

Identifying elements via laser-induced breakdown spectroscopy

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Abstract: As a way to stimulate materials with the goal of making a spectroscopic analysis possible, laser-induced breakdown spectroscopy (LIBS) is a new and promising method. Its basic operation involves using a high energy laser pulse tightly focused on the target material to produce a plume of plasma consisting in part of excited matter, the existence of which will enable spectral lines characteristic of the material to be studied.

| E [mJ] | P [GW/mm ²] |
|----------|---------------------------|
| 5 | 0.69 |
| 6 | 0.83 |
| 10 | 1.39 |

Table 1: The lasers pulse power density P , for the energy values used for our measurements obtained with the relation in equation (3).

Characteristics of the laser beam

Focused laser beam width

The unfocused laser beam of wavelength $\lambda = 532$ nm has a diameter $d_0 \simeq 4$ mm. It enters an lens whom we assume to be diffraction limited and of focal length $f = 100$ mm. In there the light will converge on the focal plane where the light rays will interfere con- & destructively due to superposition. Assuming a TEM₀₀ Gaussian beam, we have about 86% of the total power at the central maximum. The numerical aperture number NA of a Gaussian beam is related to the minimum beam diameter d ,

$$NA \simeq \frac{2\lambda}{\pi d} \Leftrightarrow d = \frac{2\lambda}{\pi NA} \quad (1)$$

The f-number $N \equiv f/d_0$, defined as the ratio of the focal length f to the diameter of the incident beam d_0 . If we then approximate airs index of refraction as $n = 1$ and use the relation in equation (1) we obtain,

$$N = \frac{f}{d_0} \simeq \frac{1}{2NA} = \frac{d\pi}{4\lambda}$$

rearranging, we obtain an expression for the beams diameter after focusing,

$$d = \frac{4f\lambda}{\pi d_0} = 16.93 \text{ } \mu\text{m} \quad (2)$$

The focused beam power density

Having estimated d in eq. (2), we can approximate the beams area as $A = \pi d^2$. Each pulse from the laser lasts for $\Delta t = 8$ ns. If each pulse delivers energy E , then its power density P can be obtained as follows,

$$P = \frac{E}{A\Delta t} \text{ [W/m}^2\text{]} \quad (3)$$

Experimental set-up

The described method can be put to use to analyse selected species of matter. Figure (1) is a schematic

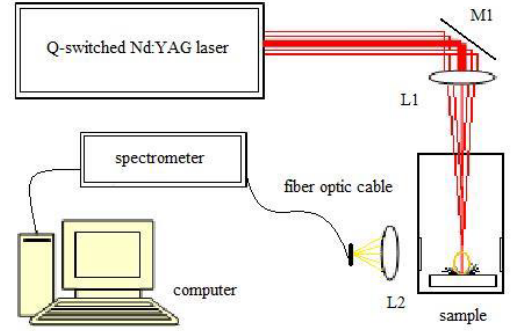


Figure 1: An illustration depicting the experimental set-up for laser induced breakdown spectroscopy

representation of how this comes about; the laser light is directed unfocused through a measuring device (L1) which measures the intensity of the light. The laser light is then focused by a lens with focal point adjusted to hit the sample at a point where a small portion of it vaporizes. Once it starts cooling and expanding it radiates spectral information, which is picked up by a fiber-optic cable (L2) that transmits the information for processing in a spectrometer and post-processing in a computer. We will analyze light at λ ranging from 500 to 1000 nm.

Gaseous pollution

Unless the experiment is made in vacuum, air will pollute the exciting plume by being itself excited; the constituents [roughly N₂ (78%), O₂ (21%), Ar (0.93%) and possibly some H₂O_(g) and CO₂] will thus contribute with their spectral lines. This is mitigated partly by showering the sample with N₂, which eliminate some of the unwanted lines. The contribution made by N₂

itself can be identified by showering the sample with a different gas, like Ar.

Laser-induced breakdown spectroscopy

Practical advantages and disadvantages

A major advantage of LIBS is that by repeatably firing the laser at the same sample spot can allow acquisition of its depth profile. One one could also acquire 2 additional spatial dimensions to the profile by scanning the laser over the samples surface.

LIBS is quick, results can be obtained within seconds. It's one of the cheapest methods of spectral analysis. It has good mobility, because LIBS yields the best sensitivity and widest elemental detection range by equipment weight. That is probably one of the reasons ChemCam was put on Curiosity, the Mars rover, because mass is currently a huge factor in space travel. It's also a subtle method, because it only requires optical contact; the sample doesn't mandate any special preparation and it's considered minimally destructive to the sample. LIBS uses non-ionizing radiation to excite the samples, which eliminates unwanted beam penetration and carcinogenic health risk. It can in principle detect all elements (and their relative abundance), only limited by the lasers power.

Disadvantages are in reproducibility and accuracy of the measurement, the former can be due to variations in the laser spark and the subsequent plasma that follows. Detection limits vary with the sample substances and typically offers between 5% and 10% accuracy.

Relation between pulse energy and relative light intensity

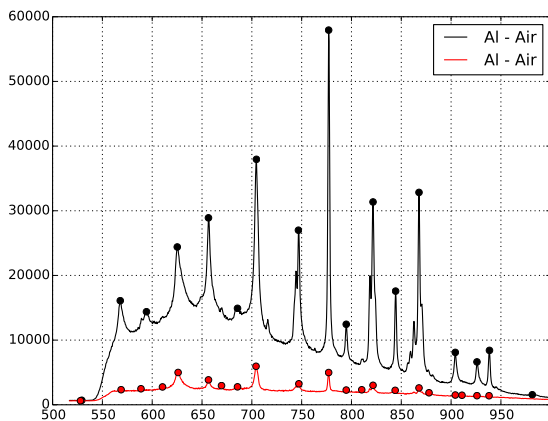


Figure 2: Comparison of the spectrum of Al in air for two different pulse energies 10 mJ and 5 mJ

Comparing the two lines in figure (2), it is clear that doubling the energy does not mean double intensity. It seems the intensity tops for the 10 mJ line are higher

relative to their respective background, than the spikes for the 5 mJ line. Also, there are few clear tops in the 10 mJ line that are barely visible in the 5 mJ one. The general shape of the spectrum, especially of the background look very similar.

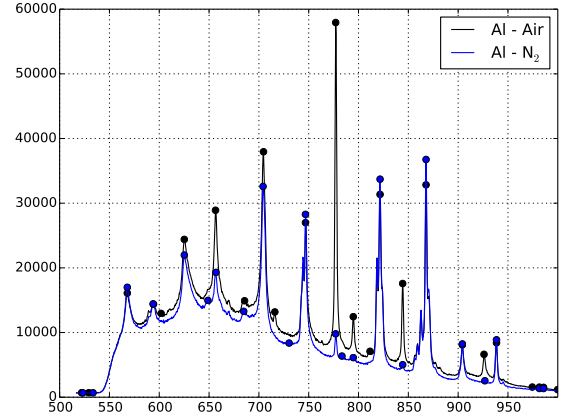


Figure 3: Air and Nitrogen comparison

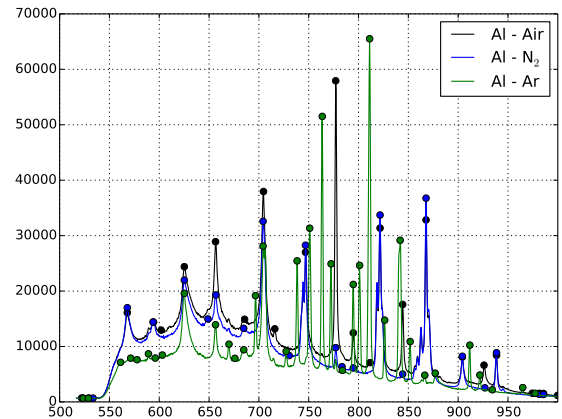


Figure 4: Air, Nitrogen & Argon on Al

Identifying spectral tops

Gaseous Nitrogen

We compare the spectral lines in figures, (3), (5), (6) & (7), who are all involve Nitrogen on different types of metals. We list down the wavelengths λ for each top that these figures have in common. Thereafter we cross-reference these values with wavelengths for known N_2 tops, in a spectral database provided by <http://physics.nist.gov/>. In table (2) we list the common λ and the corresponding λ from the database (if found). As seen in table (2) all the common tops seem to be due to N_2 , except $\lambda = 904.20$ [nm] that wasn't confirmed for N_2 . We leave the option open that this line may be due to unwanted trace amounts of some other element.

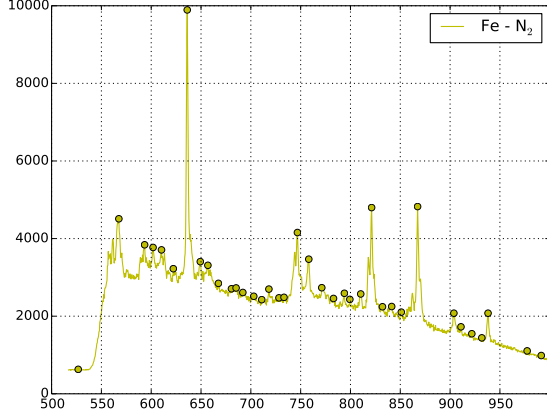


Figure 5: Iron spectra in Nitrogen gas

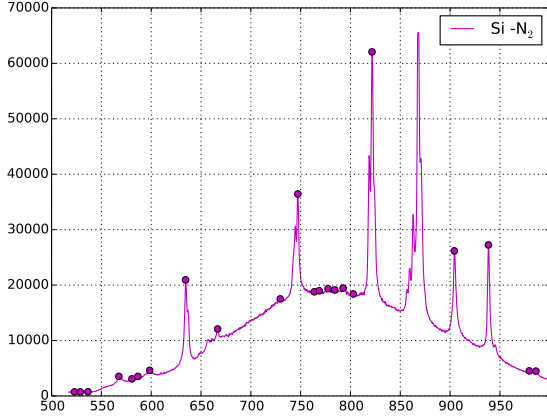


Figure 6: Silicon spectra in Nitrogen gas

| λ_{N_2} [nm] | λ web [nm] | $ \Delta\lambda $ [nm] |
|----------------------|--------------------|------------------------|
| 567.51 | 567.95 | 0.44 |
| 747.19 | 746.83 | 0.36 |
| 821.63 | 821.63 | 0.00 |
| 867.78 | 868.02 | 0.24 |
| 904.20 | N/A | N/A |
| 938.50 | 939.27 | 0.23 |

Table 2: A list of tops in common for figures (3), (5), (6) & (7), whom we expect to be due to N_2

Copper

Next we look back at figures (5), (6) & (7) in an attempt to confirm the remaining tops (not found to be due to N_2) are due their respective metals. We begin with copper. By inspection, we find the tops unique to figure (7) and compare them to the spectral database. Results are summarized in table (3)

Iron

We now repeat this process for Iron. Looking through biggest tops of Fe in the spectral database, we realize they are not apparent in figure (5). The tops we found

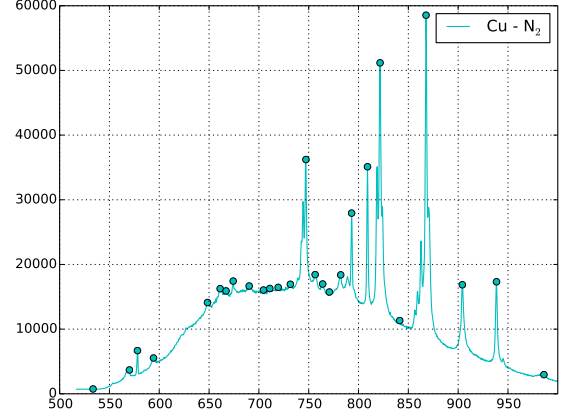


Figure 7: Copper spectra in Nitrogen gas

| λ_{Cu} [nm] | λ web [nm] | $ \Delta\lambda $ [nm] |
|---------------------|--------------------|------------------------|
| 578.12 | 578.22 | 0.10 |
| 793.06 | 793.31 | 0.25 |
| 809.04 | 809.26 | 0.22 |

Table 3: A list of tops in (7) not found to belong to N_2 compared with values for Cu in the spectral database.

in both are summarized in table (4)

| λ_{Fe} [nm] | λ web [nm] | $ \Delta\lambda $ [nm] |
|---------------------|--------------------|------------------------|
| 636.16 | 635.87 | 0.29 |
| 758.14 | 758.60 | 0.46 |

Table 4: A list of tops in (5) not found to belong to N_2 compared with values for Fe in the spectral database.

Silicon

Same procedure goes for Silicon. We compare figure (6) to the spectral database. This time we only find one top, $\lambda_{Si} = 634.46$ nm which is close to the top $\lambda = 634.71$ nm obtained from the database.

Argon

Argon has quite a few tops as evident in figure (4), we suspect some of them may be influenced by trace amounts of N_2 and/or O_2 in the Argon fume. In table (5) we list the biggest tops identified to be due to Argon,

| λ_{Ar} [nm] | λ web [nm] | $ \Delta\lambda $ [nm] |
|---------------------|--------------------|------------------------|
| 739.34 | 738.40 | 0.94 |
| 763.61 | 763.51 | 0.1 |
| 794.64 | 794.81 | 0.17 |
| 811.13 | 811.53 | 0.4 |
| 841.78 | 842.46 | 0.68 |
| 911.74 | 912.30 | 0.55 |

Table 5: A list of tops found contributed by Argon gas

Oxygen

The remaining noticeable and unidentified tops are most likely due to Oxygen or Aluminum. To find possible candidates we use the rule of elimination and the spectral database. For Oxygen, we search for tops in the air lines in figure (2) that are neither contributed by N₂ nor Ar and are matched by the database. Results are listed in table (6)

| λ_{O_2} [nm] | λ web [nm] | $ \Delta\lambda $ [nm] |
|----------------------|--------------------|------------------------|
| 777.08 | 777.19 | 0.12 |
| 844.30 | 844.63 | 0.33 |
| 925. 97 | 926.084 | 0.11 |

Table 6: List of tops likely due to Oxygen

Aluminum

Likewise, if N₂ and Ar seem to both contribute to the same air spectral top, likely means it is due to the Aluminum. These tops are listed in table (7)

| λ_{Al} [nm] | λ web [nm] | $ \Delta\lambda $ [nm] |
|---------------------|--------------------|------------------------|
| 625.15 | 624.34 | 0.81 |
| 704.61 | 704.21 | 0.4 |
| 746.77 | 747.14 | 0.37 |

Table 7: List of top likely contributed by Aluminum

References

- [1] TEM Mode, Beam Diameter, Focal Spot Size and Depth of Focus. AML - Columbia University. Web. 16. April, 2014, from <http://aml.engineering.columbia.edu/ntm/level2/ch02/html/l2c02s07.html>
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