

LIBS chemical characterization of the JET first wall after its last experimental campaign, with special focus to the divertor zone: first results and next steps

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- Brief recap of the Laser-Induced Breakdown spectroscopy technique
- The LIBS device developed for JET
- Depht profiling analysis of different materials inside the JET VV
- Depth profiling analysis of the JET divertor
- (ongoing) quantification of the hydrogen isotopes through the calibration free (CF) technique
- Conclusions

Brief recap of the LIBS technique

LIBS is a rapid technique of chemical analysis using a focused short laser pulse (typical $\tau_{pulse} \le 10^{-9}$ s) which induces a micro-plasma on the sample surface (e.g. PFCs) that can be spectrally analyzed giving the chemical composition of the sample. Laser and optics can be close to or several meters away from the target.





Brief recap of the LIBS technique



LIBS is a rapid technique of chemical analysis using a focused short laser pulse (typical $\tau_{pulse} \leq 10^{-8}$ s) which induces a micro-plasma on the sample surface (e.g. PFCs) that can be spectrally analyzed giving the chemical composition of the sample. Laser and optics can be close to or several meters away from the target.

- > All chemical elements can be detected simultaneously even at trace level
- Hydrogen isotopes detection
- Microdistructivity, only few µg of sample are needed: further analyses with other techniques can be done
- No sample preparation is necessary
- > Depth profiling and stratigraphy capabilities
- Remote detection, either from optical ports or <u>through robotic probes</u>
- Suitable for hostile environments, hard Rad compatibility
- > Semi quantitative and quantitative analysis demonstrated
- Data acquisition in real time (seconds)
- Data analysis can be automatized





Beryllium CFC tungsten coated

Inconel tungsten coated

Tungsten 📃 Inconel beryllium coated





In the case of the LIBS project, MASCOT has been used to deploy inside the JET VV a LIBS tool able to sample the FW and the divertor with the main task to detect the residual D-T and the eroded and redeposited materials on the whole surface of the VV accessible to the tool

Main requirements of the LIBS tool:

1) compact system

2) weight ≤ 10 kg

3) No water cooling tubes for the laser head

The MASCOT telemanipulator robot is a two-armed machine remotely operated from a control room, where a kinematically similar master manipulator is used to control motions, and provide high-fidelity force feedback systems. In addition to a CCTV viewing system, JET uses synthetic views created by a real-time virtual reality (VR) system, constantly updated with position data relating to the robotic systems. MASCOT has generally been used for maintenance operations of the JET first wall such as replacement of worn components of the first wall or of the divertor.





- The LIBS head includes a compact Nd: Yag laser head carried inside the VV together with some optical components.
- A hollow Aluminium cone houses the final focusing lens, to ensure the correct focusing distance between the lens and the JET-PFC.
- Ar gas is fluxed (2I/min) on the target during the LIBS measurements, to reduce the interference of the environmental hydrogen to the LIBS signal and increase the signal-to-background ratio, according to literature data.
 - The laser power cable, the laser-PC communication cable, the optical fiber and a fluxing tube for Ar gas connected the LIBS head inside the VV with the rest of the system (spectrometers, control PC, electronics, etc) outside the VV.



	Description
1)	Compact Nd:Yag – laser (λ = 1064 nm)
2)	Circular diaphgram
3)	1" dia. HR-IR 45° mirror (45°)
4)	2" dia. HR-IR HT-VIS dielectric mirror (45°)
5)	2" dia. lens (f = 75 mm) inside the cone
6)	2" dia . Lens (f = 100 mm) collecting the LIBS light on the optical fiber
7)	Optical fiber (20 m)
9)	Ar Gas tube













Depth profiling data analysis: procedure



- The <u>typical depth resolution</u> for LIBS depth profiling falls between <u>100 and 500 nm per laser</u> <u>shot</u>
- Given the large number of LIBS spectra acquired during the experimental campaign at JET the depth profiling analysis has been performed through the development of scripts capable of processing the large number of spectra automatically, in a short time.
- For each spectrum the intensity trend of peculiar and characteristic emission lines of the most meaningful chemical elements in the VV (e.g. W, Be, C, Mo, Ni, Cr, T-D-H etc) was monitored and reported as a function of the number of applied laser shots.

Depth profiling data analysis: procedure



The procedure has been developed to perform multiple depht profiling analyses of the acquired spectra looking at intense and free of interference emission lines of the elements.



Depth profiling data analysis: procedure



A list of the emission lines considered for each element is shown below. The rationale for choosing these lines is that they should be intense and as free from spectral interference as possible.

400.85

400.9

Atiom/Ion	Wavelength (nm)	Motivation
Be I	332.12	Be deposits on the divertor
Be I	457.27	area
WI	400.87	W substrate and redeposited
WI	407.44	material from erosion
T_{α} - D_{α} - H_{α}	656-656.3	Unburned (or implanted) fuel
ΜοΙ	550.65	
ΜοΙ	553.3	Mo interlayer (if present)
ΜοΙ	557.04	
Cr I	425.43	Income lateratural meterial
Cr I	428.97	inconel structural material
Ni I	341.47	
Ni I	345.85	Inconel structural material
Ni I	346.16	
He I	587.58	Reaction product



401

401.05

400.95

Depht profiling of point 357 - Oct1_VW - MIDDLE - (Inconel_reference)





Depht profiling of point 360 - 02ONG8B - R4 C2 (W_reference)



Depht profiling of point 492 - 2X08 - R7 C3-C7 (Be reference)





Depht profiling data analysis: divertor cross section





Depth profiling data analysis for the divertor: procedure



the operating scheme of the procedure already illustrated has been implemented as follows



Results: Be profile on the divertor (normalized to the <u>max intensity</u>)







Results: Be profile on the divertor





Results: W profile on the divertor (normalized to the <u>max intensity</u>)





- **140N G8A** 14IWG1B 1.0 HFGC LH 14W 0.8 relative intensity 0.6 14IWG3A 140N G7A relative LBSRP_14W LH 14BWG4A 0.4 C1 & C21 intensity - 1.000 Bulk Be W - coated CFC Bulk W - 0.2 - 0.9000 SURF Lx201.2 -1.2 *HFGC_LH14W_R3G HFGC_LH14W_R2G HFGC_LH14W_R2G HFGC_LH14W_R2G H41WG1BR7C1 141WG1BR3C1 140NG3A_R1C2 140NG3A_R1C2 140NG3A_R2C2 140NG8A_R3C2 140NG8A_R3C2 140NG8A_R4C2 140NG4A_R4C2 140NG4A_R4C2 140NG4A_* - 0.8000 Divertor 1c - 0.7000 [₩] 12a 11a 8B 11b 1A 8a 8B_7b -0.6000- 0.5000 1A_3a -0.40007A_7 3A 6a - 0.3000 B12_167 200 - 0.2000 1000 applied laser shots -0.1000500 - 0.000 2.2 3.0 3.2 2.4 2.6 2.8 Major radius [m]
- Results: W profile on the divertor

Results: **T-D-H profile** on the divertor (normalized to the **max intensity**)



3.2



Results: T-D-H profile on the divertor (normalized point by point)





Calibration free analysis: procedure

The CF procedure (Appl. Spec. 53(8), (1999), 960-964) aims to quantitatively estimate the chemical elements detected in the LIBS plasma. CF will be applied to estimate the concentration of T+D+H (the latter being present as residual impurity in the spectrum) respect to W (bulk material of the divertor PFCs) and respect to Be (bulk material of the first wall and major eroded material on the divertor PFCs).

CF is based on the experimental intensities of the emission lines.

Indeed, if the LIBS plasma can be considered in local thermodinamic equilibrium (LTE) these intensities can be expressed as follows:

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

where, $I_{\lambda}^{ki} = \exp$. intensity of the k \rightarrow i transition, $C_s =$ concentration of the species, A_{ki} = transition probability for the given line, g_k is the k level degeneracy, E_k the upper energy level of the transition, k_B^T = Boltzmann constant, $U_s(T)$ is the partition function for the emitting species at the plasma temperature T_e .

The emission lines of each species can be plotted as points in a graph (**Boltzmann plot, BP**) and their linear fits give an intercept, q_s which is related to the relative concentration of the species through the following equation:



(Appl. Spec. 53(8), (1999), 960-964)

$$C_s = \frac{U_s(T_e)}{F} e^{q_s}$$

Calibration free analysis & Matlab procedure: rescale the experimental intensities



the operating scheme of the procedure is illustrated below:

Read Aryelle txt file (one by one)

Rescale the experimental emission intensities taking into account the response of the whole spectroscopic system

Consider the three W I emission lines 426.94 nm, 429.46 nm, and 430.21 nm and compute $\rm n_{\rm e}$

Make the extended Boltzmann Plot (BP) for W I and W II and compute T_{e.}

Make the BP for W + (H+D+T) and, from the intercepts, compute the [H+D+T]/[W] concentration ratio

Include other elements: Be as dust in the divertor region and as bulk material in the first wall...

Calibration free analysis procedure: evaluate the electron temperature T_e



To apply the CF procedure it is necessary to consider the atomic and ionic emission lines of each element under analysis, complete of their spectroscopic parameters and the partition function of the emitting species at the plasma temperature; this was done for W I, W II, Be I, Be II, H(D,T), the data being retrieved from the NIST website (<u>https://www.nist.gov/pml/atomic-spectra-database</u>). Below (left) an example of the data for W I and (right) the partition functions of W I and H at typical temperatures of the LIBS plasmas.

Observed Wavelength Air (nm)	A _{ki} (10 ⁸ s ⁻¹)	Acc.	<i>E</i> i (eV)	<i>E_k</i> (eV)	$g_i - g_k$		W.txt		:	× +					W_I_UT.txt			H_I_UT.txt	
														File	Modifica	Visualizza	File	Modifica	Visualizza
400.1380	5.6e-03	в	1.507891 -	4.605562	9 - 9	File	Modifica	Visualizza	а										
400.87506	1.63e-01	в	0.365913 -	3.457880	7 = 9	4001	290	1 6056	0	1 5070	0	0 0056		6962	715003702	21.92	6962.	715003702	2
401.9227	6.7e-03	в	0.412313 -	3.496218	5 - 3	4001		4.0050	9	1.3079	7	0.0050		7542	941254010	24.46	7542.	941254010	2
402.8786	2.48e-02	в	1.181329 -	4.257920	1 - 3	4008		3.4579	9	0.3659	/	0.1630		8123	167504319	29.44	8123.	167504319	2
403.5356	2.90e-02	в	1.916797 -	4.988377	7 - 9	4019	.22/	3.4962	3	0.4123	5	0.006/		8703	393754627	33.91	8703.	393754627	2
						4028	.786	4.2579	3	1.1813	1	0.0248		9283	620004936	38.9	9283.	620004936	2
403.6855	1.49e-01	В	2.387469 -	5.457908	9 - 7	4035	.356	4.9884	9	1.9168	7	0.0290		9863	846255244	44.43	9863.	846255244	2.01
404.3894	1.42e-01	c	2.387137 -	5.452232	5 - 5	4036	.855	5.4579	7	2.3875	9	0.1490		10444	1.07250555	50.51	10444	.07250555	2.01
404.5594	2.88e-02	в	0.365913 -	3.429715	7 - 5	4043	.894	5.4522	5	2.3871	5	0.1420		11024	1.29875586	57.17	11024	.29875586	2.03
404.7938	5.0e-04	c	0.207090 -	3.269126	3 - 5	4045	.594	3.4297	5	0.3659	7	0.0288		11604	1.52500617	64.4	11604	.52500617	2.06
405.3932	4.9e-02	в	1.856810 -	4.914315	5 - 3	4047	.938	3.2691	5	0.2071	3	0.0005		12184	1.75125647	72.21	12184	.75125647	2.11
						4053	.932	4,9143	3	1.8568	5	0.0490		12/64	1.97750678	80.61	12764	.97750678	2.19
405.523	1.79e-03	c	1.655011 -	4.711538	7 - 9	4055	.230	4.7115	9	1.6550	7	0.0018		12020	.203/5/09	89.58	12025	.203/5/09	2.33
406.0705	5.9e-02	В	2.458319 -	5.510728	7 - 7	1060	705	5 5107	7	2 / 583	7	0 0590		1/50	5 65625771	109 22	1/5/05	65625771	2.54
406.4791	1.59e-01	В	2.387469 -	5.436811	9 - 7	4000	701	5 1368	7	2 3 2 7 5	ó	0.1500		1508	5.88250802	119.86	15085	.88250802	3.3
406.9950	3.60e-02	В	0.598844 -	3.644317	7 - 5	4004	050	2 6442	, E	A E000	7	0.1350		15666	5.10875832	131.03	15666	.10875832	3.91
407.0608	5.7e-03	В	0.207090 -	3.252077	3 - 5	4009	.950	2.2521	5	0.0900	2	0.0000		16246	5.33500863	142.7	16246	.33500863	4.73
						4070	.608	3.2521	5	0.2071	3	0.0057		16826	5.56125894	154.85	16826	.56125894	5.81
407.1928	3.29e-02	В	1.916797 -	4.960794	7 - 5	40/1	.928	4.9608	5	1.9168	_	0.0329		17406	5.78750925	167.47	17406	.78750925	7.21
407.4358	1.0e-01	B	0.365913 -	3.408091	7 - 7	4074	.358	3.4081	7	0.3659	7	0.1000		17987	7.01375956	180.53	17987	.01375956	8.97
408.8330	4.13e-03	c	0.412313 -	3.444095	5 - 3	4088	.330	3.4441	3	0.4123	5	0.0041		18567	7.24000987	194	18567	.24000987	11.17
410.2702	4.9e-02	В	0.771099 -	3.792260	9 - 7	4102	.702	3.7923	7	0.7711	9	0.0490		19147	46626018	207.86	19147	.46626018	13.85
410.2942	4.2e-04	с	0.598844 -	3.619823	7 - 5	4102	.942	3.6198	5	0.5988	7	0.0004		19727	69251048	222.09	19727	.69251048	17.1
	NI:	ST	' da'	ta		W٧	/ (Å)	E _k (eV)) g _k	E _i (eV)	g _i	A _{ki} (10 ⁸ 9	5 ⁻¹)		Т (К)	U(T)	Т	(K)	U(T)

Calibration free analysis & Matlab procedure: compute n_e

To make the BP of each chemical species more reliable to obtain it is a common procedure to make the <u>extended BP</u>, where atoms and ions are displayed together in the same BP, once the coordinates of the ions are modified as follows:

$$E_{k-ions} = E_{k \to i} + E_{ionization}$$

$$\ln\left(\frac{I_{k\to i}}{g_{k\,A_{k\to i}}}\right)_{ions} = \ln\left(\frac{I_{k\to i}}{g_{k\,A_{k\to i}}}\right) - \ln\left[2\left(\frac{mk}{2\pi\hbar^2}\right)^{\frac{3}{2}}\frac{T^{\frac{3}{2}}}{n_e}\right]$$

therefore, the electron density, n_e is the needed parameter to include ions in the BP of the species.

Through the knowledge of n_e it is also possible to have the relative concentration of atoms and ions of the same chemical species through the **Saha-Boltzmann equation**:

$$\frac{C_{ions}}{C_{atoms}} = \frac{2U_{ions}(T_e)}{n_e U_{atoms}(T_e)} \left(\frac{mk_B T}{2\pi\hbar^2}\right) e^{-\frac{E_{ion}}{k_B T}}$$
(*E*_{ion} = ionization energy, m = electron mass)

necessary to correctly quantify the concentrations of the chemical species

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Multi-element Saha–Boltzmann and Boltzmann plots in laser-induced plasmas

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$$\ln\left(\frac{\varepsilon^{z}\lambda}{\mathrm{Ag}_{j}}\right)^{*} = \ln\left(\frac{\varepsilon^{z}\lambda}{\mathrm{Ag}_{j}}\right) - B^{z}(T, N_{\mathrm{e}})$$
(2)

where

$$B^{z}(T, N_{\rm e}) = z \ln \left[2 \left(\frac{mk}{2\pi\hbar^2} \right)^{3/2} \frac{T^{3/2}}{N_{\rm e}} \right]$$

$$\tag{3}$$

and

$$E_{j}^{z^{*}} = E_{j}^{z} + \sum_{k=0}^{z-1} (E_{\infty}^{k} - \Delta E_{\infty}^{k})$$
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ACTA PART B

SPECTROCHIMICA

Calibration free analysis & Matlab procedure: compute n_e

The electron density was computed according to the following formula:

$$n_e = \frac{\Delta \lambda_{FWHM}}{w_{FWHM}^0} (10^{23} m^{-3})$$

where $\Delta \lambda_{FWHM}$ is the experimental line broadening (reduced by the instrumental broadening which was estimated through the emission lines of the low pressure Hg lamp)



and w_{FWHM}^0 is the Stark parameter of the three W I lines at 426.9, 429.4, 430.2 nm from the Nishijima and Doerner publication (J. Phys. D: Appl. Phys. 48 (2015) 325201 (6pp)):

able 1.	Summary	of W]	I Stark	FWHM.
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λ (nm)	$T_{\rm e}({\rm eV})$	$n_{\rm e} (10^{23} {\rm m}^{-3})$	w _{FWHM} (nm)	$w_{\rm FWHM}^0$ at $10^{23} {\rm m}^{-3} ({\rm nm})$
426.9	0.73-0.99	0.12-0.41	0.00940-0.0248	0.0634 ± 0.0022
429.4	0.73-1.0	0.12-0.41	0.00727-0.0226	0.0513 ± 0.0022
430.2	0.83-0.99	0.19-0.41	0.00537-0.0157	0.0330 ± 0.0026

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Stark width measurements and Boltzmann plots of W I in nanosecond laser-induced plasmas

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Abstract

We report the first measurements of Stark broadening widths of W I lines (426.9 nm, 429.4 nm, and 430.2 nm) as a function of electron density, n_e . The electron density is obtained from Stark broadening of a C II line at 426.7 nm in nanosecond laser-induced tungsten carbide plasmas. A linear relation between the W I Stark widths and n_e is confirmed. The electron temperature, T_e , is evaluated from Boltzmann plots of W I transitions with an oscillator strength $f_{ik} < 1.0 \times 10^{-2}$, since systematically lower population densities are observed for W I transitions with $f_{ik} \ge 1.0 \times 10^{-2}$, indicating that absorption occurs. This is consistent with an overestimated n_e derived from Stark broadening of the 429.4 nm line ($f_{ik} = 2.45 \times 10^{-2}$) at a high ambient gas pressure.

Keywords: W I Stark width, W I Boltzmann plot, laser-induced plasma

(Some figures may appear in colour only in the online journal)

Calibration free analysis & Matlab procedure: compute T_e



Searching in the database accessible by the procedure, the experimental spectrum is compared with the theoretical one and if the spectral distance between experimental and theoretical lines is below a certain threshold (typically 50 pm) the lines are identifed. Using these lines the extended BP for W (and, in the next steps, for Be) can be setup.



Calibration free analysis & Matlab procedure: evaluate [T+D+H]/[W]



Once the Extended BP for W is setup, the sum of the spectral signal of the Balmer alpha emission T_{α} , D_{α} , H_{α} is included in the BP because the Aryelle spectrometer cannot spectrally resolve the three emission lines but consider the T+D+H signal as a single spectral emission. By applying CF the relative concentration [T+D+H]/[W] is obtained and rescaled in percentage.



Calibration free analysis & Matlab procedure : Expected Results and information



With these procedures the following information on the PFCs of the divertor can be obtained:

- 1) Atomic concentration (%) of T+D+H with respect to W (bulk material)
- 2) (ongoing) Atomic concentration (%) of T+D+H with respect to Be (redeposited material)
- 3) In-depth atomic concentration (%) of T+D+H with respect to W (bulk material) and Be (ongoing)
- 4) Electron temperature and electron density of the LIBS plasma
- 5) Estimated processing time per spectrum ≈ 15 sec per spectrum



Conclusions

- Depht profiling of points:
 - 357 Oct1_VW MIDDLE (<u>Inconel reference spectrum</u>)
 - 492 2X08 R7 C3-C7 (<u>Be reference spectrum</u>)
 - 20 2X08 R7 C3-C7 (<u>W reference spectrum</u>)
- Depth profiling of the plasma facing components (PFCs) of the divertor profile for Be, W, T-D-H
 - 1. Be superficial contamination of the divertor section mainly on tile 0 and 1
 - 2. The thickness of the Be layer is estimated to be 10 50 μm
 - 3. T-D-H contamination of the divertor section mainly on tile 0 and 1
 - 4. The max contamination of material eroded from the first wall is in the first shots
- CF analysis for the quantification of the residual (T-D-H) content in the PFCs:
 - Pros:
 - 1. the procedure to estimate the relative concentration of T-D-H for W and Be based PFCs over a large (huge) number of spectra is developed and requires a few tenths of seconds for each spectrum
 - Cons:
 - 1. To be reliable the CF analysis need a precise procedure to rescale the intensities of the experimental LIBS spectra (ongoing)

Partnership

WK Atomic Energy Authority

Thank you for your attention !

INSTYTUT FIZYKI PLAZMY I LASEROWEJ MIKROSYNTEZY

IM. SYLWESTRA KALISKIEGO

