WP-PWIE Review Meeting 17-21 November 2025

Optimization of the LIBS technique in air, He, and Ar at atmospheric pressure for hydrogen isotopes detection on tungsten coatings

Salvatore Almaviva

ENEA, Italian National Agency for New Technologies, Energy and Sustainable Economic Development

This work has been carried out within the framework of the EUROfusion Consortium, funded by the European Union via the Euratom Research and Training Programme (Grant Agreement No 101052200 — EUROfusion). Views and opinions expressed are however those of the author(s) only and do not necessarily reflect those of the European Union or the European Commission. Neither the European Union nor the European Commission can be held responsible for them.

Summary

- Introduction and motivation
- The Double-spectrometer LIBS system at ENEA Frascati
- Detection of D by LIBS on a D enriched W coating under air, Ar and He as background gas
- Calibration free (CF) procedure for the estimation of the D content

- Conclusions

Introduction and motivation

- It is well known that one of the problems of current and future generation tokamaks that will operate with a D+T plasma is the retention of tritium on PFCs.
- The "post-mortem" analysis techniques used to date for the characterization of PFCs and their tritium content could be, in the future, fruitfully combined with laser-based techniques, capable of carrying out chemical analyses and detect tritium *in-situ,* in real time, without the need to take samples from the first wall, increasing the duty cycle of the fusion machine.
- Among these techniques, LIBS can perform chemical analyses of PFCs in different areas of the first wall, up to a depth of several tens of microns studying the in-depth chemical composition of the samples and reveal the presence of T due to the processes occurring in the vicinity of the fusion plasma (erosion, re-deposition, implantation etc.).
- The detection of tritium by LIBS is accomplished by recording the spectral emission of the Balmer alpha line (T_α) located at approximately 656.045 nm.
- Detecting T or other hydrogen isotopes (D or H) is for LIBS substantially equivalent in terms of spectral signal, therefore it is possible to perform in-lab measurements on samples without T but with D (or H) in safety conditions, obtaining useful information for the detection of T on real PFCs.
- However, in presence of a low content of T and in simultaneous presence of D and H, with Balmer alpha emissions at 656.1 (D_α) and 656.28 nm (H_α), the T_α line can be hidden and difficult to resolve from the other two, thus methods of signal and spectral resolution enhancement are advisable.
- One of these method is based on the use of background gases that provide LIBS plasmas with different properties than in air.
- Here we have studied the LIBS plasmas in He and Ar as background gases and compared the obtained LIBS spectra in terms of spectral resolution to optimize the detection of all the Hydrogen isotopes.

Ar and He: Differences and similarities mechanisms to increase spectral resolution and SNR in LIBS

Ar

- **Plasma Confinement**: Due to its higher atomic mass and lower thermal conductivity Argon reduces the rapid expansion and cooling of the laser-induced plasma plume keeping the plasma hotter and denser for a longer duration.
- **Increased Collisions and Excitation**: The higher density of the confined plasma results in an increased number of collisions between the excited species (atoms and ions). This promotes more efficient excitation and subsequent de-excitation, leading to a stronger emission of the LIBS signal.
- **Inert nature and reduced Oxidation**: As an inert noble gas, Ar does not react with the ablated species and displaces Oxygen, Nitrogen and environmental Hydrogen from the analysis area, preventing the formation of oxides and nitrides that can reduce the signal from the target elements and limiting the interference of H.
- **Higher Plasma Temperature and Electron Density**: The enhanced signal intensity is directly attributed to the increase in plasma temperature and electron density under the argon environment.
- **Reduced Background**: Argon high ionization potential produces less background emission (continuum radiation) than air improving the SNR.

Using Argon as ambient gas increases the life of the LIBS plasmas increasing the signal intensity and precision of LIBS measurements, which is especially important for the detection of trace elements.

He

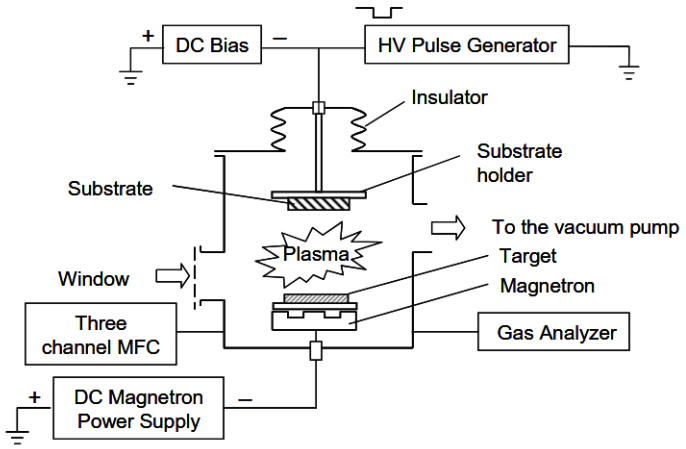
similarities

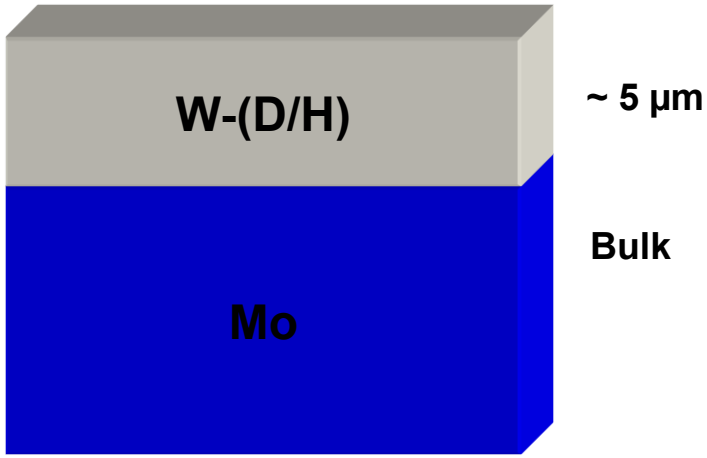
differences

- **Reduced Electron Density and Stark Broadening**: the primary reason for improved resolution is that plasma generated in a helium atmosphere generally has a lower electron density and lower temperature compared to plasmas in other gases like argon or nitrogen at the same pressure. Lower electron density in helium results in narrower spectral lines and thus better resolution.
- **Lower Thermal Conductivity**: Helium has high thermal conductivity at low pressures, which can cool the plasma more quickly, at atmospheric pressure this effect leads to a shorter-lived, more confined plasma plume. This imply the use of shorter time delays for detection, which is important for capturing rapidly decaying emission signals with higher efficiency.
- **Reduced Background**: As in the case of Argon Helium's simple atomic structure and high ionization potential produces less background emission (continuum radiation) than air improving the SNR.
- **Inert Nature**: As in the case of Argon, Helium is an inert noble gas. It does not react with the ablated sample material or the plasma species, which maintains the integrity of the emission signals.

Using Helium as an ambient gas in LIBS leads to a "cleaner," less dense plasma, which minimizes spectral interference and produces sharper, more resolved analytical lines, particularly at appropriate gate delays.

Sample preparation and composition



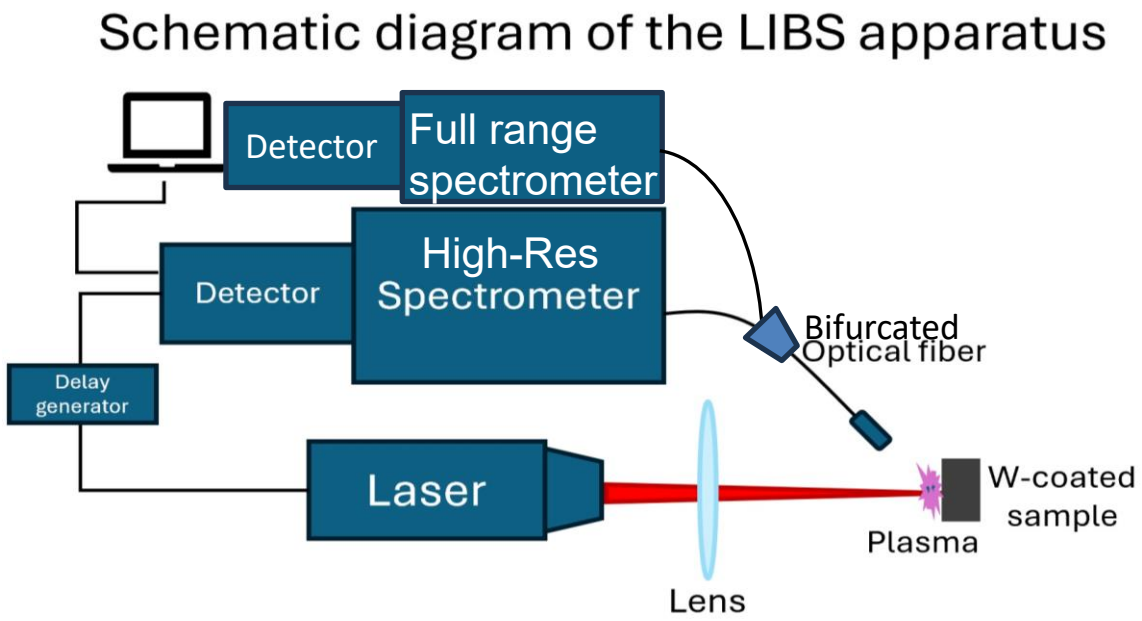


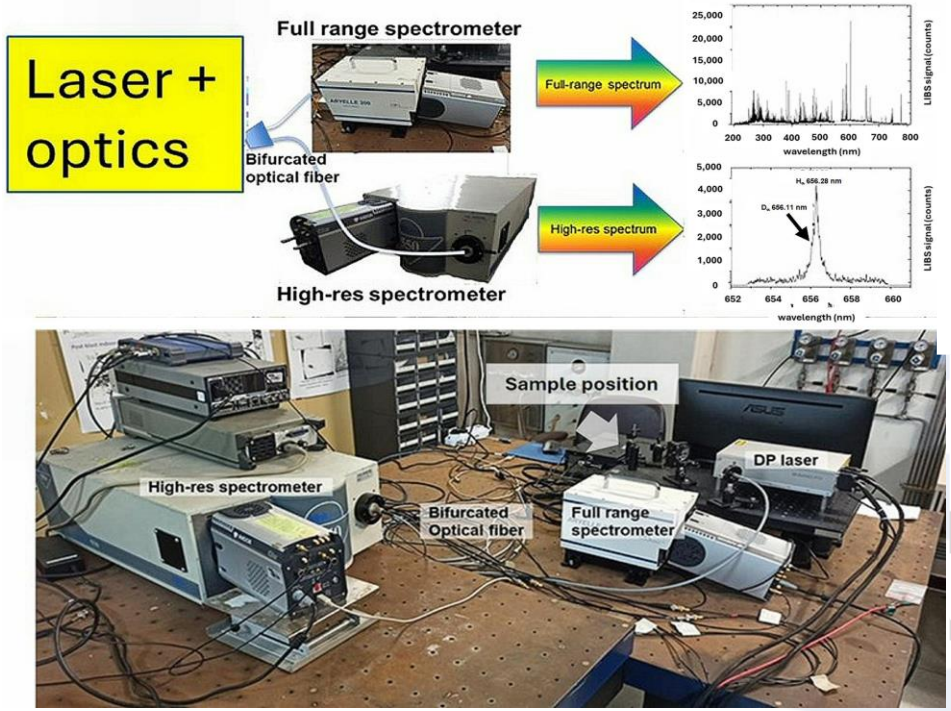
Samples simulating co-deposits of W, with D/H were produced at the National Institute for Laser, Plasma and Radiation Physics in Romania (NILPRP) by Combined Magnetron Sputtering and Ion Implantation (CMSII). The CMSII technique involves simultaneous magnetron sputtering and high energy ion bombardment. The samples consist of a rectangular Molybdenum (Mo) metal plate 11x15 mm^2 area, 1 mm thick, with a W surface layer (co-deposited with D/H), 5 µm thick, on a Mo substrate.

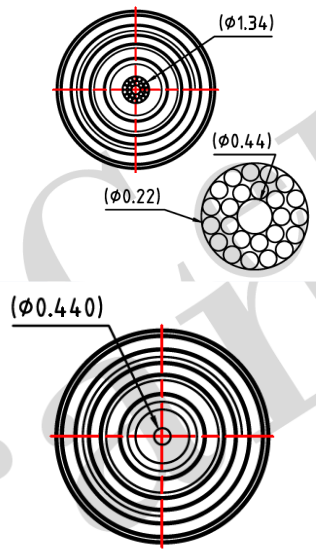
The two-spectrometers LIBS system at ENEA (Similar to the JET system)

Double spectrometers LIBS system:

1. **High Resolution:** ISA Jobin Yvon "TRIAX550" Czerny–Turner, 2400 gr/mm grating ($\lambda/\Delta\lambda$ = 50,000) resolution @ 656 nm ≈ 0.013 nm, enough to resolve the D_α - H_α - (T_α) lines. Detector: Andor "ISTAR" ICCD camera DH534-18 F (1024 × 256 pixels)
2. **Full range:** LTB "Aryelle 100" spectrometer. Spectral range (225–760 nm), resolution up to 9000. Detector: Andor "ISTAR" ICCD camera DH334T-18 F (1024 × 1024 pixels)
3. **Source**: Nd:YAG double-pulse laser (wv = 1064 nm; τ = 8 ns; f_{max} = 20 Hz; spot ø ≈ 3 mm, max pulse energy 65 (+65) mJ, min interpulse delay = 65 ns).
4. **Lenses**: focusing lens (PCLX ø ≈ 25 mm, f = 100 mm). Collection lens (PCLX ø ≈ 25 mm, f = 150 mm, UVFS).
5. **Fiber:** 2m long bifurcated optical fiber; 1st branch 24 N.A 0.22 fibers, ø ≈ 200 μm, 2nd branch 1 N.A. 0.22 fiber, ø ≈ 400 μm

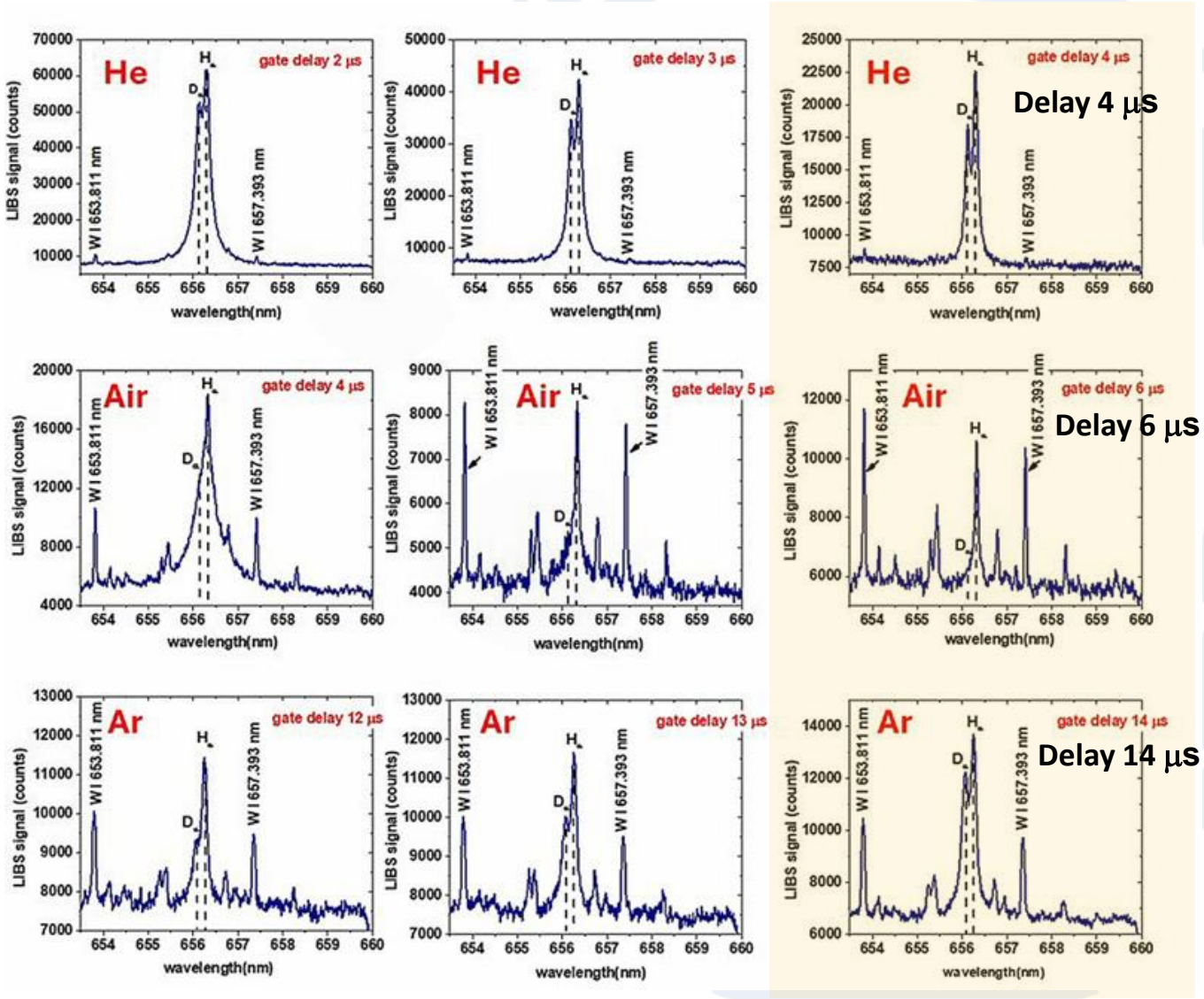






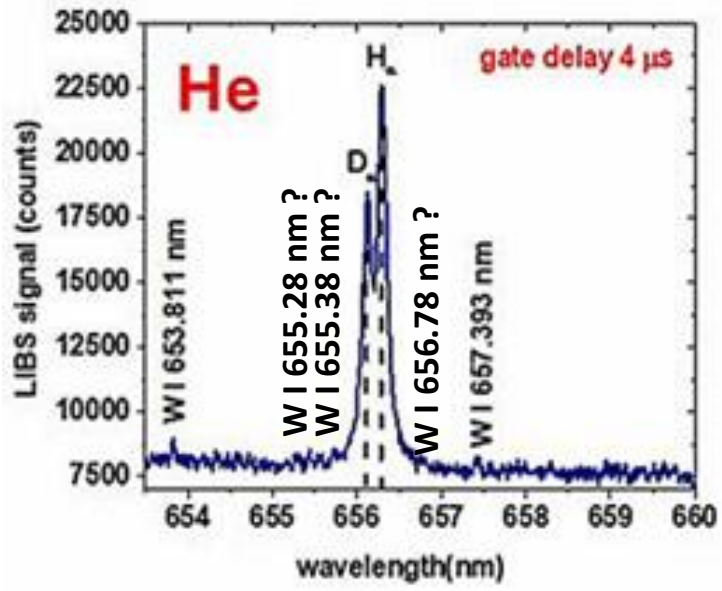
Results: High-res LIBS spectra of the D_α and H_α peaks

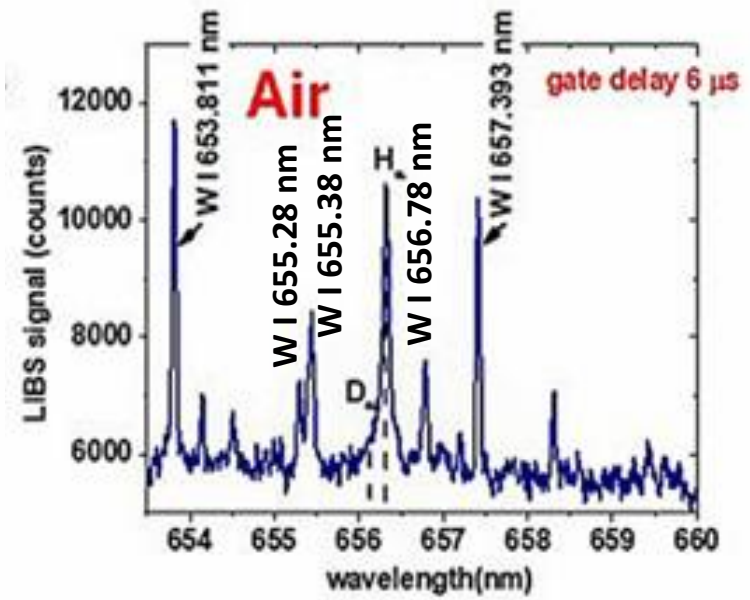
- The W-D sample was used to optimize the detection of D in presence of the H emission from the environment (water vapour), fluxing the two background gases (He and Ar) at 2l/min on the sample surface and comparing the signal with respect to LIBS in air.
- Parameters: pulse energy 50 mJ, rep. rate 2 Hz, gate width 3 µs, gate delay optimized for each gas to obtain the maximum resolution of the two D_α and H_α peaks.
- ***He gas*: Better results at shorter gate dealys with respect to air → Reduced Electron Density and temperature → reduced Stark Broadening**
- ***Ar gas:* Better results at longer gate delays with respect to air → The longer lifetime of the LIBS plasma and the higher SNR allows to move at longer gate delays balancing the increased Stark broadening still preserving a good SNR**

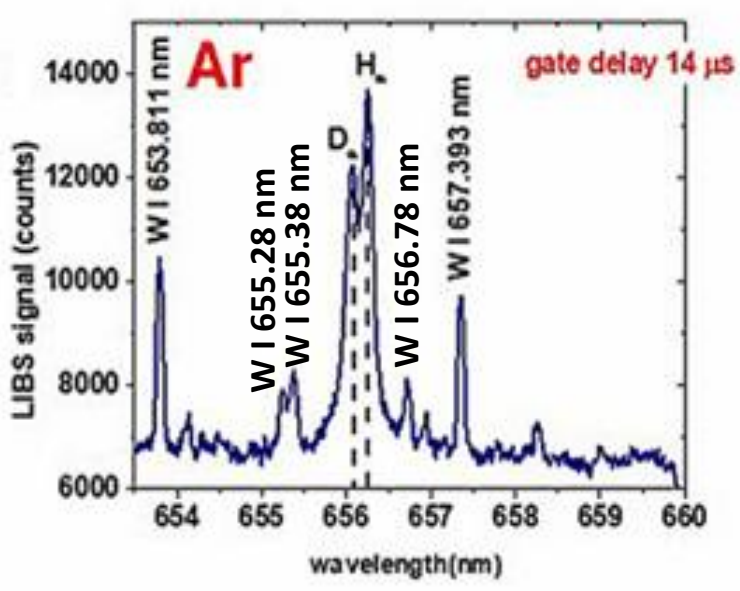


Results: High-res LIBS spectra of the D_α and H_α peaks

The spectral emissions of atomic tungsten lines at 653.811 nm, 655.28 nm, 655.38 nm, 656.78 nm, 656.97 nm, and 657.18 nm are clearly detectable in the case of Ar and air plasma, while they are poorly detectable in the case of He plasma. This result agrees with previous results in literature, the reason being that T_e and n_e decay more rapidly in He environment compared to Ar and air because of the higher higher thermal conductivity of He than Ar and air → The condition of a stable and "long" (μs…) Local Thermodinamic Equilibrium (LTE), necessary for the quantitative estimation of the elements is harder to reach in case of He gas.







Results: High-Res LIBS spectra of the D_α and H_α (and T_α peaks)

To quantitatively estimate the capability of resolve the two D_α and H_α peaks in the case of He and Ar, the ratio between the width of the two peaks and their spectral separation was taken into consideration according to the formula currently applied in chromatography to evaluate the resolution of two nearby peaks:

$$R_S = \frac{2 \cdot \Delta\lambda}{(w_{D\alpha} + w_{H\alpha})}$$

where $\Delta\lambda$ is the spectral separation of the two peaks (0.18 nm), and $w_{D\alpha}$ and $w_{H\alpha}$ are the FWHMs of the two peaks, obtained fitting them with two Lorentzian functions.

Background Gas	Gate Delay (μs)	R_s (D_α – H_α)
He	2	0.95
He	3	1.15
He	4	1.52
Ar	12	1.12
Ar	13	1.15
Ar	14	1.31

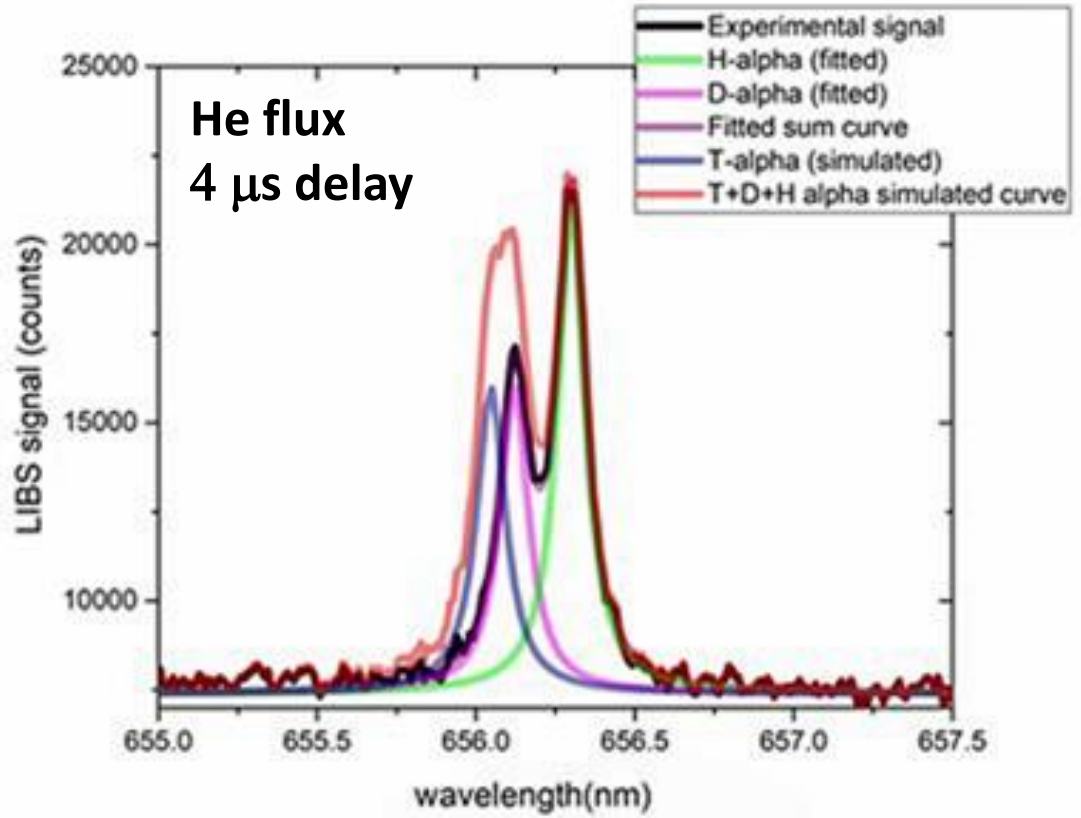
short-living plasma make the peaks width (and R_s) quickly changing

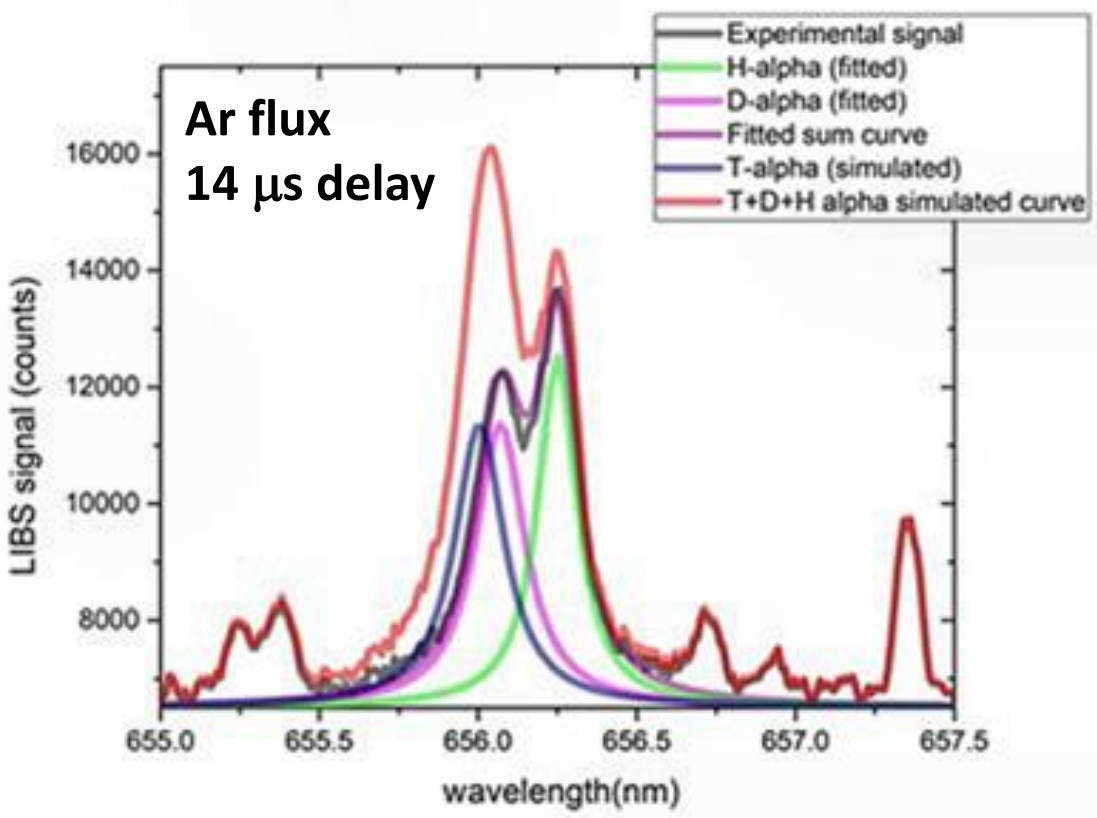
long-living plasma make the peaks width (and R_s) more stable

Results: simulation of a H+D+T spectrum

Starting from these values, we estimated the resolution that would be obtained if the T_α line were present with the same concentration as deuterium. The T_α line (656.045 nm) is expected to have the same linewidth as the Dα line, with a spectral separation $\Delta\lambda = 656.1–656.045 = 0.055$ nm.

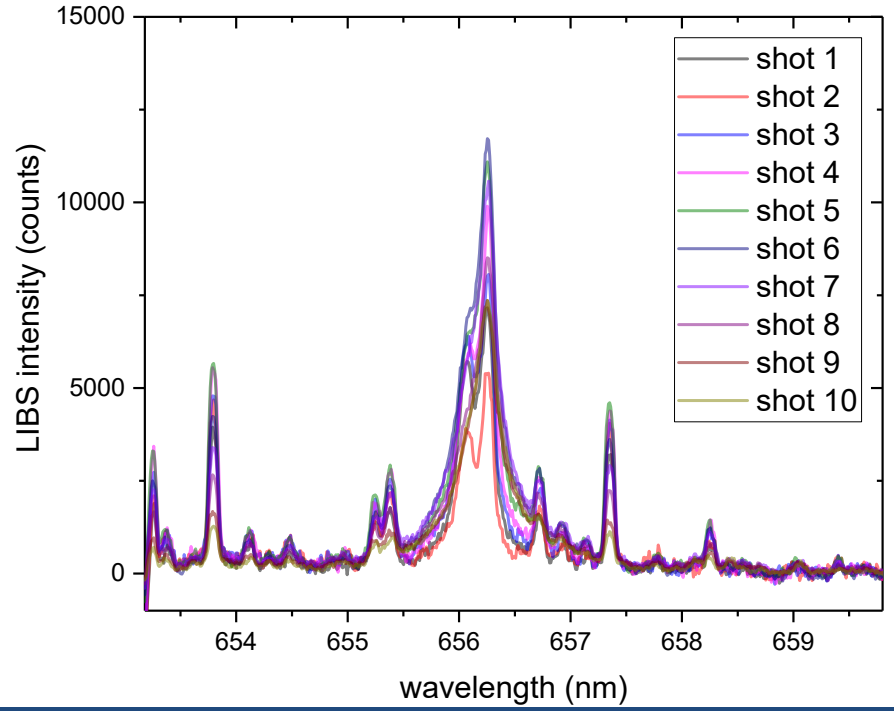
A simulation of the LIBS signal in the presence of T was performed by adding to the experimental signal an additional, hypothetical T_α peak, centered at 656.045 nm with the same FWHM and intensity of the experimental D_α peak → to resolve the peaks longer delays (lower electron density) is necessary.

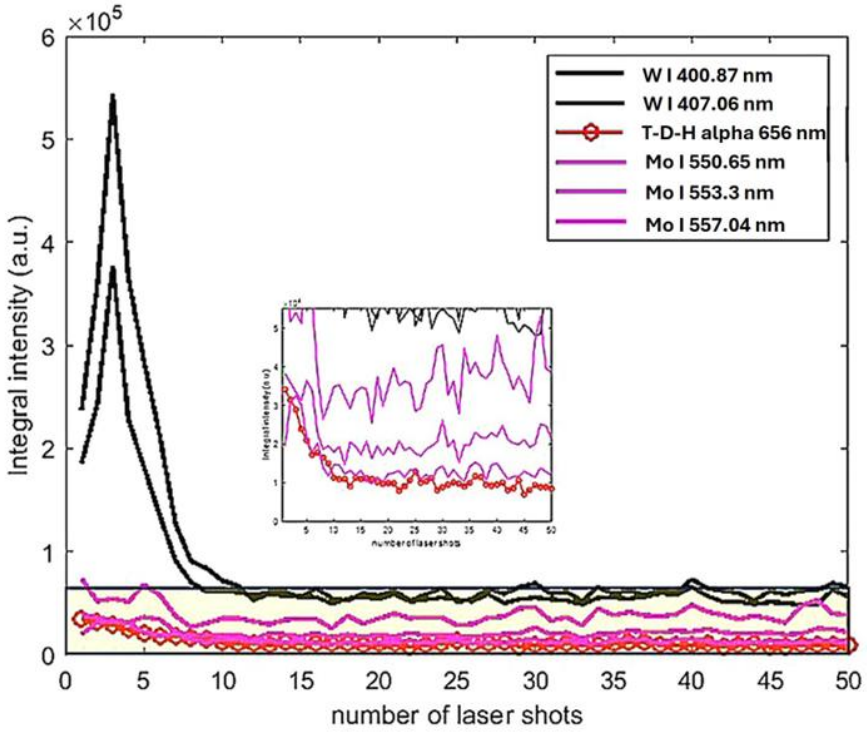




Results: depht profiling analysis

- Depth profiling analysis in LIBS is an analytical technique used to determine the elemental composition of a material as a function of its depth from the surface, by sequentially ablating thin layers of sample delivering a series of laser pulses in the same point and analyzing the elemental composition of the plasma generated by each pulse.
- Depth profiling was applied delivering 50 subsequent laser shots on the same point to estimate the average ablation rate of the superficial W layer with D using both the spectra acquired with the Echelle spectrometer and the TRIAX 550 monochromator
- After 10 laser shots the W signal related to the two lines dropped sharply suggesting that the 5 μm thick W coating was completely ablated -> **average ablation rate ≈ 500 nm/shot**





Results: CF-LIBS analysis

- The CF technique is a methodology used for a quantitative estimation of the chemical species present in a LIBS spectrum by using the experimental line intensities
- CF was applied to the series of spectra in Ar as a background gas with gate width 3 µs and gate delay of 14 µs because well-resolved $D_\alpha - H_\alpha$ emission lines were detected as well as W I emission lines at 653.811 nm and 657.393 nm; therefore, the quantitative estimation of D and H with respect to W was feasible.
- In CF-LIBS the laser-induced plasma is required to be optically thin and in local thermo-dynamic equilibrium (LTE). In these conditions, the line integral intensities of the emission lines are related to the concentration of the species through the following expression:

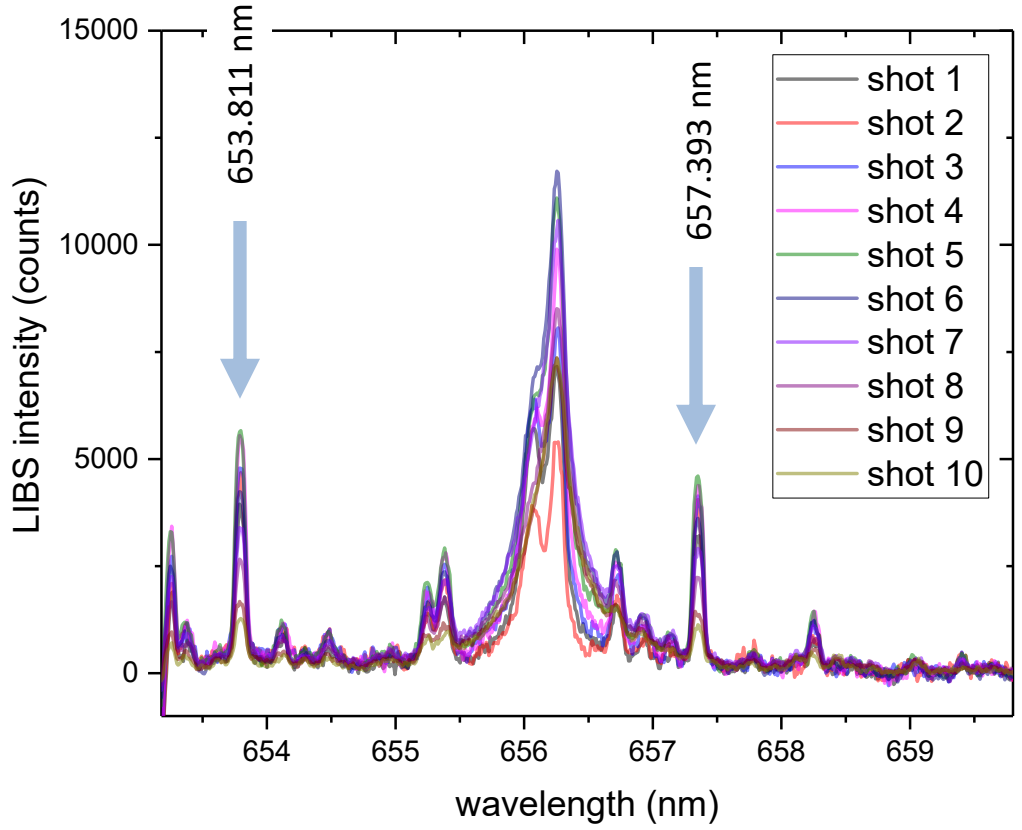
$$I_{ki} = C_s A_{ki} g_k \frac{e^{-(E_k/k_B T)}}{U_s(T)}$$

- The optical thinness of the LIBS plasma is generally evaluated from the intensity ratio of two lines of the same chemical element in the same charge state (ionic or atomic) and should be equal to the following expression:

$$\frac{I_{ki1}}{I_{ki2}} = \frac{A_{ki1} g_{k1}}{A_{ki2} g_{k2}} e^{-\frac{(E_{k1} - E_{k2})}{k_B T}}$$

Results: CF-LIBS analysis

The intensity ratio of the two W I emission lines at 653.811 nm and 657.393 nm, whose spectroscopic parameters were retrieved from the NIST database was used to check the optical thinness of the LIBS plasma. These parameters, together with the theoretical and the experimental intensity ratios, are reported in the table below: theorethical and experimental ratios are comparable → the plasma can be considered optically thin



$$\frac{I_{ki1}}{I_{ki2}} = \frac{A_{ki1} g_{k1}}{A_{ki2} g_{k2}} e^{-\frac{(E_{k1}-E_{k2})}{k_B T}}$$

λ (nm)	A_{ki} (10^{-8} s)	g_k	E_k (eV)	I_1/I_2 (theo.)	I_1/I_2 (exp.)
653.811	2.7×10^{-3}	9	4.354	0.975	1.09
657.393	9.9×10^{-3}	3	4.487		

Results: CF-LIBS analysis

To evaluate the LTE of the LIBS plasma, it is necessary to apply the so-called McWhirther criterion [31], which is a necessary but insufficient condition that can be expressed as follows:

$$n_e\left(cm^{-3}\right)_{min} > 1.6{\cdot}10^{12}T^{1/2}(\Delta E_{ki})^3$$

where T (eV) is the plasma temperature and ΔE_{ki} (eV) is the maximum energy difference between the upper and lower energy levels. In the case of the sample under analysis made of W and H(D), ΔE_{ki} (W atomic) = 2.49 eV, ΔE_{ki} (W ionic) = 4.71 eV and ΔE_{ki} (H/D) = 10.2 eV.

In addition to the above criterium, the condition for the validity of LTE need to be also verified by calculating the diffusion length, *δ (cm),* of the LIBS plasma through the following relation:

$$\delta \approx 1.4 \times 10^{12} \frac{(kT)^{3/4}}{n_e} \left(\frac{\Delta E}{M_A \langle \overline{g} \rangle}\right)^{1/2} e^{\frac{\Delta E}{kT}}$$

with k = Boltzmann constant, M_A the relative mass of the species considered (M_H=1, M_W=184), $< \bar{g} >$ the Gaunt factor and comparing it with the characteristic dimension (length) of the plasma, "*d*", which can be taken as the plasma diameter (≈2-3 mm). If *d > 10 δ* the second condition for LTE is verified

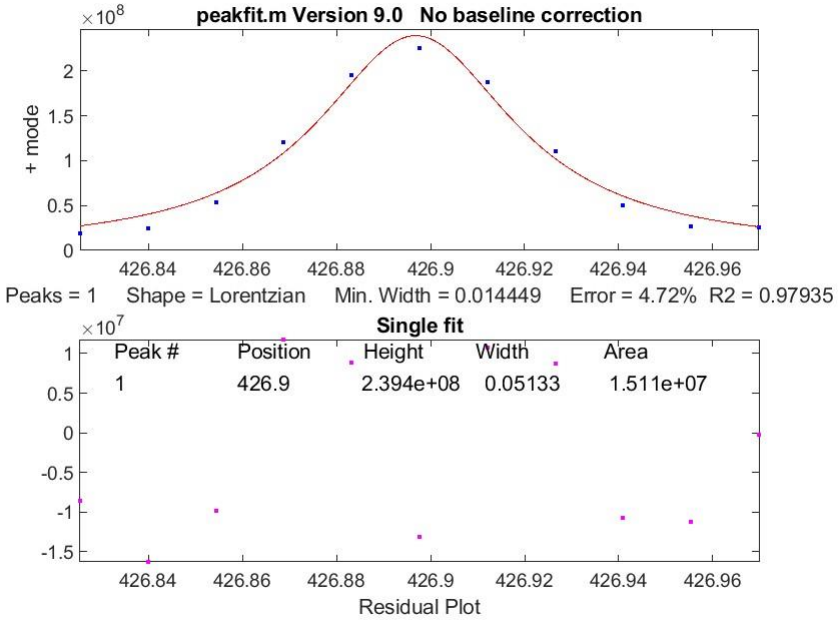
Results: CF-LIBS analysis

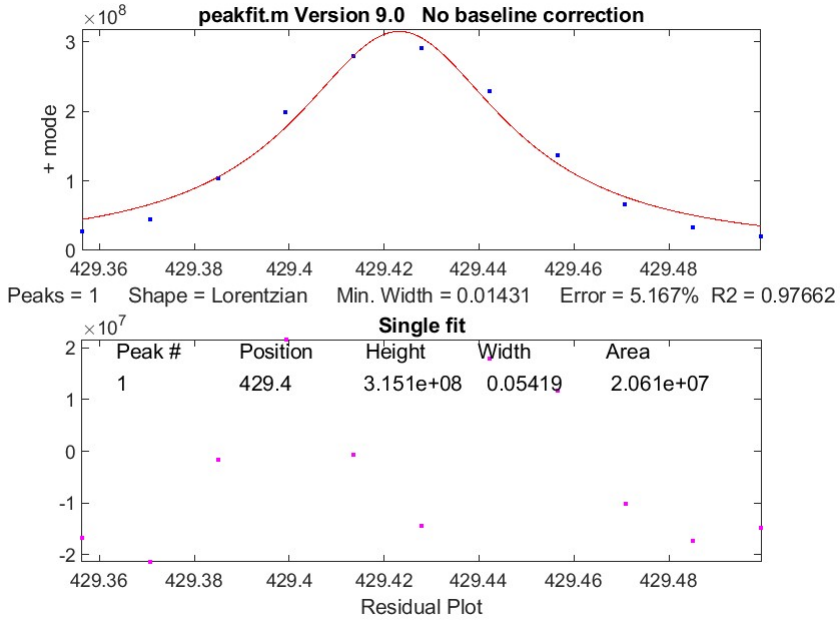
3) Calculation of the electron density of the LIBS plasma exploiting the line broadening of some reference lines of the above-mentioned chemical elements using the MATLAB "peakfit" function. The peakfit function compute the Lorentz width of some reference lines useful for the electron density calculation.

Two tungsten lines have been used in the peakfit function for W-based samples: **typical values for electron density $n_e \approx 1 \div 3 * 10^{17}$ cm^3**

W I @ 426.94nm

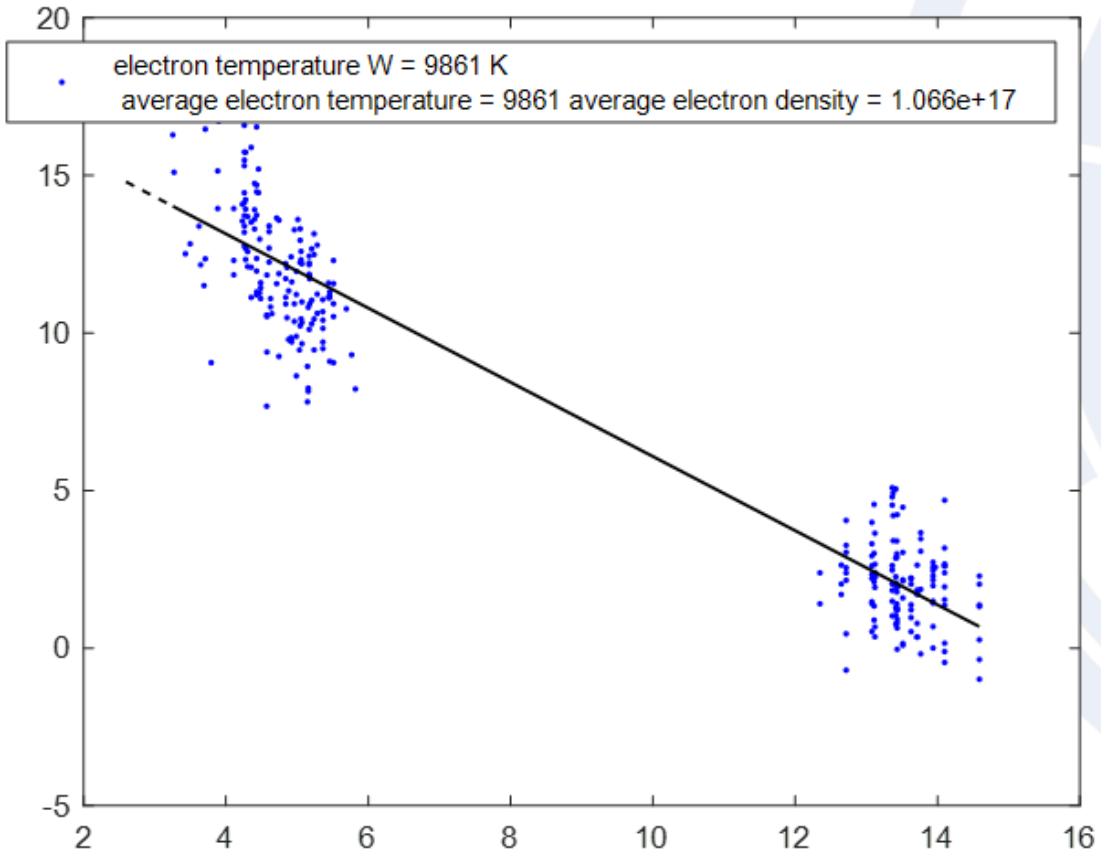
W I @ 429.46nm





Results: CF-LIBS analysis

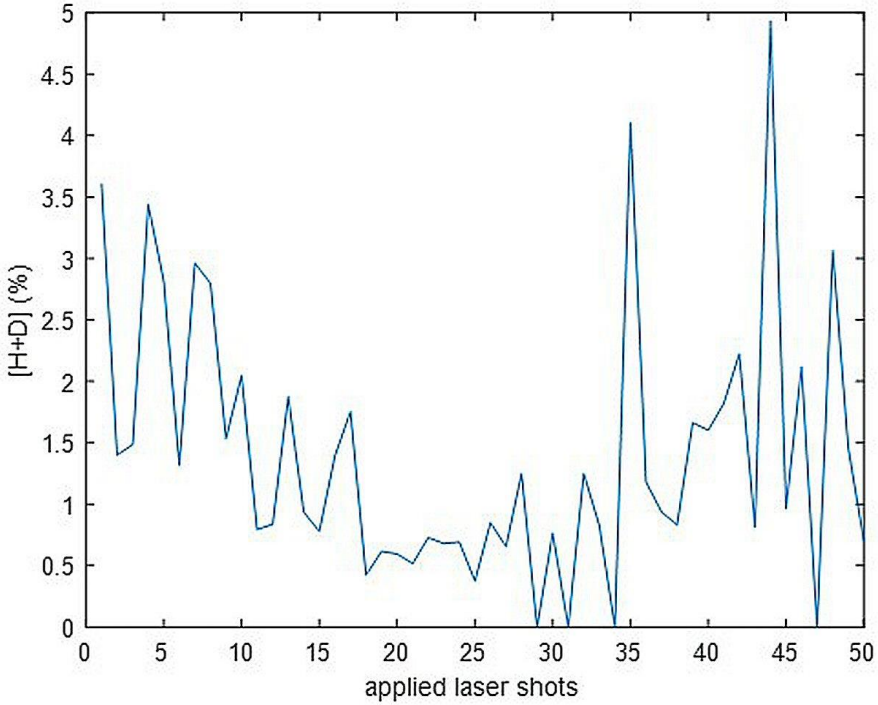
The electron temperature (T_e) of the LIBS plasma was calculated using the extended Boltzmann plot for tungsten
the calculation of T_e is based on implementation of the Boltzmann plot of atoms and ions **typical values for T_e ≈ 10000÷15000 K**



Results: CF-LIBS analysis

with $n_e \approx 1 \div 3 * 10^{17}$ cm^3 and T ≈ 10000 – 15000 K , $n_{e\,(min)} \approx 2 * 10^{17}$ and $\delta \approx 0.05$ mm, so, the condition for a plasma in LTE is fullfilled.

With both conditions satisfied (plasma optically thin and in LTE), the CF-LIBS can be applied to estimate the relative concentration of H + D ([H + D]) with respect to W for all 50 spectra of the depth profiling analysis



Giving [H + D] ≈ 0.5 ± 3.5% in the surface layer, appearing enriched in hydrogen isotopes until the 10th–15th shot, consistently with the qualitative results previously shown where the surface layer with H/D and W are above the noise level of noise within the first 15 shots. Noisy values after the 35th shot depend on the low concentration of W noisy

Conclusions

- Application of the LIBS technique to a deuterated tungsten sample, simulating the surface of a PFC of a real tokamak after an experimental campaign with fusion fuel in He and Ar as background gases
- He and Ar as background gases allows for a better separation of the H_α/D_α emission lines of hydrogen and deuterium with higher resolution than standard LIBS in air, as soon as the acquisition parameters have been optimized.
- Simulation of the presence of tritium in the spectrum, with its T_α spectral emission suggest that the detection and discrimination of the nearby T_α and D_α lines is feasible with a very "fine tuning" of the acquisition parameters.
- Depth profiling measurements gave an average ablation rate of about 500 nm per laser shot in ns-pulse regime.
- Measurements with both High-Res and full range spectrometers allowed to observe many emission lines of W and the Balmer alpha region of the spectrum with high resolution.
- Measurements in Ar Are to be preferred with respect to He because:
    1. Ar do not introduce an interfering signal, possibly being used to detect also He in the PFCs because of fusion
    2. Ar increase the plasma duration at values whitin or close to LTE conditions to apply the CF-LIBS procedure.
    3. As a consequence, both H (D-T) and W lines are clearly detected

- Finally, the application of the CF-LIBS technique allowed for a semi-quantitative estimation of the hydrogen isotopes co-deposited on the surface layer of the sample.
- Further optimizations rely on the study of longer plasma delays under Ar atmosphere (e.g. up to 20 μs) and testing the effect of the double pulse technique