Lab report: Characterization of the composition of materials by Laser-induced breakdown spectroscopy

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Abstract—An analysis of the composition of different aluminum samples was made using the laser-induced breakdown spectroscopy (LIBS) technique. Correspondingly, the concentration element of the samples was found using the inductively coupled plasma (ICP) optical emission spectroscopy (OES), a widely use and refine technique. Then, combining the results of both techniques a calibration graph with the samples that have a standard specification (Al 6061, 3003, and 7075) was made. The calibration graph was used to obtain the concentration of the samples without a standard specification and compared to the measurements of the ICP/OES. With this method, concentrations of samples that cannot be analyzed with the ICP/OES can be obtained or at least reduce the processing time.

Index Terms—Laser-induced breakdown spectroscopy (LIBS), Inductively coupled plasma optical emission spectroscopy (ICP/OES).

Fig. 1. The number of articles published in the Web of Science search by laser-induced breakdown spectroscopy (LIBS) in 1963-2016.Source: [1]

I. INTRODUCTION

SPECTROSCOPY is the study of the interaction between matter and radiation for the purpose of founding the composition, physical structure and electronic structure of the matter.

One of the many methods of spectroscopy is atomic emission spectroscopy (AES), in which there is atomization/vaporization of the sample to produce excitation of the atoms to detected the emitted light.

The purpose of AES is to determine the elemental composition of a sample, examination of the emitted light provides the analysis because each element has a unique emission spectrum useful to fingerprint the element.

The position of the emission lines identifies the elements and, when properly calibrated, the intensity of the lines permits quantification.

One type of AES is the inductively coupled plasma (ICP) optical emission spectroscopy (OES) technique in which the composition of elements in (mostly water-dissolved) samples can be determined using plasma and a spectrometer. The technique has been commercially available since 1974 and thanks to its reliability, multi-element options, and high throughput, it has become widely applied in both routine research as in more specific analysis purposes [1].

The ICP/OES technique is widespread in many laboratories but in recent decades there has been a new interest in an emergent technology of the type AES [2], the laser-induced breakdown spectroscopy (LIBS) technique, for analysis in the field or in hostile areas.
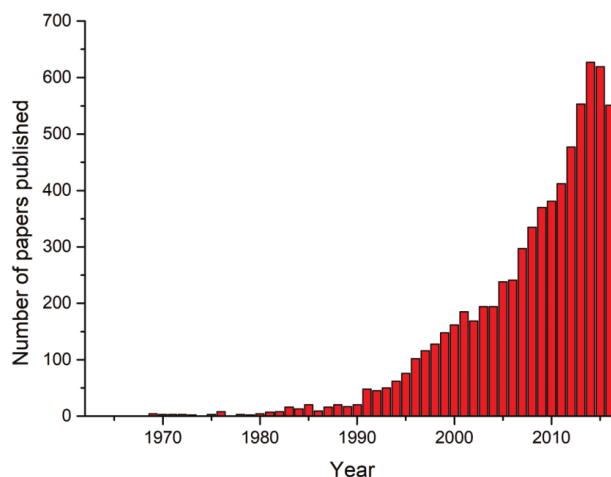
LIBS used a laser-generated plasma as the excitation source, henceforth, makes a noncontact analysis. Also, there is no need for an adjacent physical device, there are few instruments and low cost. There is no need to sample preparations, LIBS directly focused pulsed laser bombardment of the sample without processing the sample. The laser converges to the surface of the sample, and only a small amount of the sample is excited, it can be considered as nondestructive or near nondestructive [3].

LIBS is a very fast technology that provides analytical results in seconds, making it particularly suitable for rapid analysis or online industrial monitoring. But to assess the potential of LIBS, the analytical results must be compared with those of a well-known technique, i.e. ICP/OES, and this is the goal of this paper.

We use the element concentration found in the ICP/OES measurement in various samples in combination with the data found in the LIBS measurement to create a calibration graph that can be used to found the concentration of the elements in other samples, finally we compare the results to the measurements of ICP/OES.

Once done the comparison and confirmed the accuracy of the LIBS measurement, this method can be used to obtain the concentration of elements in samples found in the field or in hostile areas.

II. Materials and Methods

A. ICP/OES

ICP-OES (Inductively coupled plasma - optical emission spectrometry) is a technique in which the composition of elements in (mostly water-dissolved) samples can be determined using plasma and a spectrometer. The solution to analyze is conducted by a peristaltic pump through a nebulizer into a spray chamber. The produced aerosol is lead into an argon plasma.

In the ICP-OES the plasma is generated at the end of a quartz torch by a cooled induction coil through which a high-frequency alternate current flows. As a consequence, an alternate magnetic field is induced which accelerated electrons into a circular trajectory [4]. Due to the collision between the argon atom and the electrons ionization occurs, giving rise to a stable plasma.
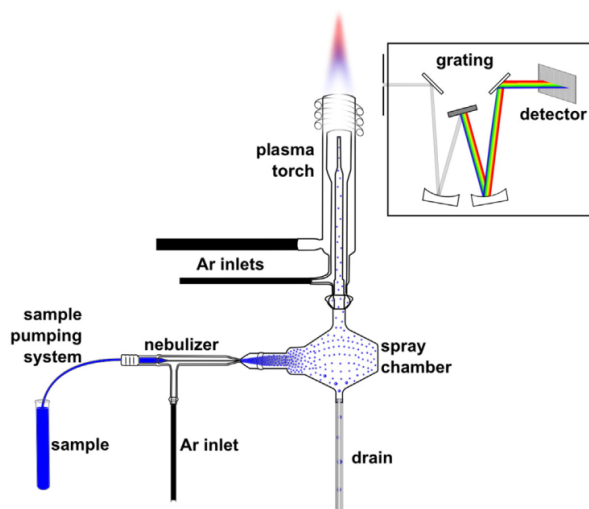

Fig. 2. Experimental setup of the ICP/OES measurement.Source: [5]

In the torch desolvation, atomization and ionization of the sample take place. Due to the thermic energy taken up by the electrons, they reach a higher "excited" state. When the electrons drop back to ground level energy is liberated as light (photons). Each element has its own characteristic emission spectrum that is measured with a spectrometer. The light intensity on the wavelength is measured and with the calibration calculated into a concentration.

An ICP/OES measurement was made for 5 samples, the concentration found in the samples with standard specification (i.e requirements to be satisfied by the sample in the industry), Al 6061, 3003, and 7075 was used in combination with the LIBS data to make a calibration graph.

Element	Concentration (%) ICP/OES		
	Al 6061	Al 3003	Al 7075
Si	0.14	0.144	0.127
Fe	0.324	0.88	0.841
Cu	0.203	0.075	0.841
Mn	0.029	1	0.15
Mg	0.81	N.D	1.26
Cr	0.11	0.013	1.28
Zn	0.114	0.039	2.52
Ti	0.019	0.01	0.015

TABLE I
THE CONCENTRATION OF SAMPLES WITH STANDARD SPECIFICATION
FOUND IN THE ICP/OES MEASUREMENTS.

Element	Concentration (%) ICP/OES	
	Al MIC6	Al K100
Si	0.289	0.056
Fe	0.141	0.013
Cu	1.3	0.089
Mn	0.6	0.283
Mg	1.43	2.9
Cr	0.019	0.056
Zn	2.05	0.029
Ti	0.049	0.018

TABLE II
THE CONCENTRATION OF SAMPLES WITHOUT STANDARD SPECIFICATION
FOUND IN THE ICP/OES MEASUREMENTS.

B. LIBS

The main physical process that forms the essence of LIBS technology is the formation of high-temperature plasma, induced by a short laser pulse.

When the short-pulse laser beam is focused onto the sample surface, a small volume of the sample mass is ablated (i.e. removed via both thermal and non-thermal mechanisms) in a process known as Laser Ablation. This ablated mass further interacts with a trailing portion of the laser pulse to form a highly energetic plasma that contains free electronics, excited atoms, and ions [1].
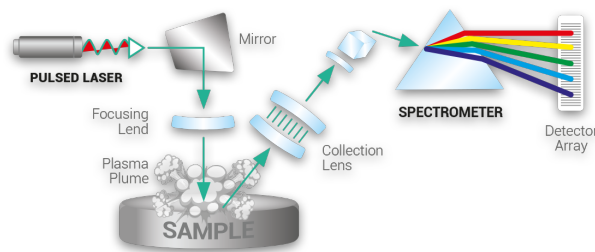

Fig. 3. Experimental setup of the LIBS measurement. Source: [6]

When the laser pulse terminates, the plasma starts to cool. During the plasma cooling process, the electrons of the atoms and ions at the excited electronic states fall down into natural ground states, causing the plasma to emit light with discrete spectral peaks.

The emitted light from the plasma is collected and coupled

with a spectrograph detector for LIBS spectral analysis. Each element in the periodic table is associated with unique LIBS spectral peaks. By identifying different peaks for the analyzed samples, its chemical composition can be rapidly determined.
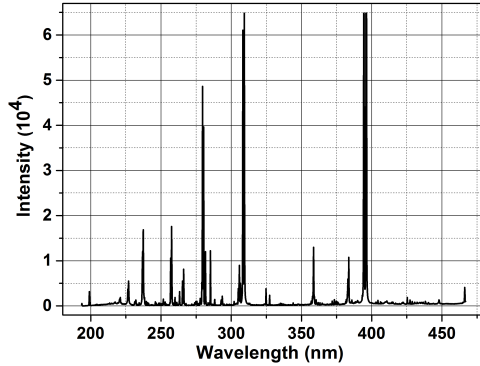

Fig. 4. Spectrum resulting from the LIBS measurement in the sample Al 6061.

In our experiment, we made 100 measurements for each sample. Then an average was made using around 10 to 20 measurements, taking the intensity of the line 281.7 nm of Al ll as a base (Fig. 5) and taking the more stable measurements.
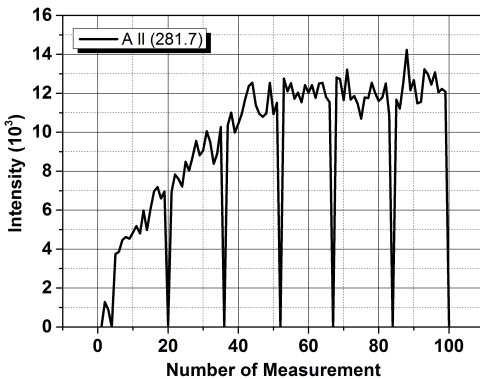

Fig. 5. Distribution of the line 281.7 nm of Al ll in the 100 measurements of the sample Al 6061. In this case, the measurements from 54-64 were chosen as the more stable and use to make the average.

Once the average of the sample was calculated, each line element was identified using the NIST Database [7].
A gaussian adjust was made to the line, taking the area above the Gaussian, and the standard deviation of the background emission adjacent to the line. This way we calculate the signal-to-noise ratio (S/N), this value corresponds to the ratio between the area and standard deviation mentioned.
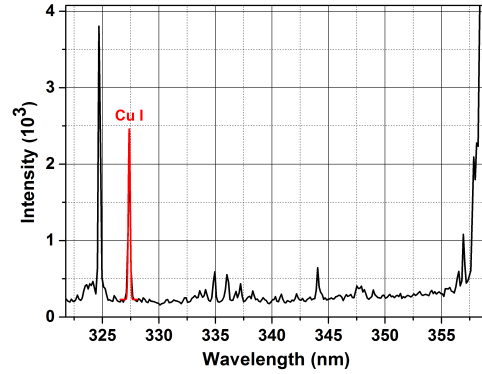

Fig. 6. Identification of the line of Cu I (327.3957 nm) in the sample Al 6061.

III. RESULTS

With the concentration measurements of ICP/OES and the signal to noise ratio obtained in the LIBS measurements of the samples Al 6061, 7075 and 3003 a graph was made for each element. Then, a linear fitting to this calibration graph was made (Fig.7).

The limit-of-detection (LOD) is the minimum concentration of an element that can be detected with the calibration graph. The LOD is calculated according to the 3σ-IUPAC criterion, is the concentration corresponding to a line intensity equivalent to three times the standard deviation of the background, σ, in the vicinity of the line,

$$LOD = \frac{3\sigma}{S} \qquad (1)$$

where S is the slope of the calibration curve for a specific emission line [8].
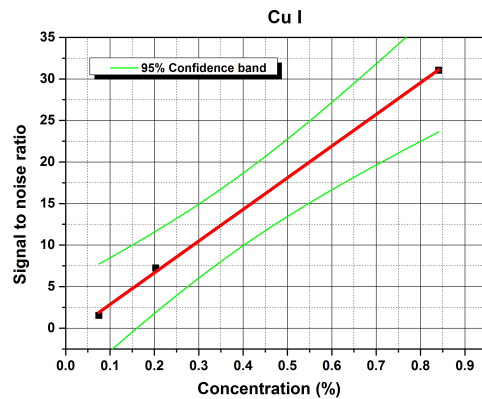

Fig. 7. Calibration graph of Cu I with linear fitting, using the data of the samples Al 6061, 7075 and 3003.

In the Cu I the linear fitting equation that was found was:

$$Y_{cu} = A_{cu} + m * X_{cu} \qquad (2)$$

where Y_{cu} is the signal to noise ratio, X_{cu} the Concentration(%) of Cu, $A_{cu} = -0.95429 \pm 0.51279$ and the slope is $m_{cu} = 38.12921 \pm 1.02278$, with a $LOD = 0.02622$.
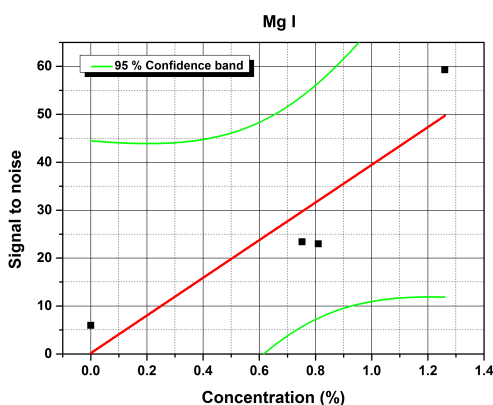
Fig. 8. Calibration graph of Mg I with linear fitting, using the data of the samples Al 6061, 7075 and 3003.

In the case of Mg I:

$$Y_{mg} = A_{mg} + m * X_{mg} \tag{3}$$

where Y_{mg} is the signal to noise ratio, X_{mg} the Concentration(%) of Mg, $A_{mg} = 0.17169 \pm 10.29876$ and the slope is $m_{mg} = 39.29114 \pm 12.28789$, with a $LOD = 0.02545$.

We can calculate the concentration of Cu I and Mg I clearing the variable X (Concentration) from Eq. 2 and 3 respectively, and using the signal to noise ratio found in the LIBS experiment for the other samples.

Sample	Concentration (%) ICP/OES		Concentration (%) Calibration Eq. 2 and 3	
	Cu I	Mg I	Cu I	Mg I
Al MIC6	1.3	1.43	0.58666 ± 0.097	0.55178 ± 0.36804
Al K100	0.089	2.9	0.0889 ± 0.026	0.43302 ± 0.3136

TABLE III
THE CONCENTRATION OF SAMPLES WITHOUT STANDARD SPECIFICATION FOUND USING THE CALIBRATION GRAPH.

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IV. DISCUSSION AND SUMMARY

The table III shows the concentration (%) of Cu I and Mg I in the samples Al K100 and MIC6. Comparing the results to the ICO/OES measurement (Table II-A), it can be see a huge discrepancies between the concentrations found in both methods. The only one that shows almost the same result is the Cu I of the sample Al K100.

It can be seen in the values for the Equation 2 the error in the linear fitting is of the order of 600 % in A_{mg} and of 30 % in m_{mg}, comparing this error to the ones in the linear fitting of Cu I. Where the error in A_{cu} is of the order of 50 % and of 2 % in m_{cu}.

The linear fitting of Mg I contains too much error to obtain relevant results, the same occurred to the other elements Fe, Cr, and Mn. The only linear fitting that did work is the Cu I. An independent measurement of the one present in this report, using the LIBS technique was made by another student, finding the same discrepancies in error.

All things considered, this error can be traced back to the concentration found in the measurements using ICP/OES method, even though the method is very refined and standard, is still possible to make a human error in the process. The percentages errors in two independent experiments using the same measurements of ICP/OES are to out of proportion to think otherwise. New measurements of ICP/OES are needed to make new calibration graph, a process that can be done with ease.

To summarize, the combination of LIBS and ICP/OES measurement to found the concentration of other samples in the field or in hostile areas is plausible as shown in our experiment, even so, more experiments and analysis are needed.

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