Comparison of signal enhancement of elements with diverse upper-level energies in Double-pulse Laser-Induced Breakdown Spectroscopy

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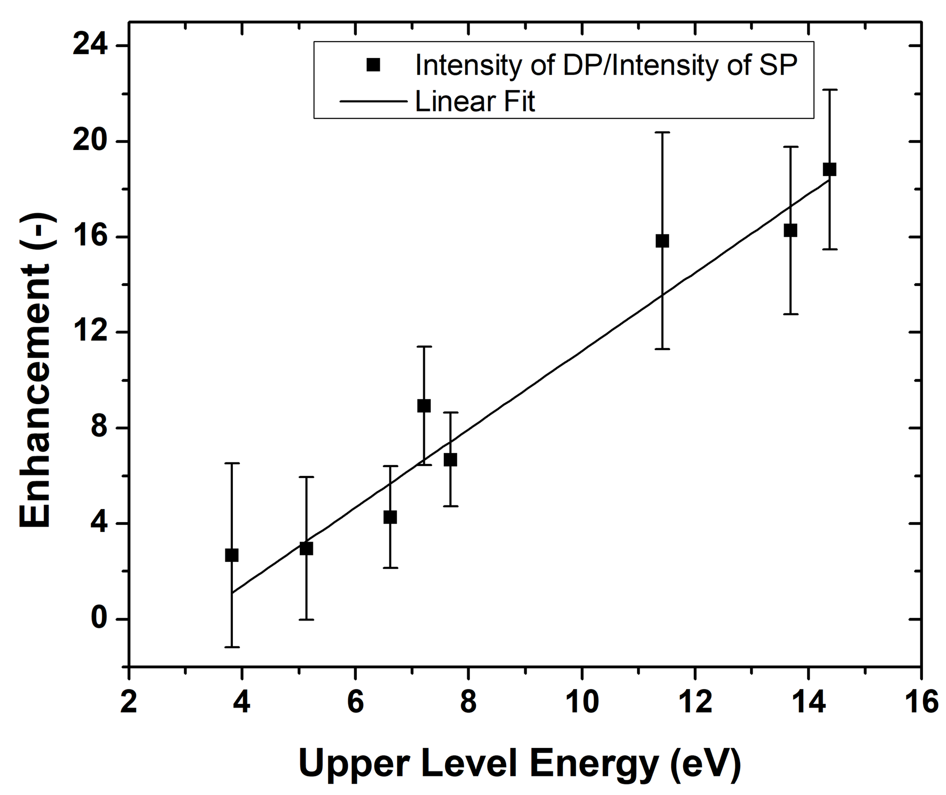
Abstract

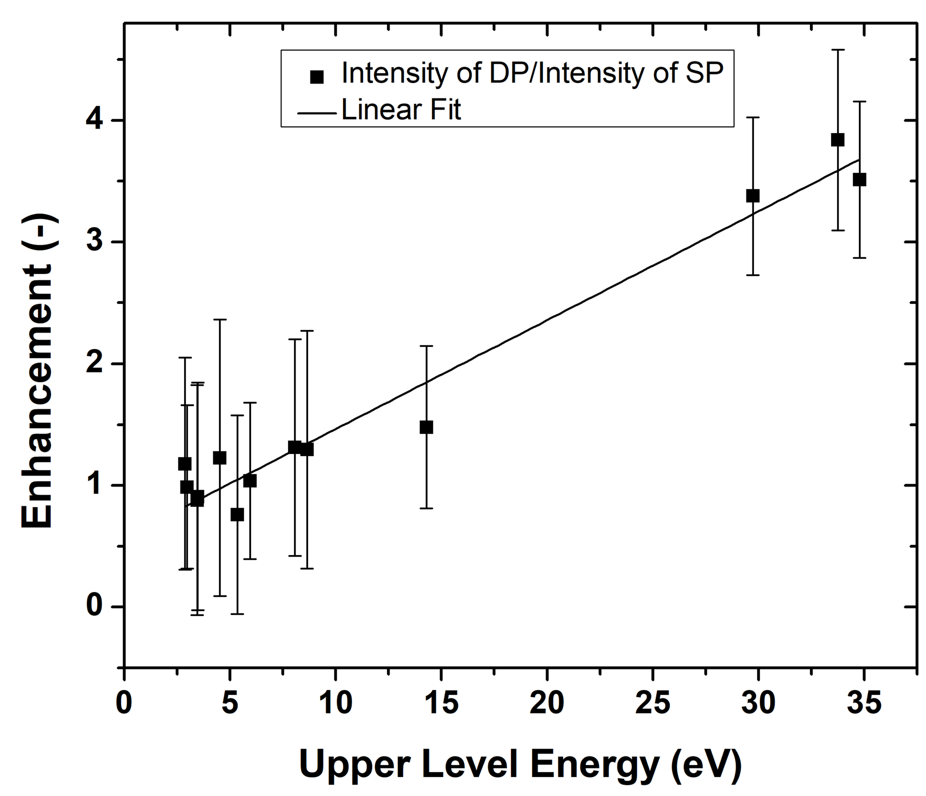
Double-pulse Laser-Induced Breakdown Spectroscopy (DP-LIBS) is a widely used approach for overcoming the sensitivity shortcomings of the conventional single pulse laser-induced breakdown spectroscopy. The goal of this work is to compare the signal enhancements in elements with diverse upper-level energies and to analyze the trend in the variation. Among three different configurations of orthogonal DP-LIBS, re-heating configuration is utilized in this work. Initially, the optimization of laser energies, interpulse-delay, and gate delay is performed. Later, under the obtained optimum conditions, single pulse and double-pulse measurements are performed for two different matrices; homogenous steel and concrete samples. The selected samples enable the selection of elements with diverse excitation energies and different spectral lines from the same matrix. In the case of the steel sample, the experiment is performed under argon atmosphere and the concrete sample is analyzed under both helium and argon atmospheres at atmospheric pressure. The trend in the variation is then analyzed by plotting the obtained signal enhancement versus the upper-level energies. The results show a linear variation of enhancement with increasing excitation energies and the reasons for deviation from the trend in the case of some elements are discussed.

Results

a)



b)



c)

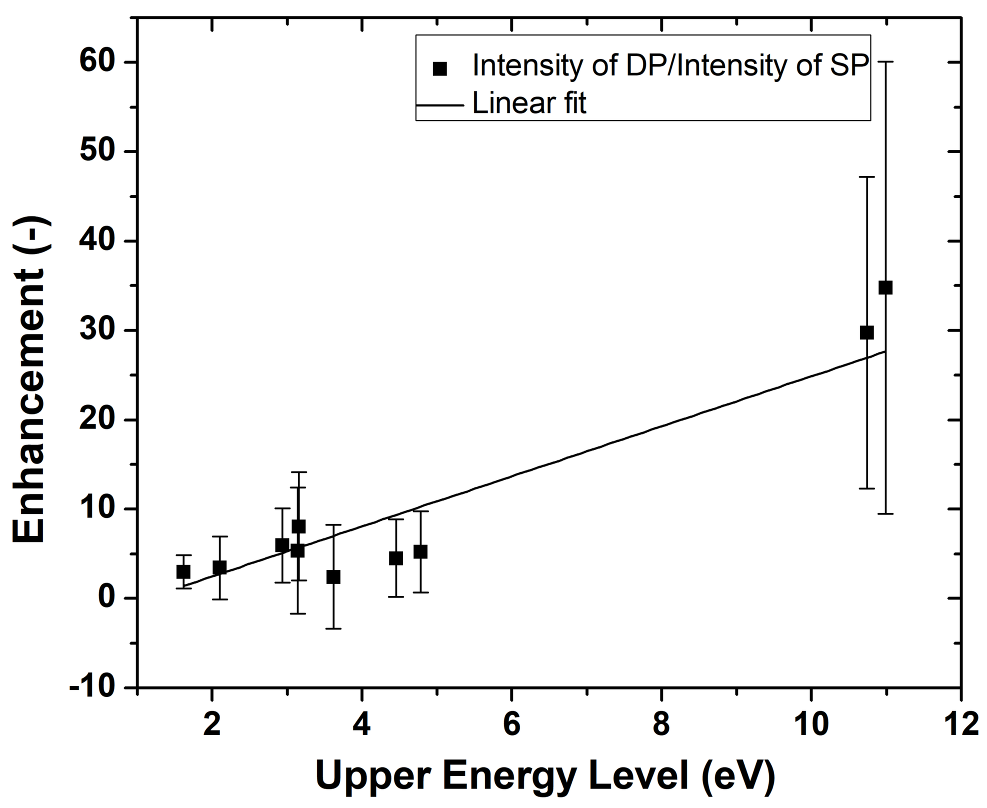


Figure: Variation of signal enhancement in different elements with increasing upper-level energies of a) Steel sample in argon atmosphere b) Concrete sample in argon atmosphere c) Concrete sample in helium atmosphere

To calculate the enhancement in LIBS signal, single pulse and orthogonal re-heating measurements were performed under optimum conditions on highly homogenous steel and concrete samples. A 5 × 5 map with 5 accumulations in one spot were created for the ablation of each sample. Steel samples were measured in argon atmosphere with argon purge in the spectrometer and concrete samples were measured in both helium and argon atmosphere at atmospheric pressure. Elements with diverse upper-level energies were selected for the analysis (Tab.1 and Tab.2) and their enhancements were compared. Results show a linear increase in signal enhancement with increasing upper-level energies irrespective of the element chosen.

Some trace elements like carbon (193.09 nm) in steel and chlorine (837.59 nm) in concrete were detected in reheating double-pulse configuration but not in single-pulse configuration which makes the estimation of enhancement impossible. Since the enhancement is also dependent on other experimental parameters like the concentration of the element in the sample, exposition time etc., small deviations from the linear trend can be observed in the case of some elements.

Conclusion

The variation of the enhancement in the signal as a function of the excitation energy of different elements were investigated in this work. The results show a linear variation of enhancement with a coefficient of determination 0.96, 0.93 and 0.71 in the case of steel in argon atmosphere, concrete in argon atmosphere and concrete in helium atmosphere, respectively. Compared to the steel sample, small variation in the linearity was observed for concrete sample in both cases.

References

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Instrumentation

System:

LIBS Discovery (CEITEC BUT, Czech Republic) consists of a Quantel CFR Ultra Nd:YAG laser (France, 532 nm, 10 ns, 20 Hz) and a Litron Bernoulli LIBS Nd:YAG laser (UK, 1064 nm, 10 ns, 20 Hz). The spectrometer used is EMU-65 (Catalina Scientific, USA) equipped with an EMCCD detector (Raptor Falcon Blue).

Samples : Highly homogenous BAM SUS-1 R Steel sample and concrete sample.

The double-pulse measurement parameters were optimized to 46 mJ ablation energy, 200 mJ reheating energy, 2 µs interpulse delay and 0.5 µs gate delay for concrete sample and 25 mJ ablation energy, 100 mJ reheating energy, 1 µs interpulse delay and 0.1 µs gate delay for steel sample. Ablation energy and gate delay were same for the corresponding single pulse measurements.

Tab.1: Analyzed elements in steel sample with their selected wavelengths, enhancement and their upper-level energies

Element	λ [nm]	Enhancement [-]	E_k [eV]
Si I	212.41	4.27	6.61
P I	213.61	8.93	7.21
Co II	241.32	18.82	14.37
C I	247.85	6.67	7.68
Mn II	259.75	15.84	11.41
Fe II	259.90	16.27	13.69
Cr I	302.15	2.98	5.13
Cu I	324.75	2.67	3.81

Tab.2: Analyzed elements in concrete sample with their selected wavelengths, enhancement and their upper-level energies

Element	λ [nm]	Enhancement [-]	E_k [eV]
Al I	396.15	5.34	3.14
Ca I	422.61	5.94	2.93
Ca I	430.25	5.22	4.77
Na I	589.59	3.44	2.10
Ca I	643.90	4.52	4.45
K I	766.48	2.97	1.61
O I	777.19	29.73	10.74
Na I	819.48	2.42	3.61
O I	844.64	34.77	10.98
Ca II	854.20	8.08	3.15

Acknowledgments

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