

ELEMENTAL ANALYSIS OF AUSTENITIC STEEL BY CALIBRATION-FREE LASER-INDUCED BREAKDOWN SPECTROSCOPY (CF-LIBS)

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Abstract. Diagnostics of the plasma-facing components (PFC) of a fusion reactor is vital for the safe operation of the device. In this paper, the calibration-free (CF) LIBS procedure was used to assess the chemical composition of an ITER-relevant material, an austenitic steel sample. The self-absorption correction of the intensities of the chosen spectral lines was done for each element, using the estimated plasma temperature and the internal reference line. Obtained results suggest that this method could be suitable for the chemical analysis of austenitic steels, but further investigation is needed to quantify its analytical performance fully.

1. INTRODUCTION

The structural materials of fusion reactors are subjected to thermal, mechanical, chemical, and radiation loads. Due to their excellent manufacturability, good mechanical properties, welding ability, and corrosion resistance, austenitic stainless steels were chosen as structural reference material for ITER (P.J. Maziasz and J.T. Busby, 2012). In addition, to diagnose the composition of the deposits on the fusion reactor's first wall, test targets made of austenitic steel (AISI 316 L) were settled at ten positions on the LHD at NIFS in Japan (V. Kh. Alimov et al., 2019). A CF-LIBS analysis of the LIBS 316L(N)-IG (ITER Grade) was conducted to evaluate the applicability of LIBS for the determination of the composition of test targets and deposits at reactor walls.

2. EXPERIMENTAL SETUP

The experimental setup is shown in Figure 1. Target AISI 316L (YUS = Č.45703, DIN = X2CrNiMo17-12-2, EN 1.4404) plates were placed on the PC controllable x-y table. The impulse from Nd:YAG Q-switch laser (Quantel, $\lambda = 532$ nm, energy 55 mJ, pulse duration 6 ns) was focused on a target with a lens whose focal length

is 15 cm. Light emitted from a plasma was collected using fiber optic cable ($\varnothing = 400 \mu\text{m}$) and detected using Andor Tech. Mechelle 5000 spectrograph equipped with Andor iStar DH734 camera. The camera was triggered using an external photodiode, and the gating of the camera was done with the help of the external Stanford Research System Digital Delay Generator DG535.

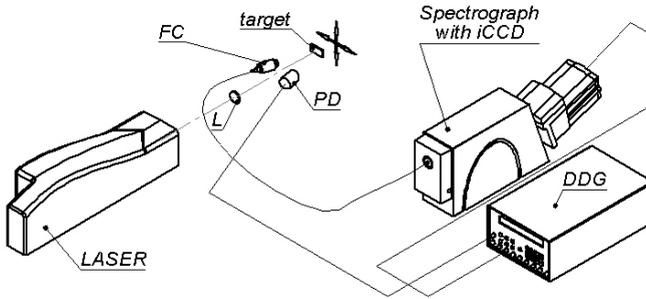


Figure 1: LIBS experimental setup

Delay was set to $0.6 \mu\text{s}$, and $3 \mu\text{s}$ and $30 \mu\text{s}$ gates were used. LIBS experiments were performed in air at atmospheric pressure.

3. RESULTS

A part of the spectrum, in the range 350 nm to 370 nm, recorded for two different delay times is shown in Figure 2.

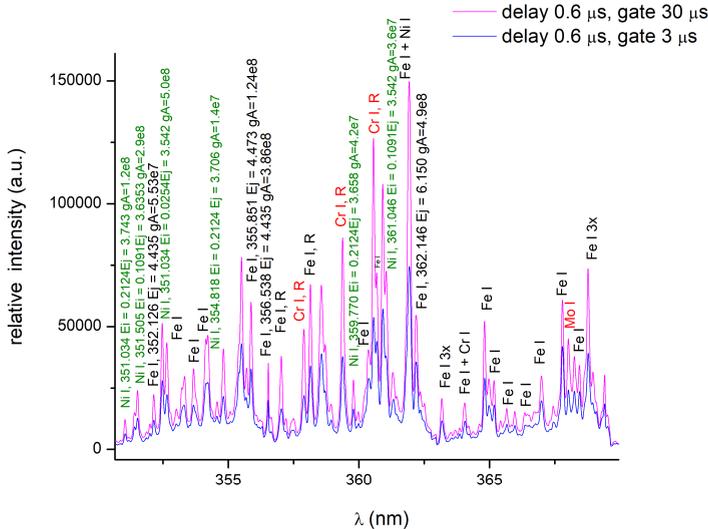


Figure 2: Part of the recorded spectrum with identified lines of Fe I, Ni I, Mo I, and Cr I.

For both delay times, 30 spectra were averaged to obtain the final one, and the gain of 100 was set to amplify the signal further and improve the signal-to-noise ratio.

Quantitative analysis was done using a calibration-free algorithm proposed by Yang et al. (Yang et al., 2018). As a first step, internal reference lines were selected manually for each plasma species. In the next step, self-absorption (SA) correction of the internal reference line was done using the following formula (Yang et al., 2018):

$$f_{\lambda}^S = f_{\lambda_R}^S (I_{\lambda}^{ki} / I_{\lambda_R}^{mn}) (A_{mn} g_m / A_{ki} g_k) e^{E_k - E_m / k_B T} \quad (1)$$

where f_{λ} and f_{λ_R} are the SA coefficients of the analytical and internal reference line; I_{mn} , A_{mn} , g_m , and I_{ki} , A_{ki} , g_k are the intensity, coefficient of spontaneous emission, and statistical weight of the upper level for reference and analytical line, respectively.

In the third step, Boltzmann plots, constructed using uncorrected intensities of spectral lines for each analyte, were used to determine excitation temperatures. After this, the optimal temperature was searched in the interval (T_{\min} , T_{\max}) using Particle Swarm Optimization (PSO) algorithm. The selection of temperature interval was based on the minimal and maximal estimated temperatures from Boltzmann plots ($T_{\min} = 7477$ K, and $T_{\max} = 18567$ K). Number of particles was set to 20, inertia coefficient was $w = 0.6$, and cognitive and social coefficients were $c_1 = c_2 = 0.5$. The optimal temperature was found to be 7920 K (0.68 eV).

Finally, using equation (2) (Yang et al., 2018) and the optimal temperature found by PSO, we were able to correct the analytical lines for self-absorption:

$$I_{\lambda}^S = (I_{\lambda_R}^{mn} / f_{\lambda_R}) (A_{ki} g_k / A_{mn} g_m) e^{E_m - E_k / k_B T_{opt}} \quad (2)$$

Results of the optimization process are shown in figure 3.

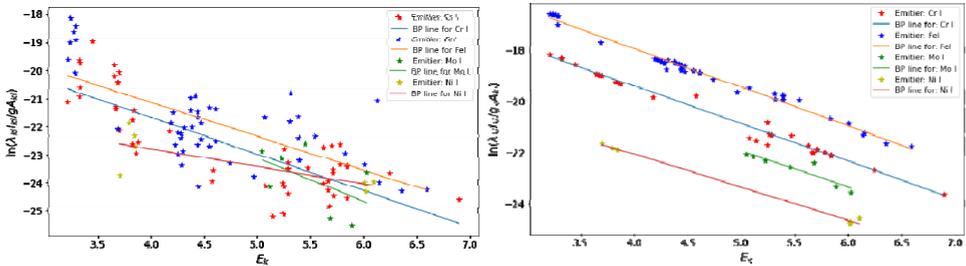


Figure 3. Boltzmann plots before any correction (left) and after all corrections (right).

After all corrections, concentrations of all species were calculated using standard calibration-free procedure (Yang et al., 2018):

$$c_s = \frac{1}{F} U_s(T) e^{q_s} \quad (3)$$

Here, F is the experimental parameter that includes the optical efficiency of the collecting system, $U_s(T)$ is the partition function of given species for temperature T , and q_s is the intercept of the Boltzmann plot.

Parameter F was determined from the following condition:

$$\sum_{s=1}^n c_s = \frac{1}{F} \sum_{s=1}^n U_s(T) e^{q_s} = 1 \quad (4)$$

By applying the described CF model to the experimentally determined intensities of spectral lines, the following elemental composition of the analyzed sample was calculated: Fe - 89.5%, Cr - 8.3 %, Mo - 1.7 %, and Ni - 0.50 %.

4. CONCLUSION

The applied CF model successfully corrected Boltzmann plots for self-absorption, but the obtained concentrations deviate significantly from the expected chemical composition of this type of steel. Careful analysis of the relative spectral intensities of the Fe, Mo, Cr, and Ni lines, considering the measured temperature value, indicates that the declared composition most likely does not correspond to the tested sample. In the next step, an independent chemical analysis of the same sample is planned to confirm the validity of the applied model for the analysis of this type of steels.

Acknowledgements

The research was funded by the Ministry of Education, Science and Technological Development of the Republic of Serbia, Contract numbers: 451-03-68/2022-14/200024 and 451-03-68/2022-14/200146, and supported by the Science Fund of the Republic Serbia, Grant no. 3108/2021.

References

- Maziasz P.J., Busby J.T.: 2012, *Comprehensive Nuclear Materials*, Editor(s): Rudy J.M. Konings, Elsevier.
- Cuicci A., Corsi M., Palleschi V., Rasteli S.: 1999, *Applied Spectroscopy* **53**, 960.
- Alimov V. Kh., Yajima M., Masuzaki S., Tokitani M.; 2019, *Fusion Engineering and Design* **147**, 111228.
- Yang J., Li X., Xu J., and Ma X.: 2018, *Applied Spectroscopy* **72**, 129.