Effect of oxidation on the surface of metallic samples in LIBS measurements.

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Abstract.

The analysis of metals with LIBS in the industry can give us very useful information during the production processes and in this way, we can optimize these processes.
LIBS is an analysis method that is performed on the surface of the sample, so surface layers that are not representative can give us erroneous analytical information. These unrepresentative surface layers can be formed by various situations. They are usually oxidation processes that are formed during the production of the material or due to long storage times in warehouses.
With this study we want to see if there are significant differences in the results of the measurements before treating the sample and after having done so, to know if we should use a pretreatment method before analyzing the samples and which one would be the most appropriate.

Introduction.

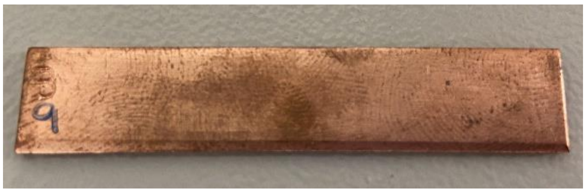
Laser-induced breakdown spectroscopy (LIBS) is an atomic emission spectroscopic technique that allows obtaining the elemental composition of a sample through the spectral analysis of the emission of plasma generated by laser ablation (Reinhard Noll, 2012)
LIBS uses a low-energy pulsed laser to generate a plasma, which vaporizes a small amount of the sample. Spectral features emitted by the excited species, mostly atoms (but more recently molecules as well), are used to obtain quantitative and qualitative analytical information. Targets have included solids, gases, liquids, slurries, and aerosols (Cremers & Radziemski, n.d.)
Several experimental factors influence the LIBS analysis. These factors include irradiation conditions like laser wavelength, pulse duration, number of pulses or energy density. Other parameters are related to the analysis environment like atmosphere (air or buffer gas) and pressure. Timing considerations during the spectra acquisition and inherent factors of the sample are important parameters. The sample parameters depend on the physical and chemical properties of the material (Lopez-Quintas et al., 2012)
Physical properties, such as sample surface roughness, oxidation, hardness, particle size, and homogeneity, as well as thermal conductivity and reflectivity, affect the ablation process required to produce the plasma and therefore the characteristics of the LIBS signal (Sheta et al., 2015)
The treatment of the sample can benefit us in different ways. The simplest refers to mechanical treatment such as surface polishing to improve the reproducibility of measurements, which is what we want to test with this study.

Experimental.

Samples preparation.

To do this study we used 22 Cu samples with a purity of 99.90% Cu and 0.015%-0.040% P. The samples were initially slightly oxidized and dirty due to having been handled and stored for some time.
First, measurements of the samples without any type of treatment have been done and then, they have been treated by manually polishing them with sandpaper and we proceeded to analyze them after this pre-treatment.

Sample before treatment



Sample after treatment

Apparatus and method.

The samples were irradiated with a 1570nm DPSS-Nd:YAG laser, which has a 4,5mJ pulse energy and pulse duration of less than 6ns. Since the sample thickness can vary from a few millimeters to centimeters, the samples are placed on motorized linear ball screw actuators, which provide means to vary the focus point on the sample, by moving the X and Z axis. The motors are driven by a microcontroller, which is communicating with an in-house developed Python software through USB serial. The same Python software also communicates with the laser via RS-232 serial interface and the spectrometer via USB interface. An optical system that collects the emitted light from the sample and transmits it to the spectrometer is located perpendicularly above the sample. The spectrometers (AVANTES-4096 CL-EVO 10 μm) can give 0.14-0.18 nm resolution for spectral analysis from 190 to 450 nm.

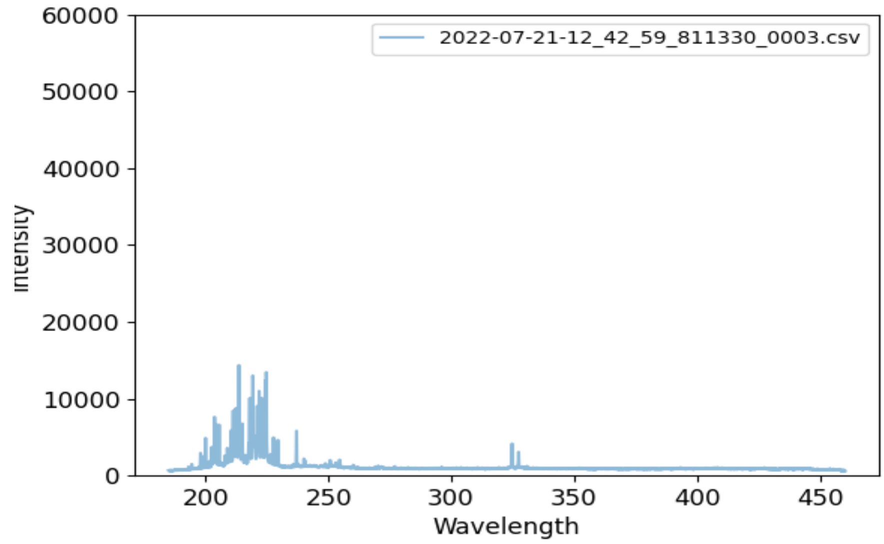
Experimental conditions for LIBS experiments.

Laser	**Quantel Falcon 157**
Type	DPSS-Nd:YAG
Wavelenght	1570nm
Pulse duration	<6ns
Pulse energy	4,5mJ
Repetition rate	5Hz
Optics	
Focusing lens material	N-BK7
Imaging lens material	UV-grade fused silica
Detection system	
Spectrometer	Avantes StarLine AvaSpec-ULS4096CL-EVO
Wavelength range	190 to 450nm
Slit size	10 µm
Gratings	1200 lines/mm
Detector	Hamamatsu S13496
Integration time	9µs
Other components	
Microstep driver	TB6600, 9-42VDC, 3.5A
X axis	Fuyu FSL30, 150mm stroke
Z axis	SFU1605, 200mm stroke
Displacement sensor	Sick OD Mini
Frame	30x30 aluminium profile
Panels	EN AW-5754 aluminium alloy, 4mm thick

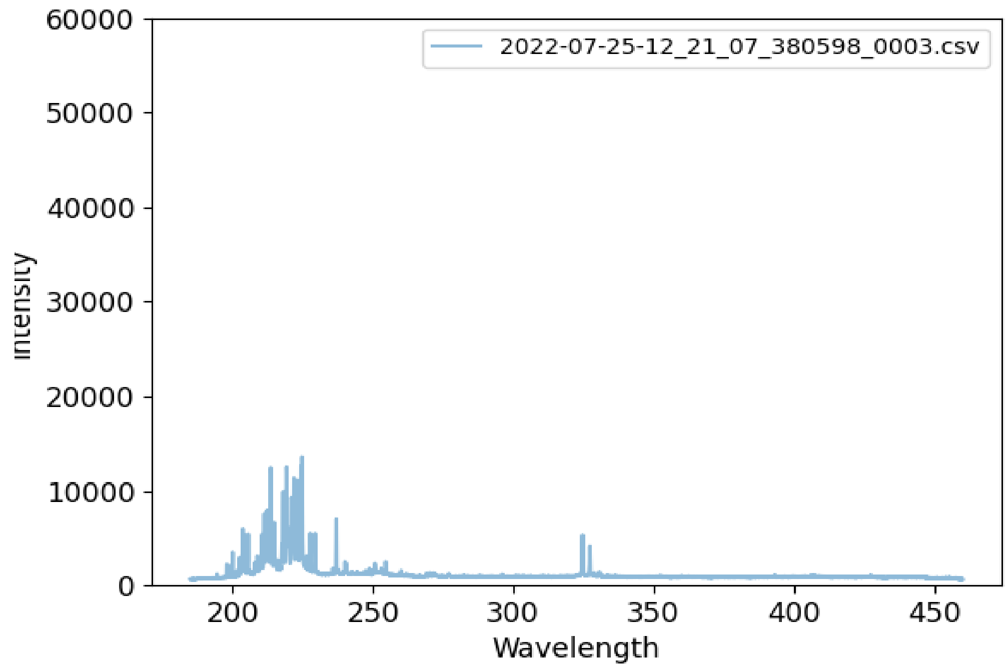
Results and discussion.

For this study we made 150 measurements of 5 shots each in 22 samples of Cu before and after pretreatment, these are some examples of the results:

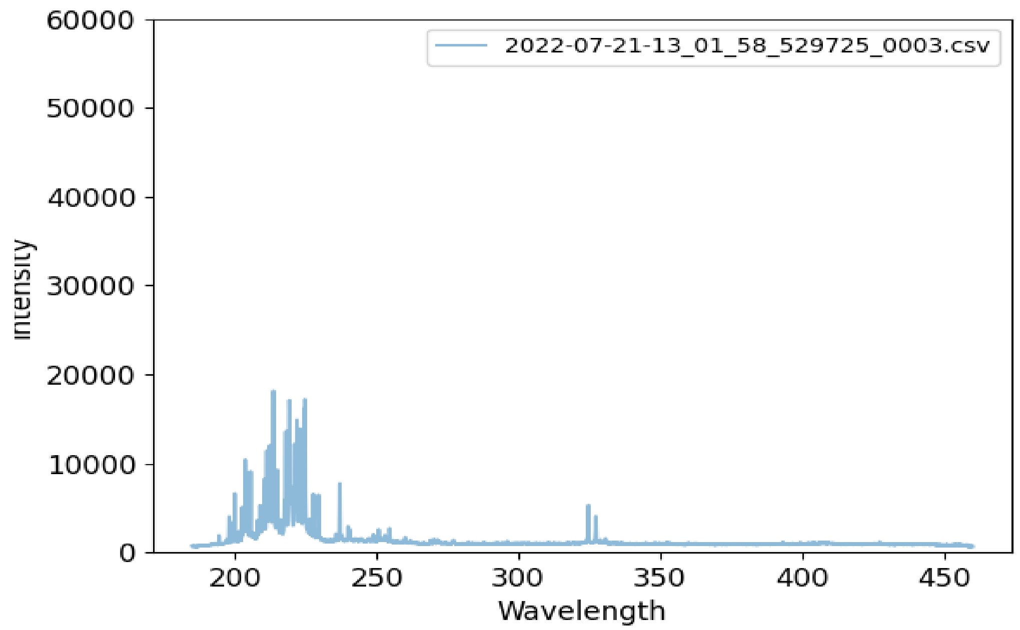
- Sample 9 before treatment.



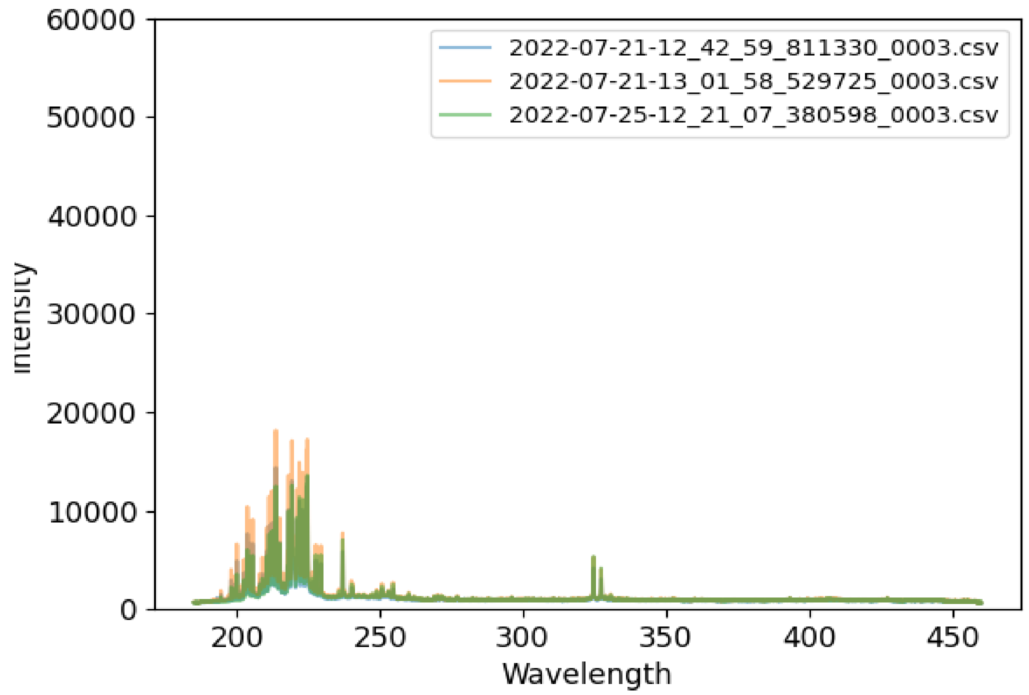
- Sample 9 with dust after the treatment.



➢ Sample 9 after treatment.



➢ Comparison of the 3 results obtained.



As we can see, both in the individual graphs and in the comparative graph of all the results obtained (blue represents the sample before treatment, orange after treatment and green the sample with the dust after being treated) of the sample 9, there is a change in the intensity of the signal obtained after doing the treatment. This has happened with all the samples analyzed in this study.

Conclusions.

As a conclusion we can say that after having pre-treated the samples, we can obtain a higher signal intensity, but no differences are observed in the wavelengths obtained, so the material of which the metallic sample is composed is detected but not the contamination it has on the surface. This will also depend on the thickness or amount of oxidation or contamination on the surface of the sample.

References.

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