Laser-induced breakdown spectroscopy analysis of dried liquids on solid surfaces

Análisis de líquidos in situ sobre superficies sólidas mediante espectroscopía de plasma inducido por láser

Diego Jijón^(1,*), César Costa Vera^(1,2)

1. Departamento Física, Escuela Politécnica Nacional, Ladrón de Guevara E11-253, Ed. Ing. Civil Piso 1, Quito, Ecuador.

2. Grupo Ecuatoriano de Estudio Experimental y Teórico de Nanosistemas -GETNano, Diego de Robles s/n y Vía Interoceánica, Quito, Ecuador.

(*) Email: judijival@hotmail.com

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ABSTRACT:

In this work, we present a comparison of analytical substrates made by scratching surfaces of silicon and stainless steel with pencils of different hardness (HB, 4B, and 9B) in terms of analytical performance in quantification of As and Fe in water. We deposited 1 μ L of aqueous solutions of As and Fe on these substrates over a concentration range of 6-1000 ppm, and then dried the samples with a conventional hair drier. LIBS spectra were collected and calibration curves for each of these cations were built from the areas of the corresponding spectroscopic peaks. In this context we discuss the influence of phenomena such the matrix effect, self-absorption, and self-reversal, upon the non-linear behavior of the calibration curves. We introduce a setup to discuss qualitatively the influence of these two last effects by retro-reflection of the spark light into the LIBS plasma. Suitable calibration curves are obtained for these two elements on the pencil-scratched-silicon substrate. As expected the pencil-scratched-steel substrate does not turn out to be convenient to analyze iron because the elementary constitution of steel already contains iron. The data to build the calibration curves were treated and modeled in agreement with existing literature. This work will improve the usability of previous methods for future industrial and environmental applications.

Key words: Self-Absorption, Self-Reverse, Quantitative LIBS, Calibration Curves.

RESUMEN:

En este trabajo se presenta una comparación de sustratos hechos a base de acero rayado y óxido de silicio rayados con diferentes tipos de lápices (HB, 4B y 9B), según su rendimiento analítico en la cuantificación de As y Fe en agua, usando espectroscopia LIBS. Se depositaron alícuotas de hierro y arsénico con concentraciones entre 6-1000 ppm en los sustratos indicados y se secaron con una secadora de cabello convencional. Se recogieron los espectros LIBS y se obtuvieron las curvas de calibración para los cationes indicados a partir de las áreas de picos espectrales adecuados. En este contexto, se discute la influencia de fenómenos físicos relacionados con el efecto matriz, la auto-absorción y la llamada auto-reversa, en la forma no lineal de las curvas de calibración. Se introduce un arreglo experimental para discutir cualitativamente la presencia y relevancia de estos dos últimos efectos por retro-reflexión de la luz del plasma LIBS. Curvas de calibración adecuadas para los elementos indicados se obtienen para la superficie de óxido de silicio rayada. Como podría esperarse, la superficie de acero rayada con lápiz no resulta ser adecuada para el análisis de Fe debido a la presencia de este elemento en la constitución del acero. Los datos para las curvas han sido tratados con un método estadístico de remoción de espurios, y modelados de acuerdo con la literatura existente. Este trabajo permitirá ampliar la utilidad de los métodos previos en aplicaciones industriales y ambientales.

Palabras clave: LIBS, Cuantificación en LIBS, Efecto Matriz, Curvas de Calibración.

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1. Introduction

LIBS (Laser-Induced Breakdown Spectroscopy), is a frequently used tool for qualitative and quantitative analysis of solids, liquids, and gaseous substances of varying chemical composition. The LIBS technique provides information about the identity and concentration of the atoms present in a compound [1–4]. This technique uses a high intensity laser pulse, focused on the sample to produce a hot plasma, which contains spectroscopic evidence of individual elementary species representative of the sample composition. The high temperatures inside the plasma excite the atomic species present, which then emits light with unique spectral characteristics that permit identifying them. Furthermore, under the right conditions, the intensity of these spectral lines allows the determination of the concentration of the corresponding chemical species. With time, the overall spectral profile generated in LIBS changes. During the first few nanoseconds, the spectrum is basically a continuous background of incoherent radiation produced by the electrons moving away from the plasma. As time goes on, the plasma cools down and the

recombination of electrons and ions produces excited neutral atoms. At this point, the spectrum begins to show spectral lines of those atomic species [5–14].

There are several problems for the construction of calibration curves for quantifying the concentration of a given element in a compound, with LIBS. Among these, we have the chemical matrix effect, whereby the presence of other competing elementary chemical species in the surrounding plasma affects the final intensity of the lines corresponding to the analyte. The variation in LIBS signals resulting from particles of different sizes in homogeneous aerosol samples or micro-crystalline deposits, can affect also the intensity of the spectral lines, and therefore, condition quantification [15–18]. Phenomena such as self-absorption and self-reverse induce a nonlinear loss of sensitivity at higher concentrations. Self-absorption occurs because photons emitted by the core atoms of the LIBS plasma have a high probability of being absorbed by the atoms from the same species in the outer layers of the LIBS plasma, and the result is a loss of signal LIBS. The self-absorption phenomenon is evident in a flattening of the top of a peak's profile, and in deformation of the

peak's wings [15–20]. On the other hand, the self-reversal effect, which is associated to an inhomogeneous plasma distribution throughout the LIBS spark, can manifest itself as indentations at the top of the spectroscopic lines. Through these modifications on the line profiles both the self-absorption and the self-reverse effects induce non-linear responses in the quantification curves that can be obtained with LIBS [17,20]. The chemical matrix effect will not be discussed further in this work, due to the fact that the two other effects are more important in this context. The chemical matrix effect is explained with some detail in references [17,30].

Several experimental setups to study the self-absorption and self-reverse phenomena have been introduced in the literature, based on the use of mirrors to reflect back the emitted light from the LIBS spark into the plasma. The signals with and without the reflection input can then be compared [19,20]. We built an experimental setup similar to that introduced by Bekefi and Moon *et al.* [19, 20], to study these phenomena in the case of a line of Cesium at 852.11 nm and two lines of K at 766.49 nm and 769.9 nm. The aim of this study was to understand at least qualitatively the extent and characteristics of their spectral signatures. We present this in the first part of this paper.

There are several previous works introducing experimental strategies to quantify the concentration of different compounds in liquids with LIBS [21]. In general, the quantitative analysis of these kind of samples is complicated in LIBS for two main reasons. First, the impact of the laser pulse on a liquid interface causes splashing. Second, the LIBS spark is quickly quenched inside liquids which limits the amount and quality of the light emitted for analysis [22–25]. A convenient alternative strategy for dealing with these problems is the measurement over dried-out deposits from the original solutions, as suggested by Vander Wal *et al.* and Jijón *et al.* [26,31]. In the second and main part of this work, following the method introduced in Ref. [26], we built calibration curves for As and Fe in aqueous solutions. Small deposits of these solutions are dried with a conventional hair drier over the pencil-scratched surfaces of stainless steel or a silicon wafer.

Pencils of different hardness (HB, 4B, and 9B) were compared in terms of analytical sensitivity for this purpose [26]. The proposal of using dry deposits on suitable surfaces for the quantitative analysis of cations has been made before by Vander Wal *et al.* [31]. These authors used a graphite planchet to perform the deposits. Other researchers have used membranes or paper substrates for the same purpose [21,27]. In the case of the use of deposits over the analytical system initially introduced in [26], namely, a pencil-scratched steel surface, the quantification of Fe in solution is expected to be complicated by the presence of such element in the composition of steel [26]. For this reason, we introduce a new similarly built system, based on a silica wafer surface scratched with a pencil lead (4B and 9B), with this new system we have been able to satisfactorily build calibration curves both for iron and for arsenic in solution, in the range of concentrations from 6 to 1000 ppm. For the construction of the calibration curves we also used the statistical outlier treatment introduced in Ref. [26] and we have used appropriate models already discussed in the literature [28–30].

2. Experimental system

The instrument used for quantification in this study is a LIBS spectrometer 2000+ of Ocean Optics Inc. (Dunedin, FL, USA) with a spectral range from 200 nm to 1100 nm and a resolution between 0.1 nm at the UV, and 0.3 nm at the NIR. The system uses a Nd:YAG laser emitting in the fundamental mode at 1064 nm, with energies per pulse up to 250 mJ, and a pulse duration of 10 ns. The software OOLIBS used for the data acquisition and peak detection and peak area calculation was provided by the equipment manufacturer. Post analysis for calibration curve building was carried out with OriginPro 8 ® (Origin-Lab Corp., Northampton, MA, USA) and Mathematica 8.0 ® (Wolfram Research Inc., Champaign, IL, USA). The salts were provided by Sigma-Aldrich (St. Louis, MO, USA), and the As and Fe solution were provided by the Laboratorio de Aguas of Escuela Politécnica Nacional (Quito, Ecuador). The characterization of the self-absorption effect was made with a special setup, which we describe in detail below.

2.1 Experimental setup for the qualitative study of self-absorption and self-reversal

We used a semi-spherical mirror positioned on the laser beam axis and in a position between the laser output window and the LIBS target, with the reflecting side facing toward the plasma. An opening at the center of the mirror allowed the laser beam to reach the target. Additionally, we included a homemade retro-reflector (cube-corner mirror), orthogonally at the top of the plasma, to reflect back the light of the spark into the plasma as shown in Fig. 1. The laser intensity used was 60 to 200 mJ. The sampling of the light from the plasma was made with an optical fibre aimed almost orthogonally to both the direction of the laser beam and the observation direction of the cube-corner mirror. A slight inclination from the exact orthogonal direction was allowed, such that the signal in the spectrometer was intense enough. Under these conditions light was reflected back into the plasma by the mirrors, then scattered and absorbed inside it and sampled by the optical fibre. The spectra were acquired with the above mentioned OOLIBS program.

As indicated, the objective of this mirror's arrangement was to send back the photons emitted by the atoms present in the LIBS plasma. In this manner, we increased the probability of photon re-absorption by the atoms in the plasma. According with the references in the literature, for photon self-absorption a flat-topped profile, whereas for self-reverse a dip at the central frequency were expected respectively [17]. The samples for these experiments were made by saturating solutions

Fig. 1. Experimental setup used for detect self-reversal in KCl and CsCl.

of KCl and CsCl in water, which were deposited on a steel substrate and let drying to form a thick crystalline deposit.

2.2 Experimental setup for LIBS quantification of As and Fe solutions

To make calibration curves for the As and Fe cations in aqueous solution we used the LIBS2000+ spectrometer describe before. Briefly, the pulses from a Nd:YAG laser were focused by a lens on the sample surface which was laid on a xyz translating stage in the sample chamber. Figure 2 shows scheme of this instrument. With the help of the translation stage and a video camera for imaging the sample which is part of the LIBS2000+ system, we could select the exact point of impact of the laser on the sample.

The laser focal point on the substrate analyzed was kept fixed, that is, we did not change the length of z (see Fig. 2). We used the same length for all measurements.

We prepared 6, 15, 50, 100, 150, 200, 400, 600, 800, and 1000 ppm solutions of As and Fe dissolved in deionized water. Aliquots of these solutions were deposited and then dried with a hair drier on the substrates indicated below. The corresponding LIBS analysis was performed over the resulting micro-crystalline deposits.

For the analysis, arsenic (As) presented only two peaks registered at 228.812 and 234.984 nm. These peaks were analyzed by LIBS from the solution deposited on the substrates of the steel surface scratched with a (HB, 4B, and 9B) pencil lead.

Fig. 2. LIBS set-up used for calibrations curves of As and Fe dissolved in water.

Table I shows the iron (Fe) peaks analyzed for this work. To evaluate the effect of the elemental composition of the substrate on the LIBS signal of the deposits, the Fe peaks were analyzed on two different systems, a steel surface scratched with a 9B pencil lead, and a silicon wafer scratched with a (4B and 9B) pencil lead. An example of the spectral region for Fe indicated in Table I is shown in Fig. 3. The spectrum corresponds to a 1000 ppm Fe solution over 9B-leadscratched stainless surface.

As expected, a great deal of interference from iron atoms of the steel was observed in the former system. This rendered the pencil-scratched steel surface impractical for iron analysis. This also limits in general the type of elements that can be addressed with this method given a particular substrate.

Fig. 3. Peak 4 obtained from the spectral data indicated in Table I for the Fe spectral analysis.

Table I

Fe peaks chosen from the spectral data for analysis with LIBS technique. Left wing and Right wing here correspond to the extreme values delimiting the peaks studied as defined in the acquisition software.

	Centroid	Left wing	Right wing
	Wavelength (nm)		
Peak 1	438.35	437.81	439.36
Peak 2	440.45	437.94	441.99
Peak 3	406.26	403.74	407.96
Peak 4	373.57	371.60	377.64
Peak 5	358.21	355.01	363.00

3. Results and discussion

3.1 The self-reversal effect

As indicated before, the self-reversal effect can be investigated using the setup indicated above, through the presence of a distinctive dip at the top of the emission peaks. The self-absorption should on the contrary, be evident through a flattening of the top of the peaks [17,30]. In our case, the former effect is thus probably responsible of the appearance of some of the peaks obtained using the dedicated setup described earlier. An example of this evident feature is shown in Fig. 4 for a 852.11 nm Cs peak. In this case the redirection of the light through the LIBS plasma causes the loss of photons exactly in the center of the peak. Of course, this also means that the area of the curve is reduced and is no longer representative, at least in a linear fashion, of the initial Cs atom population.

We found similar self-absorption effects in the 766.49 nm and 769.9 nm peaks of K from KCl. In this case we measured for two different concentrations of the water solution of KCl. One solution was saturated (over 1.161 g/mL) with the salt while the second was not saturated and was instead diluted (around 0.433 g/mL). The difference seems to indicate that the ready availability of more K atoms in the plume, coming from the initial higher concentration, correlates with greater absorption, as evident in the larger dip in the saturated solution. In this manner, we have determined that three things directly affect the extent of: 1) higher laser intensities, which provoke a larger amount of material ablation, 2) larger initial concentration of the element in the initial sample, and 3) the larger availability of photons with the "right" wavelength passing through the plasma to re-excite already unexcited neutral atoms. Due to the profile deformation observed (Fig. 4), it is clear, that under conditions propitious for self-reversal, such as high relative concentrations of the analyte, the calibration curves must show a non-linear behavior. This has been properly rationalized when modeling such curves in the literature, for instance in the work of Aragon *et al.* [28]. A saturating exponential growth (see below) should take the place of a linear calibration in such cases [28].

Fig. 4. Self-reversal is evident in the dip at the top of the peaks in this spectrum of Cs at 852.11 nm.

Fig. 5. Spectra for the K peaks at 766.49 nm and 769.9 nm for both a saturated (in black) and a non-saturated (in red) solution of KCl. The effect of the larger original availability of atoms of K in the saturated solution is evident in the larger absorption for the self-reverse to occur dip at the center of the peaks.

3.2 Quantitative analysis of As and Fe

In this work on analytical substrates, we used the method proposed in Ref. [26]. In that work, the authors introduced, for the first time in LIBS, an analytical substrate formed by scratching a lead pencil on a steel surface and proposed a suitable statistical procedure to treat the data, by eliminating outliers. The proposed statistical analysis method included the remotion of outliers by taking into account the size distribution of the micro crystals that were formed by allowing the solutions to dry onto the substrate. Briefly, to eliminate detrimental outliers a comparison is made of the representative peak areas at a given concentration with the corresponding average values at immediately higher and a lower

concentration. The registered area values at a particular concentration that are larger or smaller, respectively, than those average values are considered outliers and are removed from the analysis. In this work, we compared two substrates, stainless steel and a silicon wafer surface, scratched with pencil leads of different hardness in terms of analytical response. For this, we aimed to increased relative sensitivity and reduced variance of the representative. To clarify this, in Table II the standard deviation average for measurements for two peaks of As at 228.86 nm and 235.05 nm are shown. The results show no great statistical significant differences and there is no clear advantage in the use of one type of lead or another. Still, for the peak at 228.86 nm the standard deviation value is about half of the other cases, and suggests a better option for quantification of As by using this spectral line. The marginal differences observed in Table II are evidently correlated with the hardness of the pencil lead used, and might have to do with both a better coverage of the substrate with the particular pencil used, and a degree of overall hydrophobicity of the respective clay-graphite mixture that makes up that particular pencil lead. This certainly is the case of the 9B pencil, which due to its softness spreads more evenly and has higher graphite content than the others. This is consistent with the fact that a pure graphite surface has been demonstrated to be an excellent choice for quantifying from dry deposits [26,31].

In Fig. 6 we show the calibration curve for As obtained with the whole calibration curve method proposed. It is clear in this case that for the wide range of concentrations measured here, the behavior is nonlinear. To produce the data

Table II

Standard deviations of the signal intensity for two characteristic peaks of As at 228.86 nm and 235.05 nm. There are no major differences between the different substrate preparations, however, the lowest value is about half of the others and suggests that using a 9B pencil-lead covered substrate and analyzing the 228.86 nm peak for As is the best analysis choice.

Average (σ)			
Peaks analyzed	9B	4B	HB
Peak 1 (228.86 nm)	6.847	10.668	11.894
Peak 2 (235.05 nm)	10.675	14.214	12.854

Fig. 6. A calibration curve for arsenic concentrations from 6 to 1000 ppm. A non-linear behavior is appreciated over the concentration range. The use of the outlier treatment proposed in Jijón *et al.* [26] permitted reducing the error. Further improvement can be achieved with a larger number of spectra averaged for every point in the curve.

points shown and their corresponding error bars, the overall error will be reduced and the statistical increased. The outliers treatment was applied for all data points in this case.

To better quantify with this calibration curve, we fitted the measured points to an expression of the form shown in equation:

$$y = y_0 + A_1 \exp\left(-\frac{x}{t_1}\right). \quad (1)$$

This equation is equivalent to a empirical expression put forward by Aragon *et al.* previously [28] (Eq. (2)):

$$I = a + bc_0 \left(1 - e^{-\frac{x}{c_0}}\right). \quad (2)$$

In their work Aragon *et al.* discussed the influence of nonlinear effects from phenomena such as self-absorption. Additionally, it was shown that this equation can adjust also a linear behavior at relative low concentrations [28]:

A further discussion of the different terms in Eq. (2) can be found in Ref. [30]. Here, a and b are constants, and c_0 can be regarded a “saturated concentration” [30], in the sense that the maximum concentration used to build the calibration curve can no be much larger than c_0 [30]. Also, x represents the concentration ratio, and I is the intensity of the line of the cation analyzed. The parameters in Eq. (1) are easily connected algebraically to those in Eq. (2). It is

Table III

Parameters resulting from the fitting with Eq. (2) of the experimental results for arsenic obtained over different analytical surfaces.

Pencil lead	Coef.	$\lambda=228.86$ nm
		Value
HB	y_0	85.773
	A_1	-82.775
	t_1	314.865
	R	0.999
4B	y_0	85.051
	A_1	-80.506
	t_1	315.259
	R	0.987
9B	y_0	75.553
	A_1	-69.962
	t_1	322.808
	R	0.995

Fig. 7. A calibration curve for iron obtained over a new system consisting of a pencil-lead-scratched silica surface, where no interference from the substrate composition affects the iron signal.

understood in this interpretation that the non-linear behavior evident in these equations is brought about by effects such as the self-absorption and self-reversal phenomenon discussed above

Table III summarizes the fitting parameters for 228.86 nm in this case in accordance with Eq. (1).

The analysis of the Fe solutions presented particular difficulties due to the fact that stainless steel already contains massive amounts of iron in its composition. As mentioned earlier, the use of the stainless steel substrate is not advisable in this case because of this. Measurements not reported here over such

substrate show, as expected, a large amount of background over a large range of concentrations, which reduces largely the sensitivity and takes the limit of detection over 500 ppm for iron. In this work we introduce a new system to deal with this problem, which is made by scratching with a pencil a silica surface. The resulting calibration curve (figure 6 for iron in this case) is similar to that already shown for arsenic.

We believe that these results confirm that as suggested previously, as expected the merit of the substrate systems introduced in Ref. [26], and this work, goes to the graphite overlay from the pencil leads used to scratch the surfaces. In this regard, it will be of interest to compare more formally the analytical performance of these two different substrates. An interesting result is shown in Fig. 8, where we show the calibration equation for the Fe (see Table I) on silica wafer for both a 9B and a 4B pencil lead surfaces. Notice that the curve on the 9B-terminated surface lies higher than that of the 4B one, meaning that higher spectral signals are measured in the former case.

According to this, it is possible to advance the conclusion that the 9B substrate is more sensitive in this case.

Table IV summarizes the fitting parameters for all Fe peaks in this case. It is evident that in every case the parameter t_1 , related to the growth rapidity of the curves is larger in the 4B than in the 9B cases, reinforcing the previously advanced conclusion. The data fluctuation in both substrates, and the parameters y_0 and A_1 in the calibration curves, related to other properties of the curves are similar in all cases.

For the sake of completeness, we also analyzed the arsenic solutions on a silica wafer scratched with a 9B pencil lead. The calibration curve is shown in Fig. 9 and is very similar to that of Fig. 6. In this case, both underlying substrates produce equivalent analytical performance.

However, as discussed above, a higher sensitivity is obtained in the silica substrate for a 4B pencil lead, contrary to what was observed for iron. At this point in our research is not possible to deduce the cause of such observation, but perhaps the different roughness

of the silicon and steel surface can be a part of the answer.

The limit of detection (LOD) for the arsenic element in a solution were calculated using Eq. (3), following the prescription in references [17,21]:

$$LOD = \frac{3\sigma}{m}, \quad (3)$$

where σ is the uncertainty (standard deviation) in the peak area for the lowest concentration, and m is the slope of the calibration-line for small concentrations. The LOD calculated in this way for arsenic on the silica substrate and 9B pencil lead was 3.2 ppm. For iron on the same system the LOD can be estimated to be lower than 5 ppm.

Fig. 8. Fe peak1 functions of silicon wafer scratched with a (4B [dashed], and 9B [solid]) pencil lead.

Fig. 9. Calibration curve for arsenic obtained over the same pencil-scratched silica wafer surface as in Fig. 8. A very good result is found, comparable to the case of the steel based substrate, in this case.

Table IV

Parameters resulting from the fitting with Eq. (1) of the experimental results for iron obtained over the silica surface scratched with different pencil leads.

Peak	Coef.	4B	9B
		Value	Value
Peak 1	y_0	437.858	442.556
	A_1	-340.573	-361.506
	t_1	373.563	204.688
	R	0.979	0.987
Peak 2	y_0	979.302	872.590
	A_1	-809.287	-723.316
	t_1	549.619	270.890
	R	0.983	0.994
Peak 3	y_0	672.584	657.317
	A_1	-537.761	-537.301
	t_1	508.497	286.925
	R	0.985	0.983
Peak 4	y_0	199.151	227.597
	A_1	-125.973	-173.078
	t_1	485.708	332.885
	R	0.980	0.974

4. Conclusions

The investigation reported here with a setup to enhance the reabsorption of light by the LIBS plasma showed dips on characteristic peaks under our conditions. This is consistent with a major role of the self-reversal phenomenon on the nonlinearity of the calibration curves for quantifying cations in water. These results are consistent with previous works aimed to understanding the nonlinearity of such calibration curves. A reliable calibration function can be suggested from these observations which we have used to fit our experimental data. The analytical performance of stainless steel and

silica substrates scratched with pencil leads of different hardness and graphite content was investigated and compared accordingly for arsenic and iron dissolved in water. Both kinds of substrates show similar performance, except in the case of cations in the solution that are also present in the substrate, namely, iron on stainless steel. This supports the conclusion that the analytical merit of these newly introduced analytical systems lies on the overlaying pencil layer and also hints to the need of a proper substrate and pencil lead combination selection according with the cation to be analyzed. It is important to indicate that with these two different substrates a large number of cations can be quantified with LIBS. These analysis benefit greatly of a proper statistical treatment of the results, as discussed in the paper and in previous works.

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