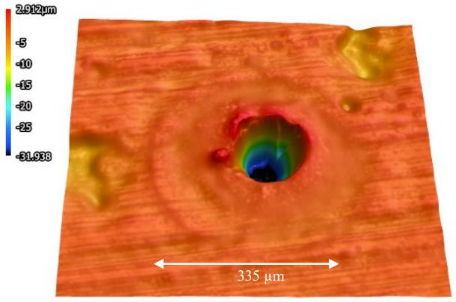
ps LIBS @ 532 nm, 30 ps duration,
energy- 1 mj, 3 mJ, 10 mJ
Ar 5 mbar press.,
Equal Delay / Gate Time from 200 ns to 450 ns

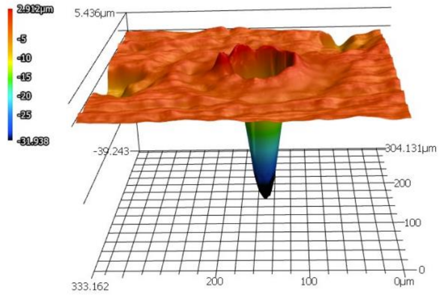
Sample Index	Substrate	GDOES Layer Thickness (μm)	Layer Composition ($at.\%$) W	Ta	D
EU2-72	Mo	6,68	90.20	9,80	–
EU2-73	Mo	6,99	97.48	2.52	–
EU2-75	Mo	1,09	83	7	10



LIBS spectrum of the EU2-72 sample (W I, Ta I, Mo I ines)
Delay 200 ns, Gate Time 200 ns
thickness- 6.6 µm, approx. 20 shots to cross for 3 mJ

ps LIBS - depth profiling of WTa(D)/Mo





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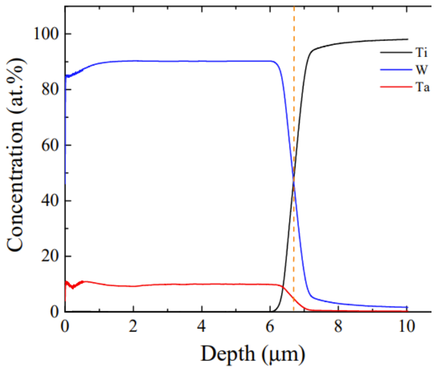
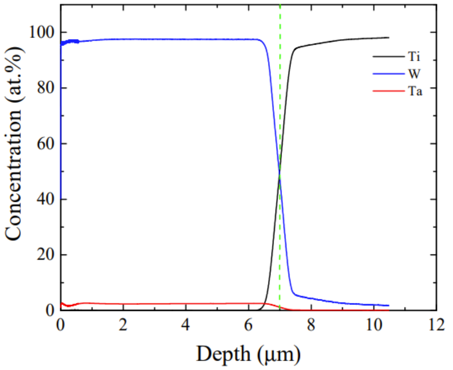
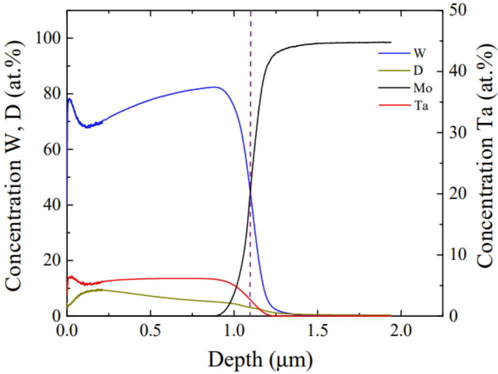


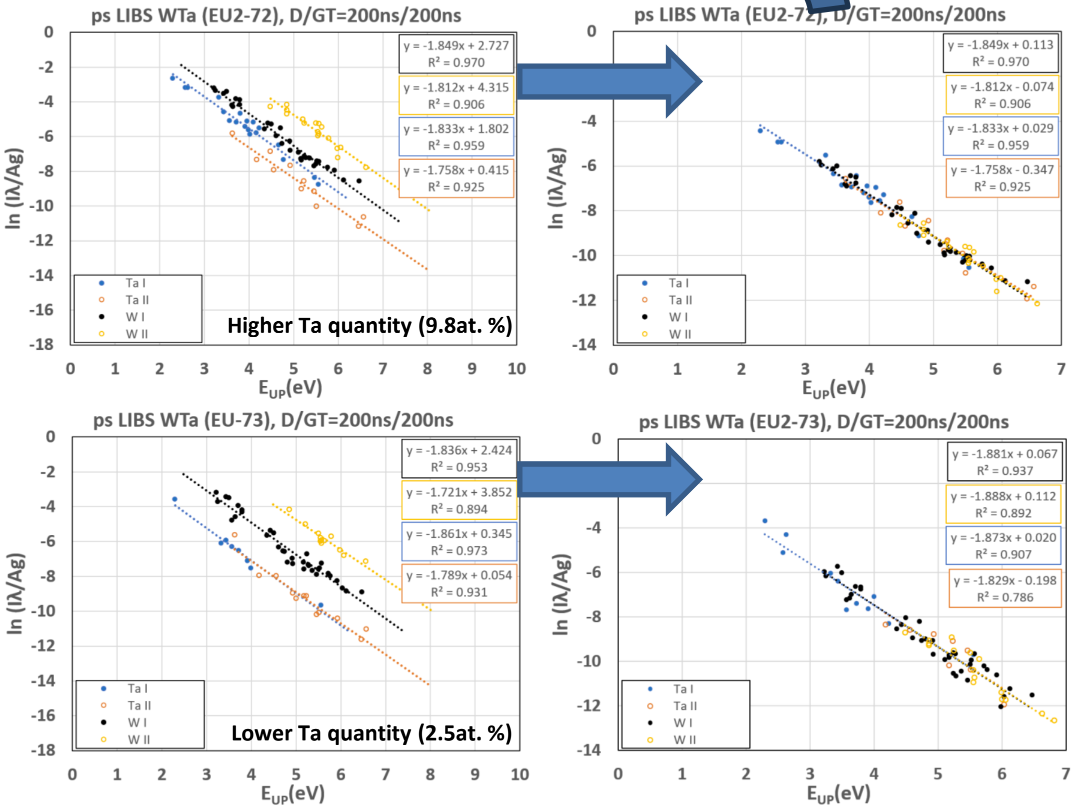




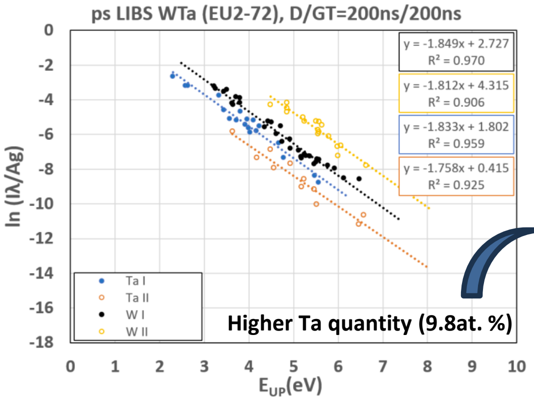
Depth profile measured by GDOES, Confocal microscopy and LIBS:
Ablation rate: min 130 nm/puls (1 mJ) max 290 nm/pulse (3 mJ)

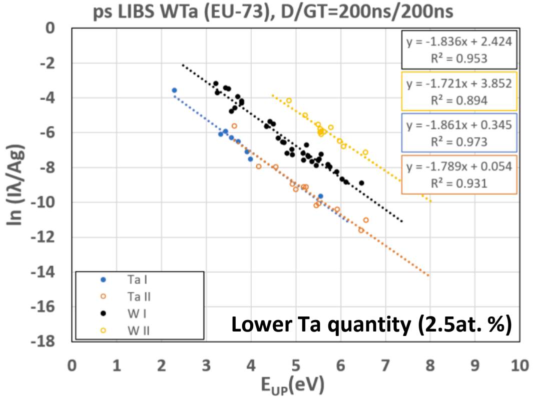
ps LIBS - depth profiling of WTa(D)/Mo

Sample	Laser Energy (mJ)	Gate Delay (ns)	T_e (eV)	N_e $(\frac{10^{16}}{cm^3})$
EU2-72	1	200	0.531 ± 0.045	1.79
		300	0.536 ± 0.047	1.46
		450	0.502 ± 0.081	0.69
	3	200	0.549 ± 0.038	1.69
		300	0.541 ± 0.044	2.35
		450	0.519 ± 0.074	1.99
EU2-73	1	200	0.533 ± 0.054	0.17
		300	0.517 ± 0.061	0.80
		450	0.503 ± 0.100	1.89
	3	200	0.550 ± 0.045	1.69
		300	0.525 ± 0.065	0.68
		450	0.524 ± 0.080	1.06



ps LIBS - depth profiling of WTa(D)/Mo

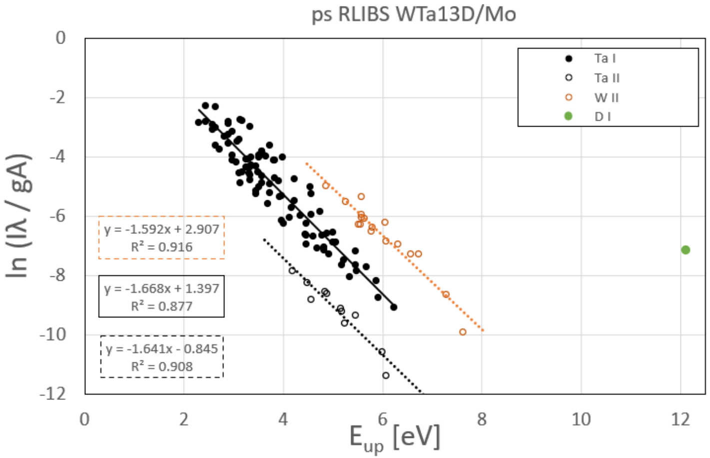




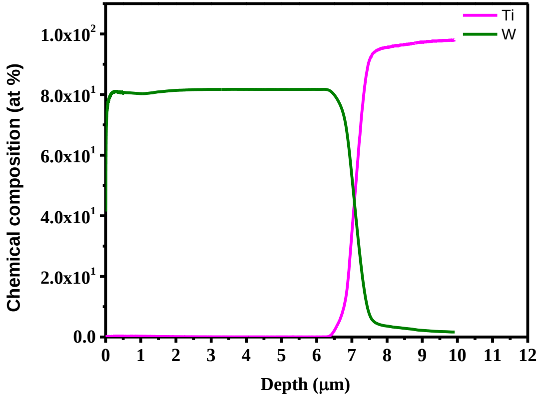
GDOES conc. (at. %)		CF-LIBS conc. (at. %)		Rel. Error (%)	
W	Ta	W	Ta	W	Ta
90.20	9.80	89.87	10.13	1.4	12.7
		89.61	10.39	1.8	15.1
		89.68	10.32	2.7	23.9
		89.87	10.13	1.4	12.7
		89.61	10.39	1.8	15.1
		89.68	10.32	2.7	23.9
97.48	2.52	96.45	3.55	1.0	26.8
		96.71	3.29	1.1	31.1
		96.52	3.48	1.8	24.1
		96.46	3.54	0.5	14.1
		97.05	2.95	0.8	26.1
		97.26	2.74	0.6	22.7

ps CF-LIBS non resonant - WTa13D10/Mo sample

Ar 5mbar pressure - at MU Brno



Depth profile via GDOES – 7 µm



Exp. Conditions: Nd:YAG ps laser @ 532 nm, up to 1-10 mJ, Ar 5 mbar, D time = G time = 350 ns

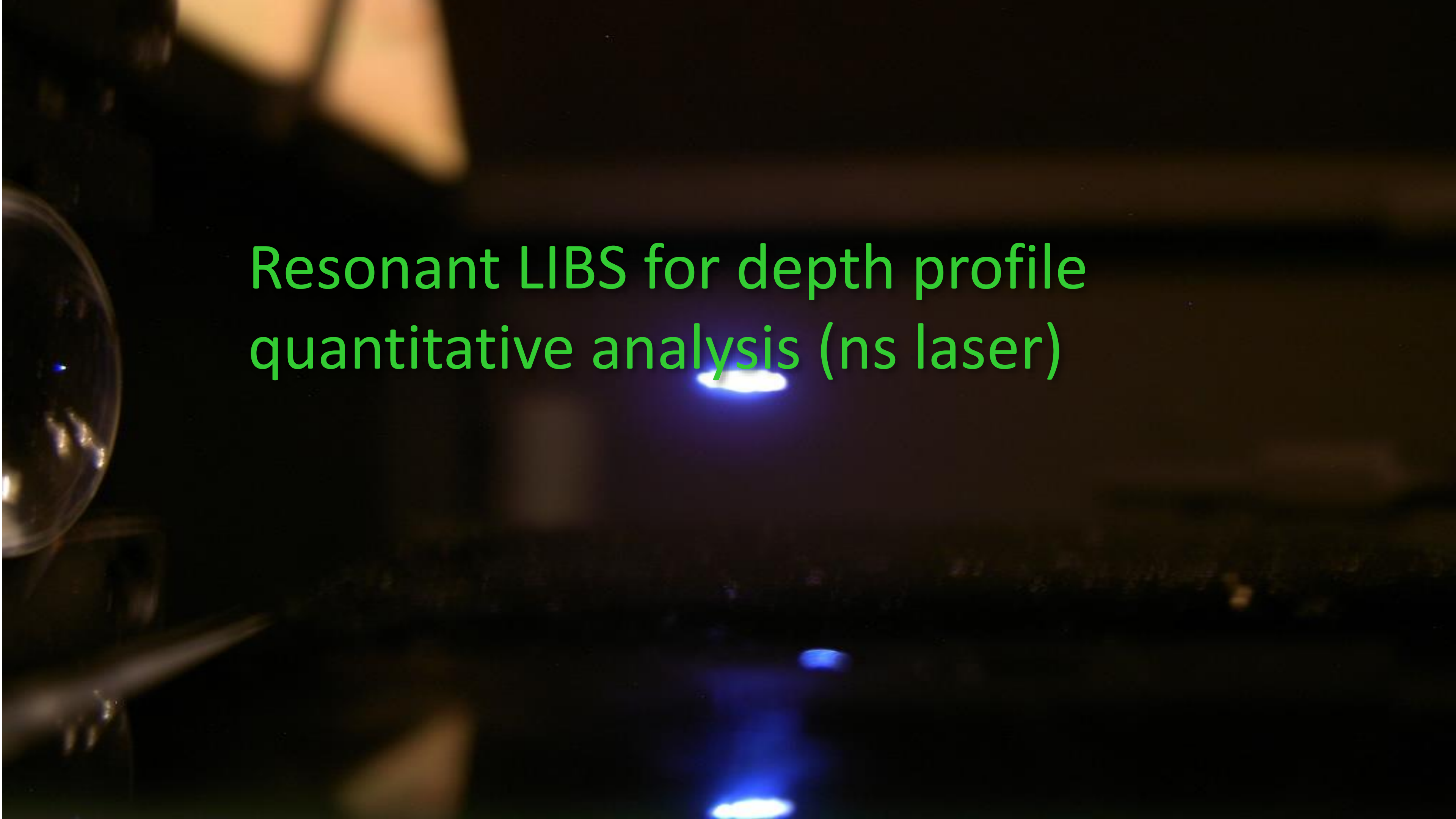
Averaged spectrum from layer. Well separated D/H alpha line.

Selection of lines: self abs. and interference free lines

T_e = 0.6 eV averaged from W I-II and Ta I- II

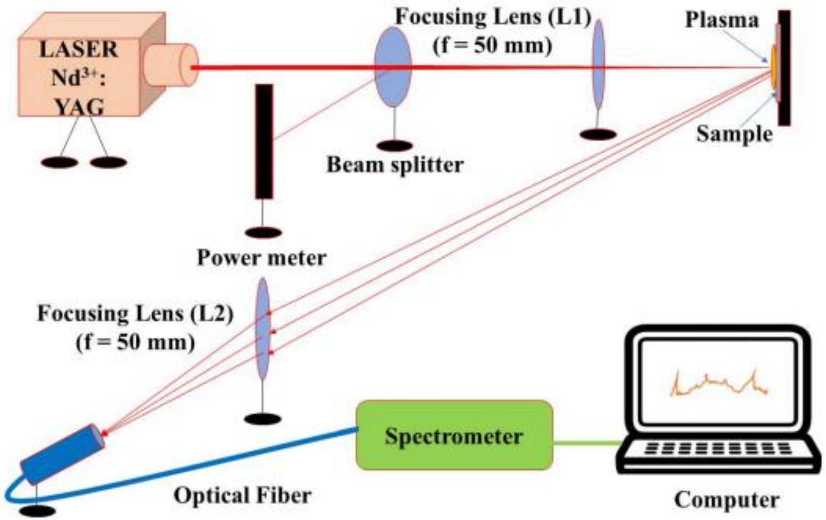
T_e = 1.04 eV from Ar I used for quantification of D I

CF LIBS quantification (W 77.8 at.%, Ta 11.5 at.%, D 10.7 at.%)


Resonant LIBS for depth profile
quantitative analysis (ns laser)

Resonant - LIBS depth profile analysis of WTa/Mo samples

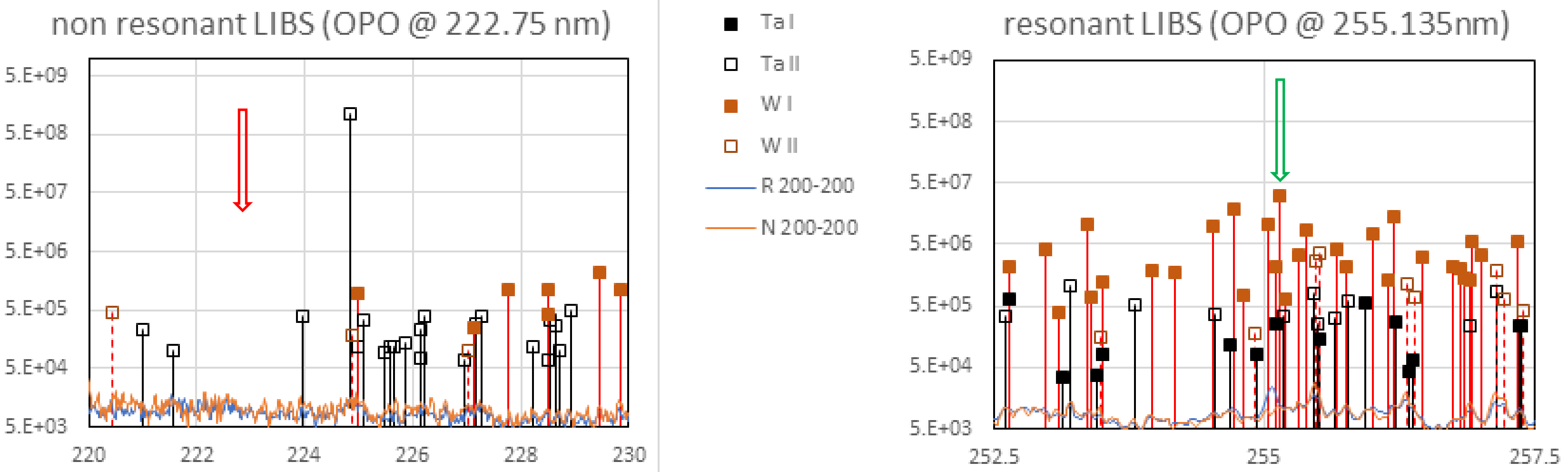
- resonant LIBS measurement in collaboration with INFLPR Boucharest (E. Grigore, F. Baiasu) and MU Brno (W. Khan, P. Dvorak).
- ns tunable OPO laser (EKSPLA NT342C-10-SH) pumped with a flash lamps.
- Typical laser beam diameter is 7 mm and has a repetition rate of 10 Hz.
- Time-resolved plasma spectra were obtained using a echelle spectrometer (ME 5000, Andor Technology) and an iCCD camera (iStar DH734, Andor Technology, temporal resolution 5 ns)
- A beam-splitter was placed in the path of laser, that reflect small part (approximately 9% of the laser beam radiation toward power meter to measure the laser energy.



Schematic Diagram of the LIBS setup

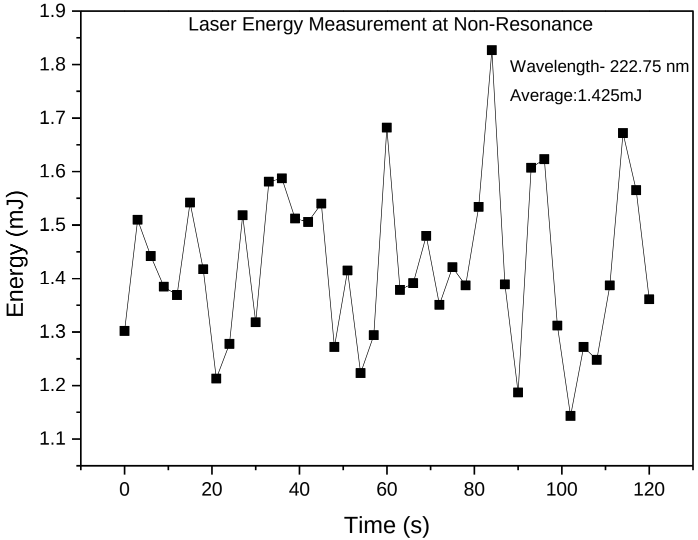
Resonant - LIBS depth profile analysis of WTa/Mo samples

- ✓ LIBS spectrum for sample W20%Ta/Mo (4µm)
- ✓ 150 shots , atm. pressure air

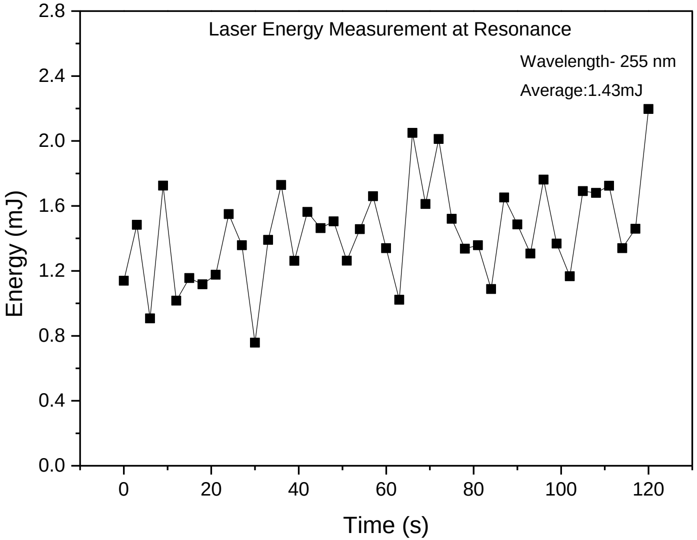


Resonant - LIBS depth profile analysis of WTa/Mo samples

Laser energy profile at non-resonance
Average energy- 1.425 mJ

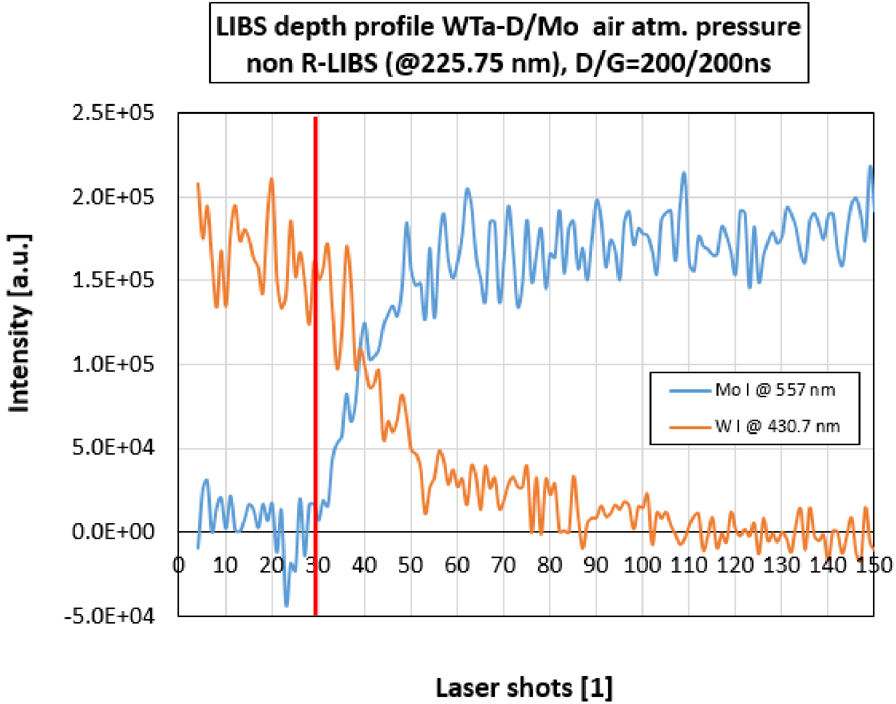


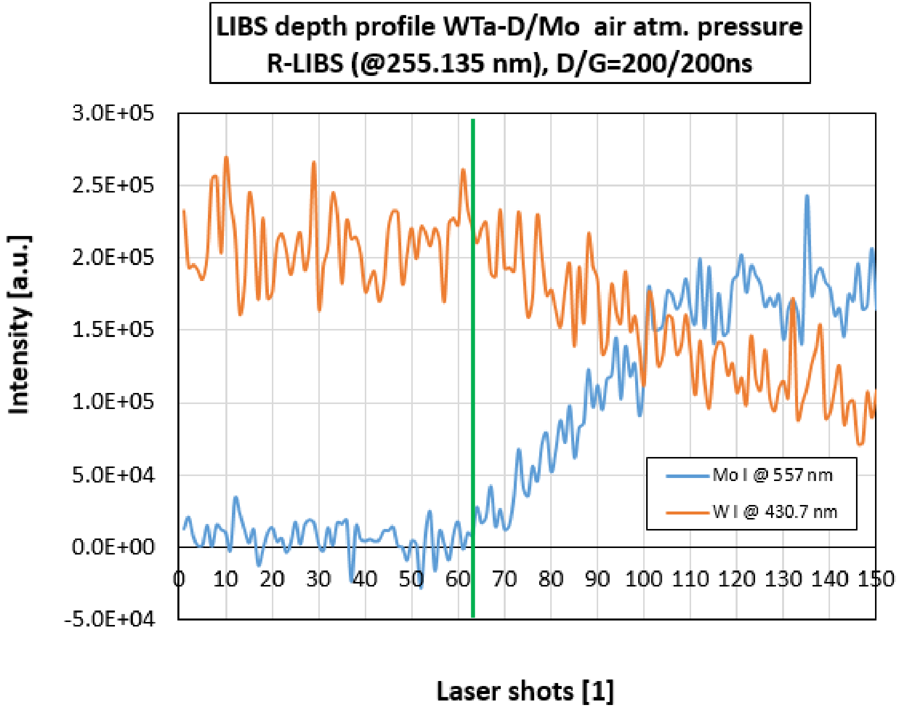
Laser energy profile at resonance
Average energy- 1.43 mJ



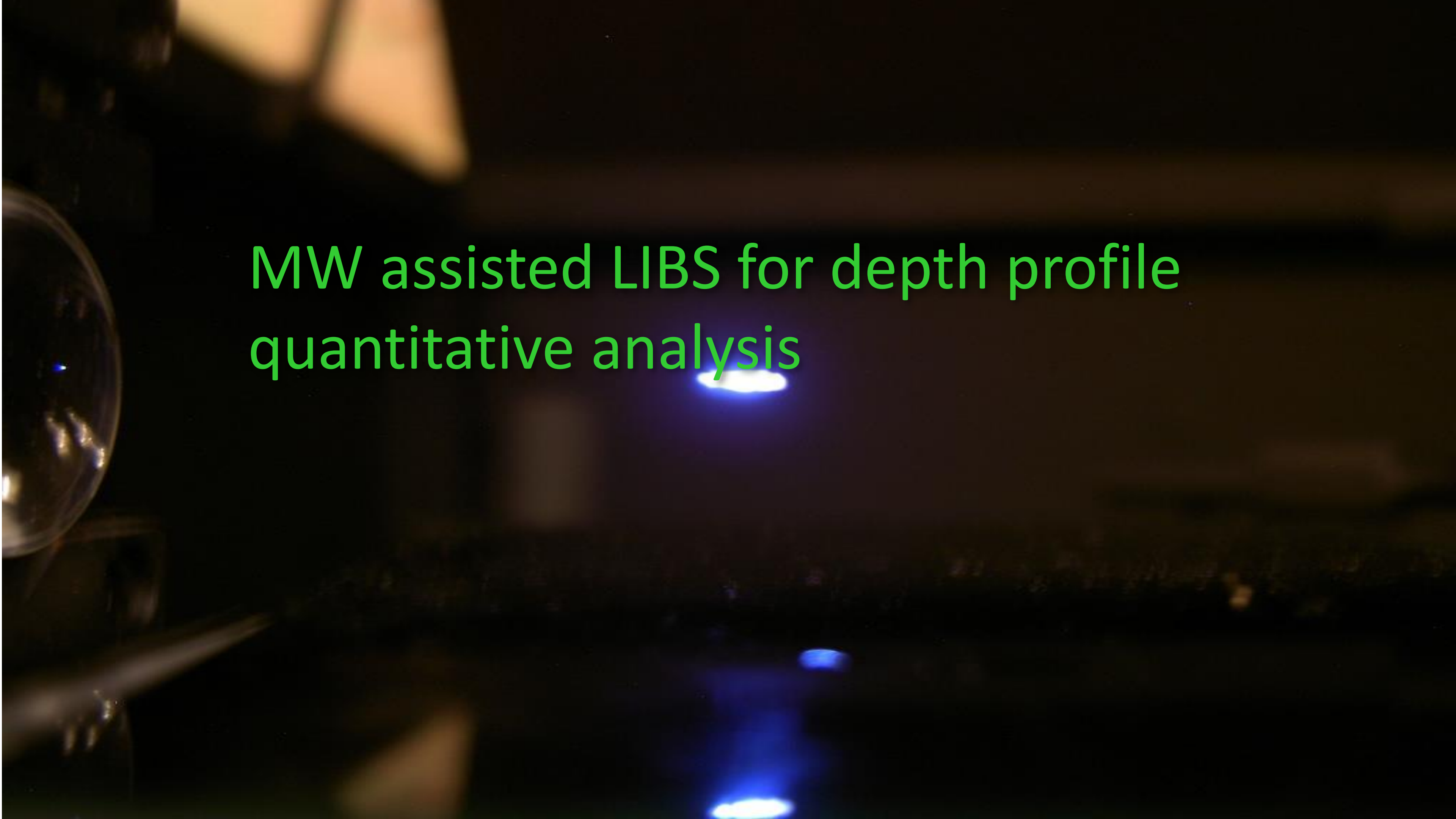
Resonant - LIBS depth profile analysis of WTa/Mo samples

- ✓ R-LIBS and non R-LIBS depth profile for sample WTa/Mo (4 µm)
- ✓ Ablation rate more than 2 times less in the case of RESONANT LIBS giving the same plasma emission





MW assisted LIBS for depth profile quantitative analysis



Microwave assisted LIBS

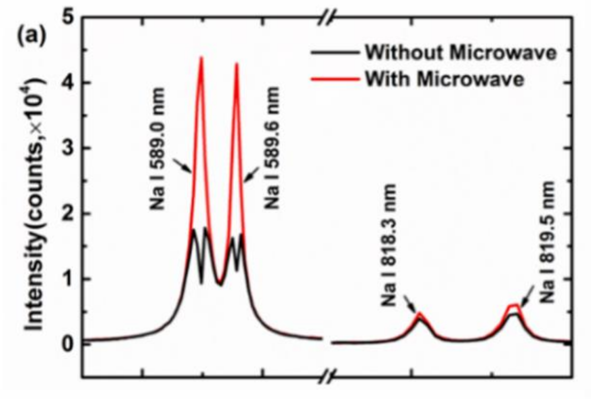
The presence of the MW radiation:

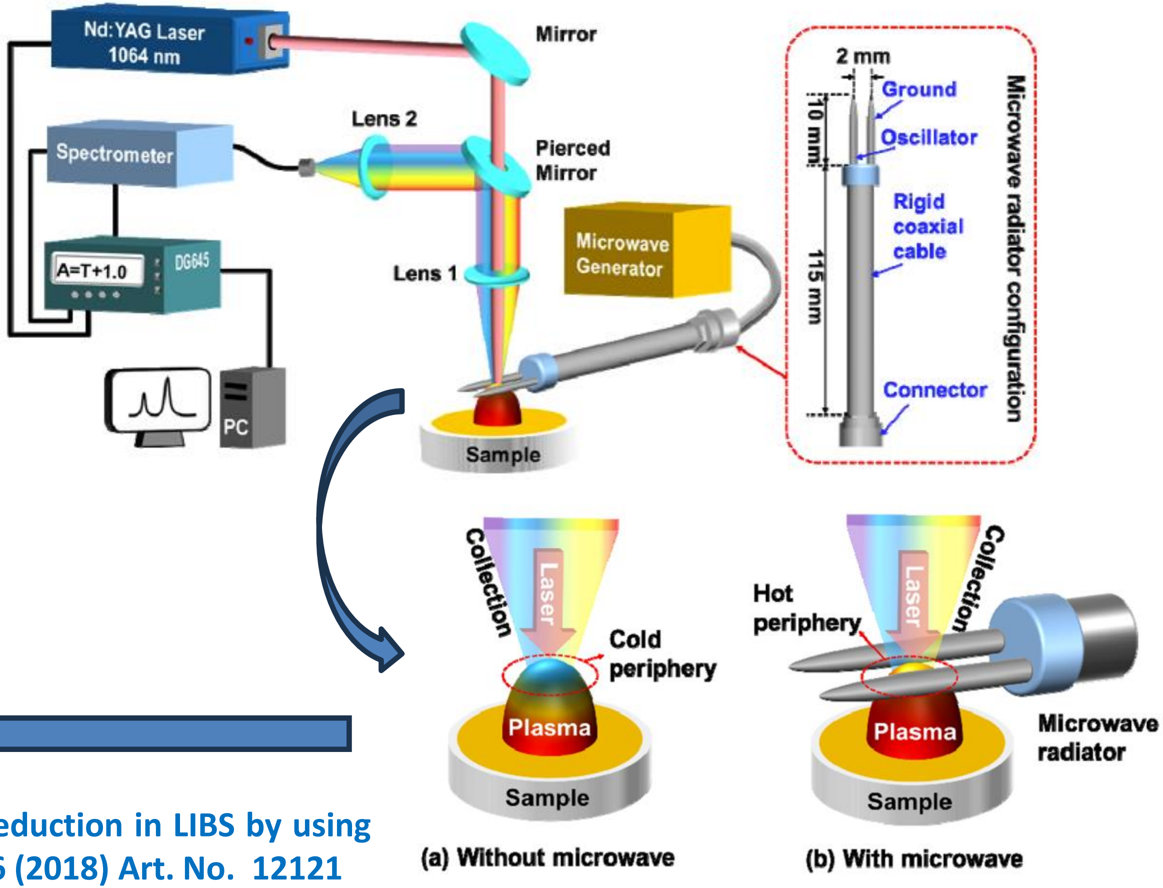
1/ extends the plasma lifetime

2/ increases the plasma size

3/ resulting in **improvement** in sensitivity **by a factor of 10x to 1000x** depending on the sample

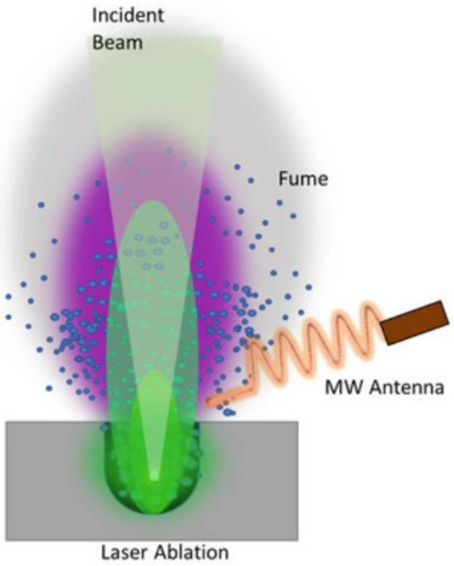
4/ and self-absorption reduction.

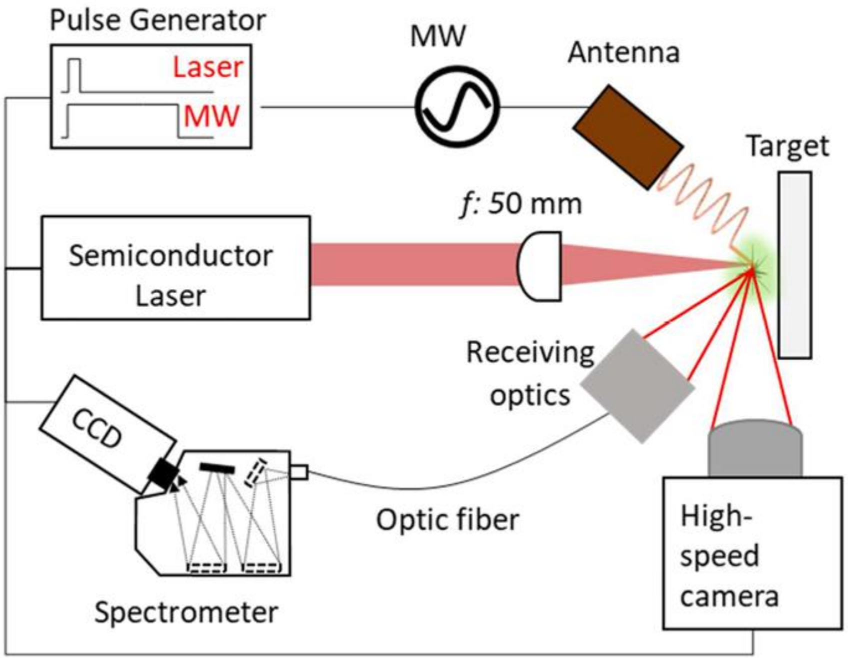




Y. Tang et al., Multielemental self-absorption reduction in LIBS by using MW assisted excitation, OPTICS EXPRESS Vol. 26 (2018) Art. No. 12121

Microwave assisted LIBS

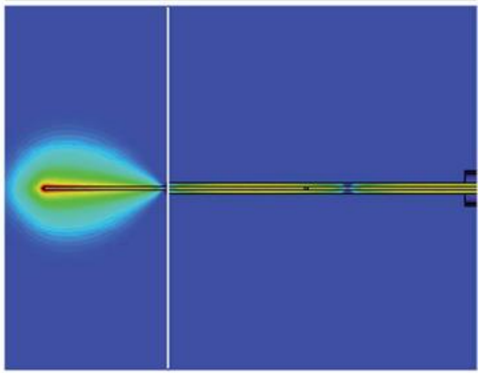


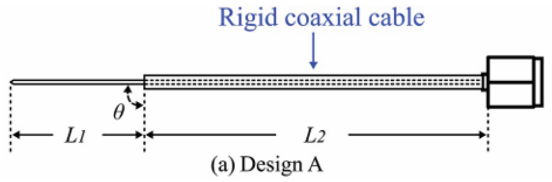


Different types of the antenna:
capacitor-like antenna (Antenna No. 1),
square-shaped flat spiral antenna (Antenna No. 2),
circular shaped flat spiral antenna (Antenna No. 3),
octagonal-shaped flat spiral antenna (Antenna No. 4),
directly mounted helical coil (Antenna No. 5),
bent-mounted helical coil (Antenna No.6),
conical spiral antenna with an increasing diameter (Antenna No. 7),
conical coil with decreasing diameter (Antenna No.8).

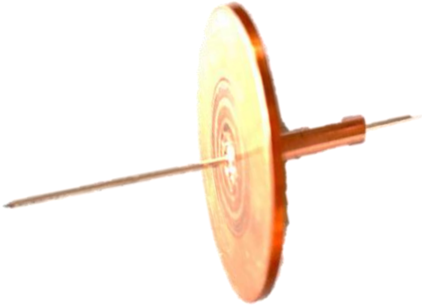
Y. Ikeda et al., Antenna Characteristics of Helical Coil with 2.45 GHz Semiconductor Microwave for MW-LIBS, Materials 15 (2022) Art.No. 2851

Microwave assisted LIBS – antenna shape

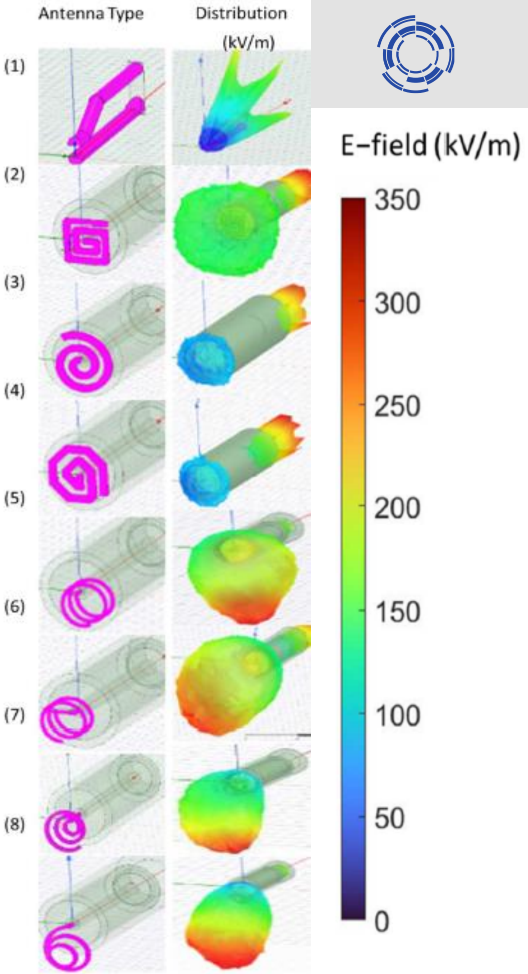




S.J. Chen, Z.T. Alwahabi et al.,
JAAS 32 (2017) 1508-1518



S. Soni, P. Veis et al.,
Comenius Univ.

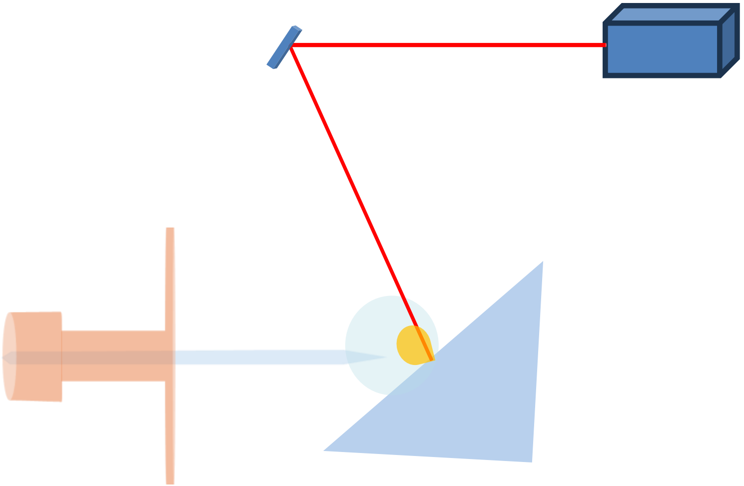


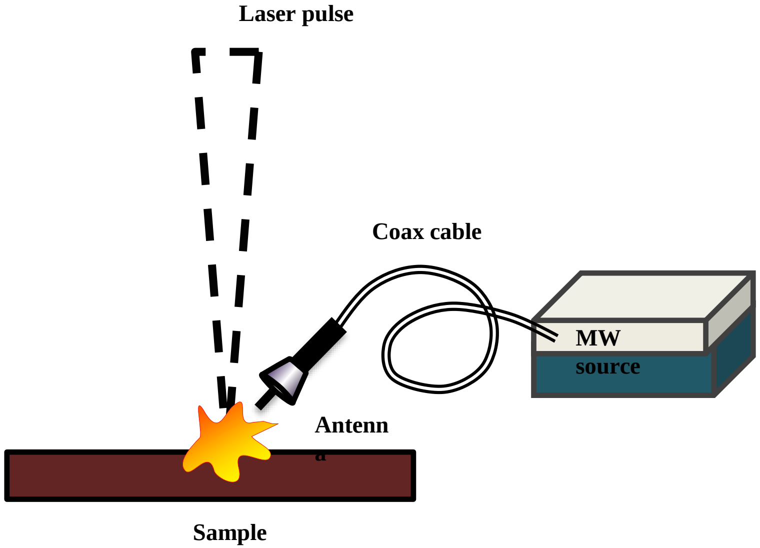
Y. Ikeda et al., Materials , 15 (2022) 2851.

Microwave assisted LIBS – solutions, setup

Microwave sources

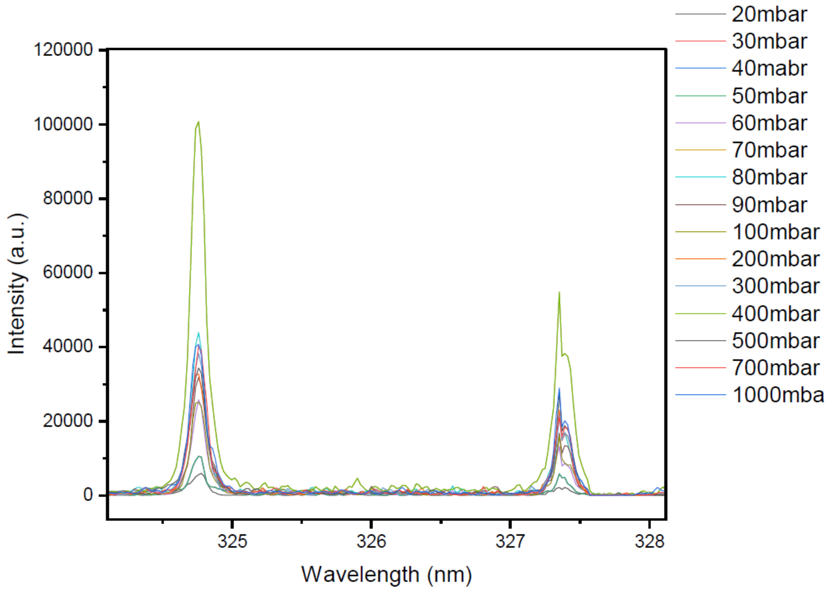
Magnetron source	**Solid-state electronics based**
Well explored	Compact
High power output	Flexible
Bulky	Cost-effective
Expensive	Antenna based
Less flexibility	Coax cable MWF guiding

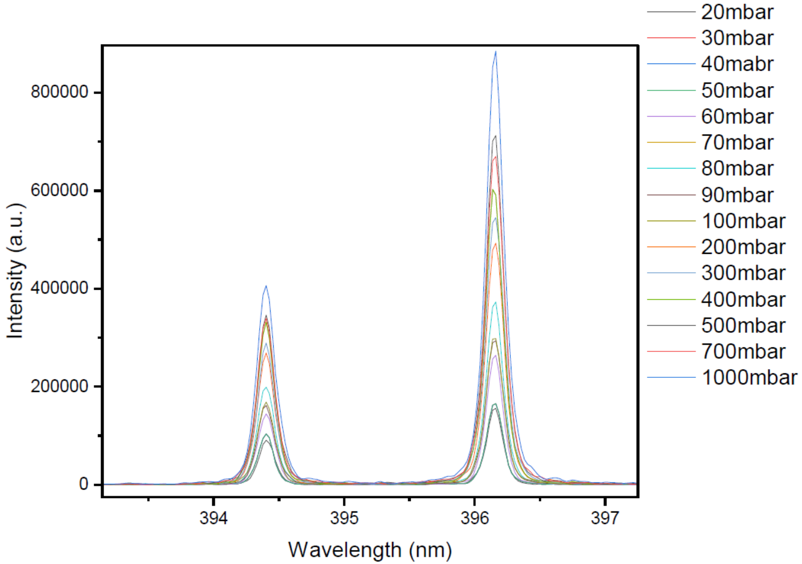




Microwave assisted LIBS – first observations

- The maximum power output = 50W
- F= 2.434 GHz

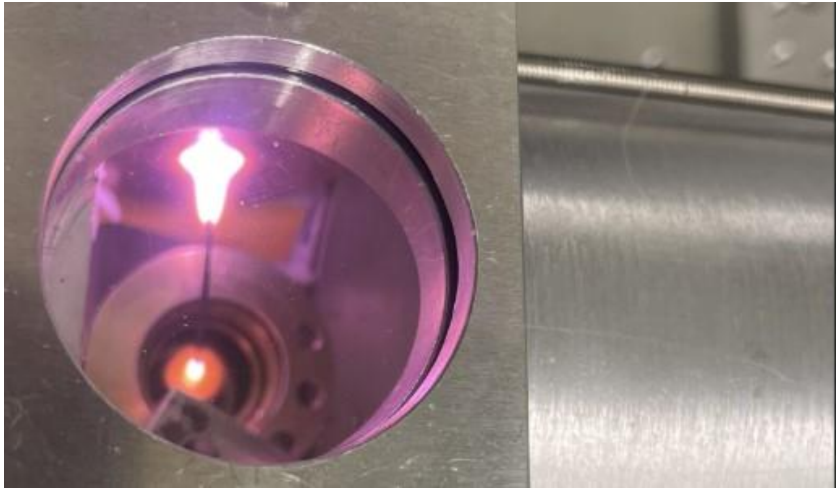




- Detected also Cu sputtered from antenna at different Ar pressure
- Al enhancement with MW-LIBS at different pressure

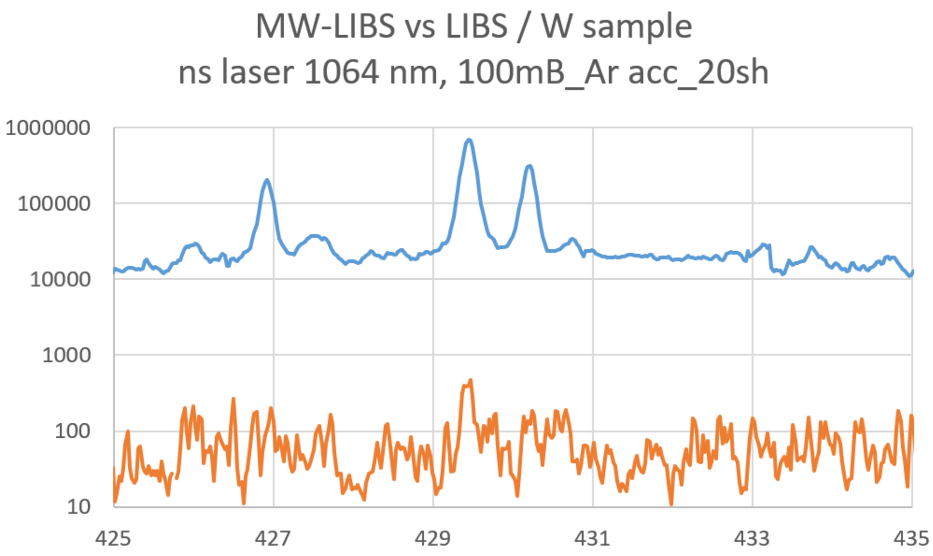
Microwave assisted LIBS – photos

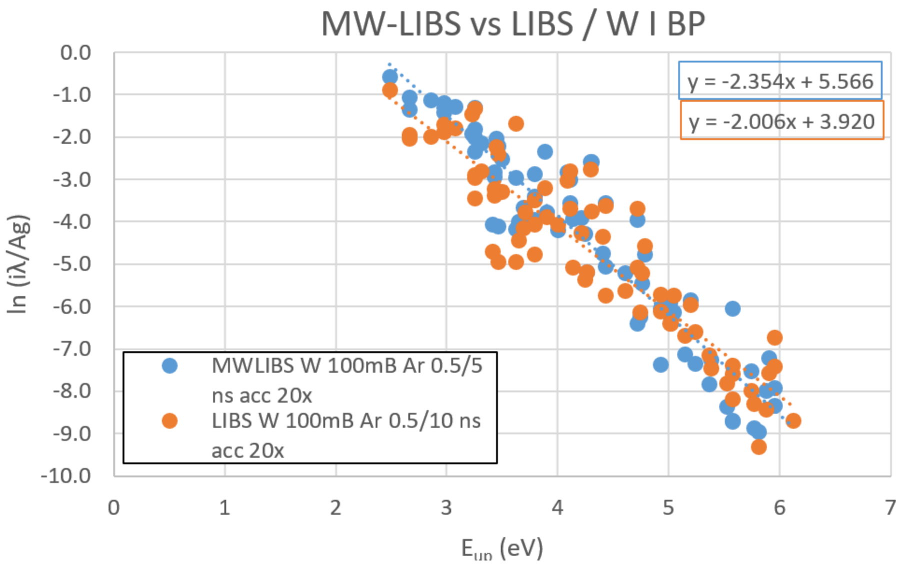
- At low Ar pressure



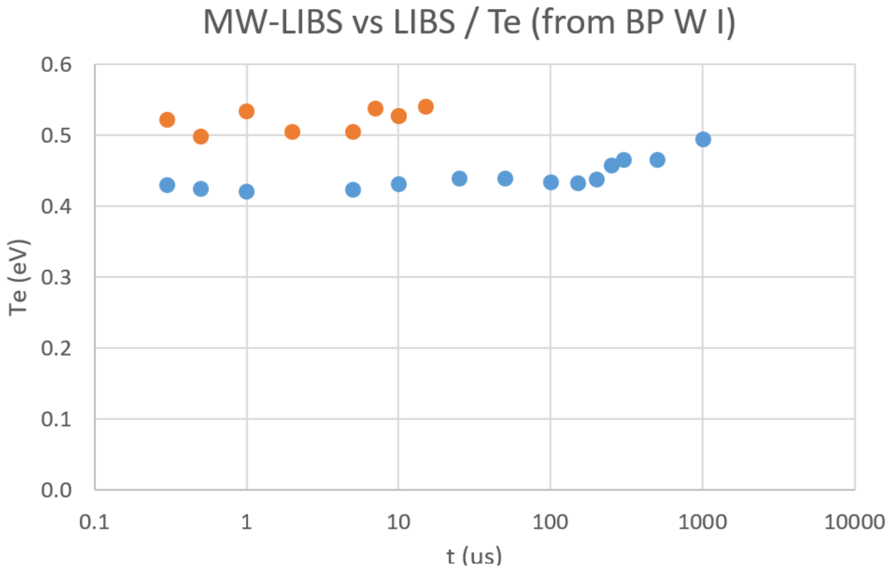
- At atm. Pressure - Ar

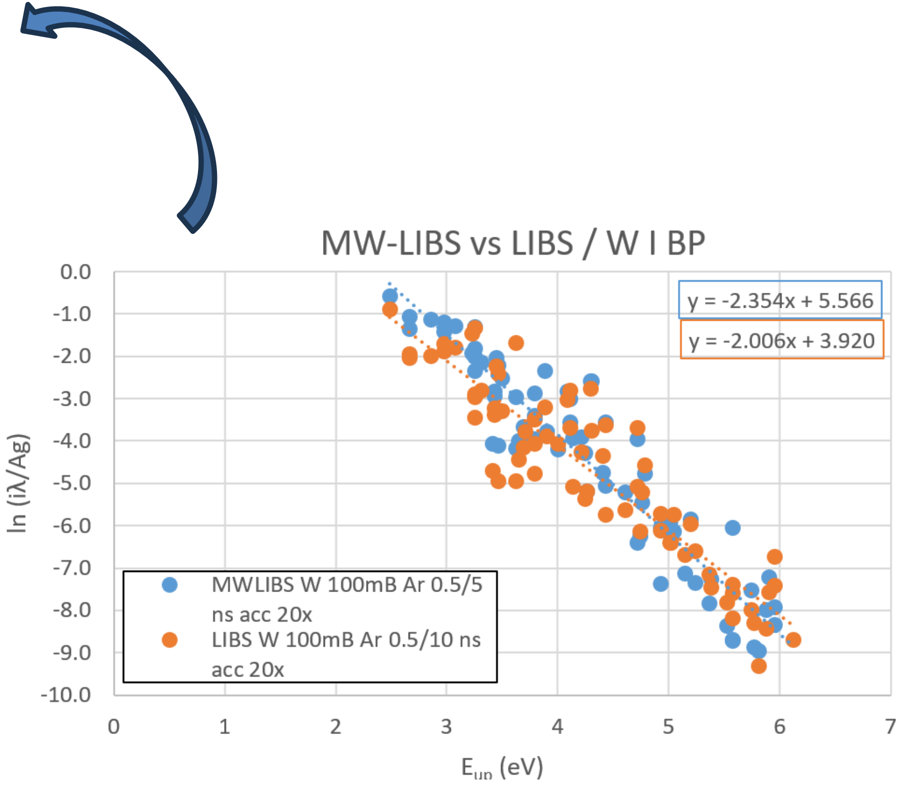
Microwave assisted LIBS – W sample



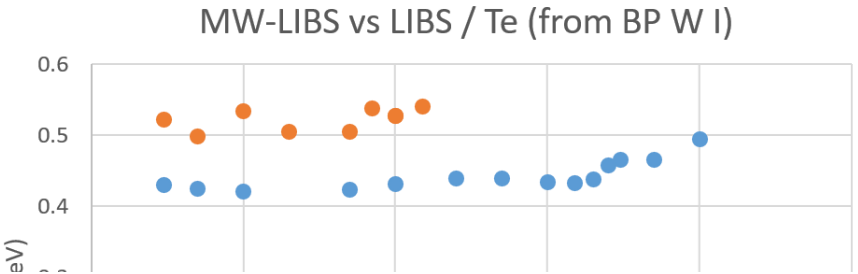


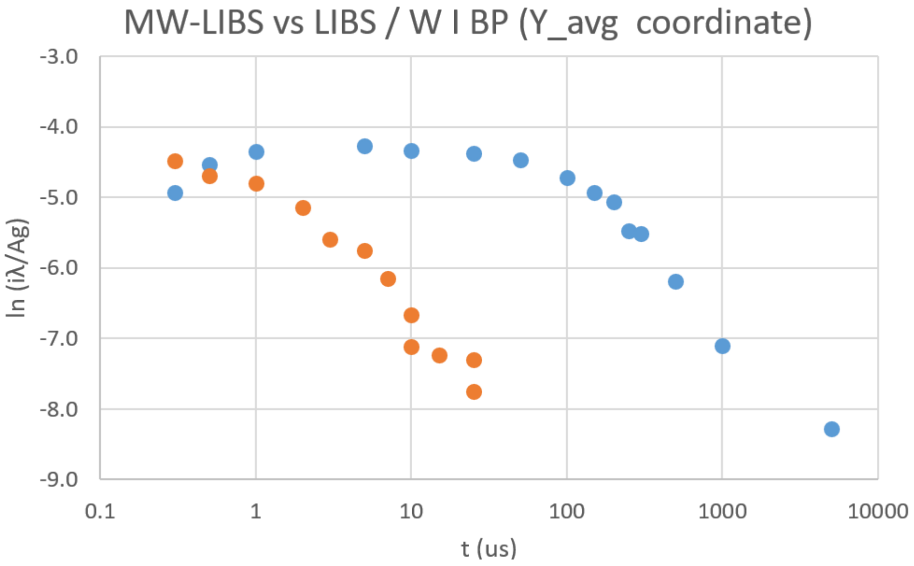
Microwave assisted LIBS – W sample

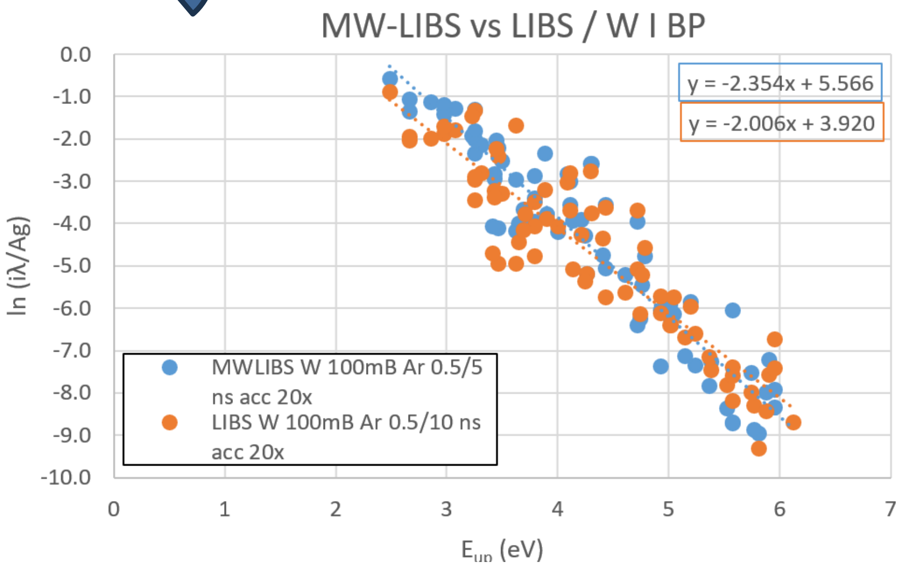




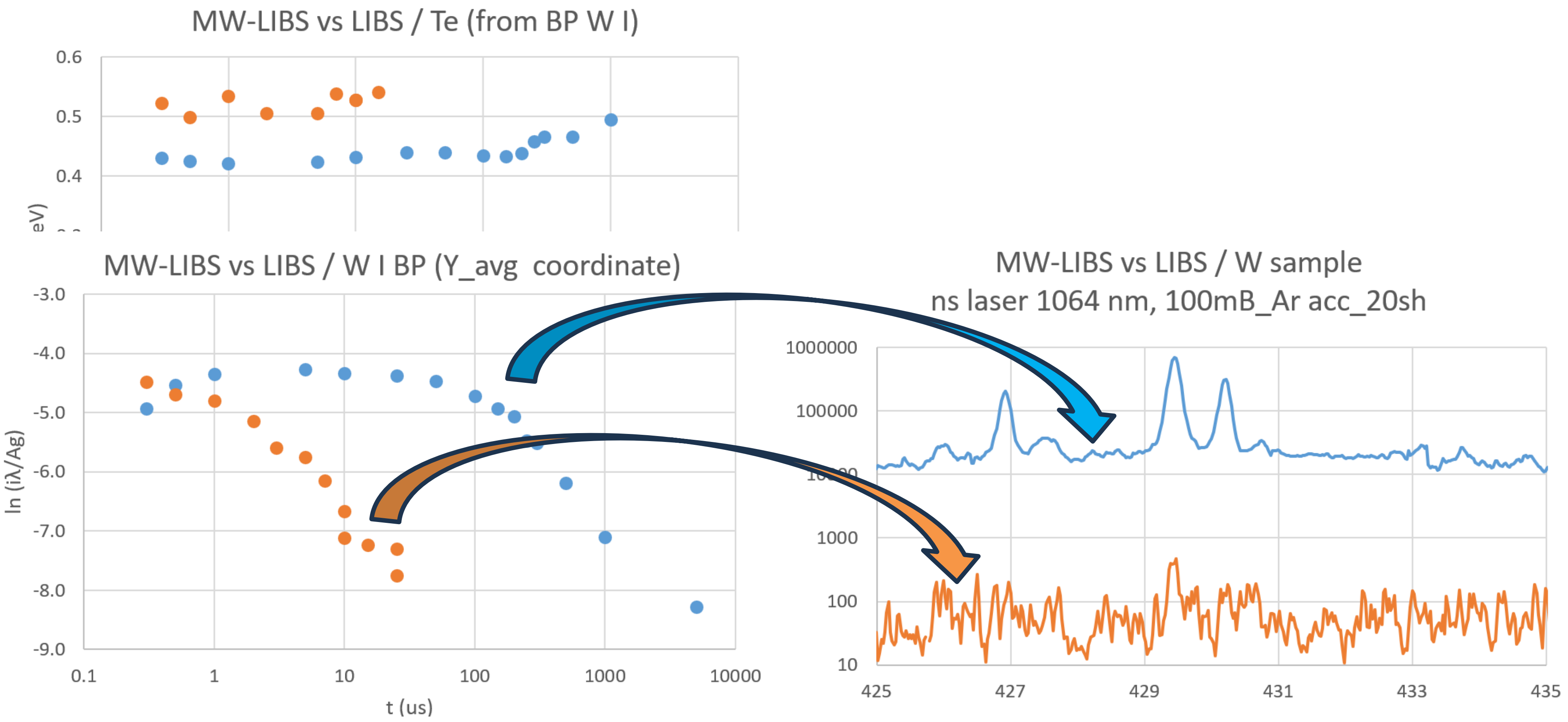
Microwave assisted LIBS – W sample







Microwave assisted LIBS – W sample



Conlclusion

- **Bulk, surface and depth profile analysis in combination with CF LIBS for quantification at intermediate and atmospheric pressure (including Ha/Da isotope line separation).**
- **Comparison of ps- and ns-LIBS.**
- **Re excitation, improvement of OES and minimisation of ablation rate by Resonant LIBS.**
- **Strong improvement of OES by MW LIBS.**

Thank you very much for your attention!

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