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Comparative analysis of the efficiency of fixing methods of metal-doped silica nanoparticles by Laser-Induced Breakdown Spectroscopy

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ABSTRACT

Silica nanoparticles have been studied for several applications since they can be obtained from rice husk biomass. These nanoparticles are dope with different metals for industry applications or as adsorbent of impurities. Quantitative analysis of them is carried out for evaluating their efficiency as adsorbents. LIBS technique can analysis this kind of samples by fixing the powder for the study. Two different methods of fixation (pressed tablets and fixation by carboxymethyl cellulose) were studied in this work with silica nanoparticles doped with Cu and Fe. Calibration curves were made and a simple linear regression was performed for obtain the correlation coefficient and slope of the linear fit for each method and metal. Limits of detection were calculated and the prediction ability of the models were evaluated by the analyzed of "unknown" samples. Results showed that pressed tablets had better correlation coefficients and prediction ability than fixation by CMC. Also, this method showed a good repeatability and reproducibility. Despite that, fixation by CMC showed a better LOD for copper but for iron.

Keywords: Laser-Induced Breakdown Spectroscopy, silica nanoparticles, simple linear regression, quantitative analysis, LIBS.

1. INTRODUCTION

Laser-Induced Breakdown Spectroscopy (LIBS) is an analytical technique that is being applied in industry[1], environmental diagnostic[2] and multitude of fields[3]. The LIBS method is based on the formation of plasma within focusing a laser pulsed into a liquid, gas or solid[4]. LIBS technique present some advantages over other Atomic Emission Spectroscopes, such as little or no sample preparation[5], multielemental analysis and virtually non-destructive. However, matrix effects[6] and self absorption have been their disadvantages as a quantitative analytical technique. Several researches have been focused of LIBS analysis of solid, especially powders[7, 8].

Silica nanoparticles have been used widely in the last decades for different applications. Since they can be synthesized from rice husk biomass, several studies of them had been carried out[9, 10]. These nanoparticles are fine powders that cannot be analyzed directly by LIBS without a fixing method. Pressed tablets and fixation by gelation has been commons methods for the study of powder by LIBS[11]. For LIBS quantitative analysis figure of merits are set. These figures of merits are: limit of detection (LOD), correlation coefficient (R^2), mean square error for evaluating the prediction model, repeatability and reproducibility[12, 13].

In this work, two different methods of fixation had been studied and compared: pressed tablets and carboxymethyl cellulose (CMC) fixation. Calibration curves were made for the studies of Cu and Fe, and simple linear regressions were carried out. Finally, unknown samples of silica nanoparticles with Cu or Fe were analyzed.

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2. METHODOLOGY

2.1 Experimental Setup

A schematic of the experimental setup is shown in Figure 1. Laser pulses from a Q-switched neodymium-doped yttrium aluminum garnet (Nd:YAG) laser operating at 355 nm wavelength and 10 Hz repetition rate were focused on samples placed in a x-y-z moving platform. The platform was moved following a pattern of 12 steps in x-axis and 6 steps in y-axis while the z was fixed, each step was 0,5mm, to ensure that each laser pulse would interact with fresh sample. The laser output energy was varying and the Q-Switch was 160. A plano-convex lens of 4,5 cm focal length was used to focus the laser onto the sample surfaces at normal incidence. Plasma emission was collected through a fiber optic connected to an Andor's Mechelle ME5000 spectrograph (wavelength range 200-975 nm) set up at 800 ns of delay time, 4μs gate pulse width, MCP Gain (0-255)=200, exposure time of 0,002 s and 10 accumulations.

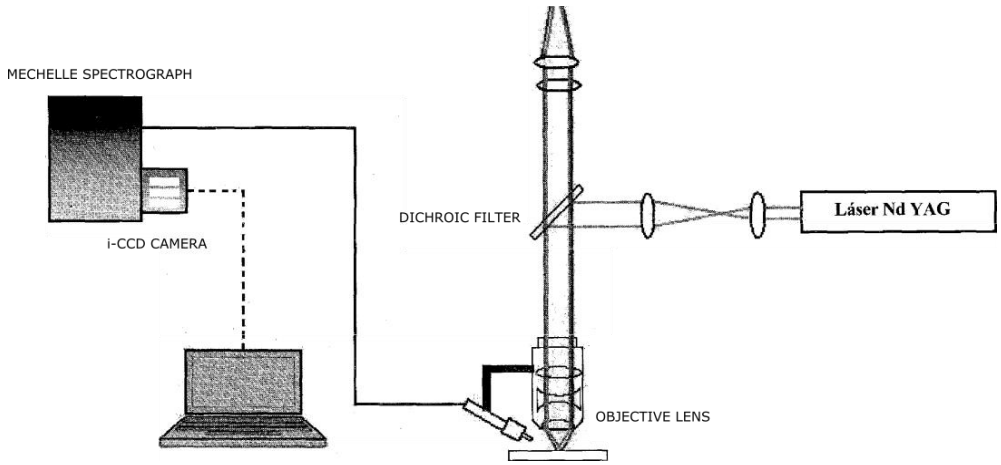

Figure 1. Set up of acquisition for LIBS analysis[14].

2.2 Delay time and Gate pulse width optimization

Optimizations of the delay time and gate pulse width were carried out by preparing 8 pressed tablets of 7% of copper in a NPs SiO_2 matrix. Each mixture was ground and homogenized for 5 minutes in a Vortex 2000 for ensure particle uniformity. For pressed samples, each mixture was compacted into a tablet by 4000 psi during 2 minutes. Samples were analyzed directly by LIBS. Gate pulse width was set at 5 μs and the delay time was varied from 500-800 ns, four samples were studied. Then, the best delay time obtained was set and the gate pulse width was varied from 3-6 μs.

2.3 Calibration curves

Calibration curves for each metal were made for both methods: tablets and carboxymethyl cellulose (CMC) fixation. Tablet samples of known copper concentration were prepared by mixing Copper (II) sulfate pentahydrate ($CuSO_4.5H_2O$) salt and NPs SiO_2, ground and homogenized for 5 minutes in a Vortex 2000, and compacted into tablets by 4000 psi for 2 minutes. Iron tablets were prepared by mixing Iron (III) oxide (Fe_2O_3) and NPs SiO_2; ground, homogenize and compacted following the same procedure. For CMC calibration curves, copper (II) oxide was used instead of the salt. Metal-NPs SiO_2 mixtures were prepared as same and mixed with a 10% m/m of CMC solution, were placed in aluminum molds and dried by 5 hours.

2.4 Unknown sample preparations

Silica nanoparticles were doped by impregnation with Copper (II) sulfate pentahydrate. Following the same procedure of ground and homogenize, the samples were fixed by pressed tablets and CMC fixation.

3. RESULTS AND DISCUSSION

The plasma spectrum of measurements in LIBS contained the information about the elements of the samples. The information is available as emission lines located at specific wavelengths and the intensity of them[15]. An emission spectrum of the copper samples which known composition is shown in Figure 1, where obtained lines were compared with the National Institute of Standards and Technology (NIST) electronic database[16]. Spectral lines at 510 nm, 515 nm and 521 nm can be observed. This fact evidence the presence of Cu(I) in the sample.

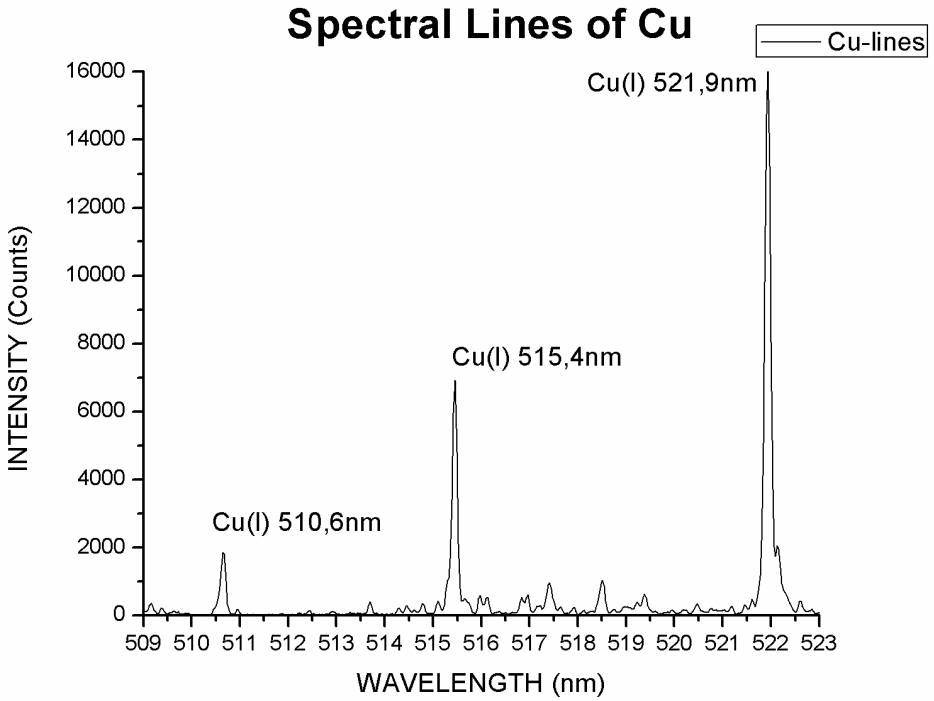

Figure 2. Spectral lines of Cu in a measure of a tablet sample for calibration curve.

Iron emission lines of the samples are shown in Figure 2, where the lines 430 nm, 432 nm and 438 nm where observed and compared with NIST electronic database. For both metals, the working spectral line was 521 nm (Cu) and 438 nm (Fe).

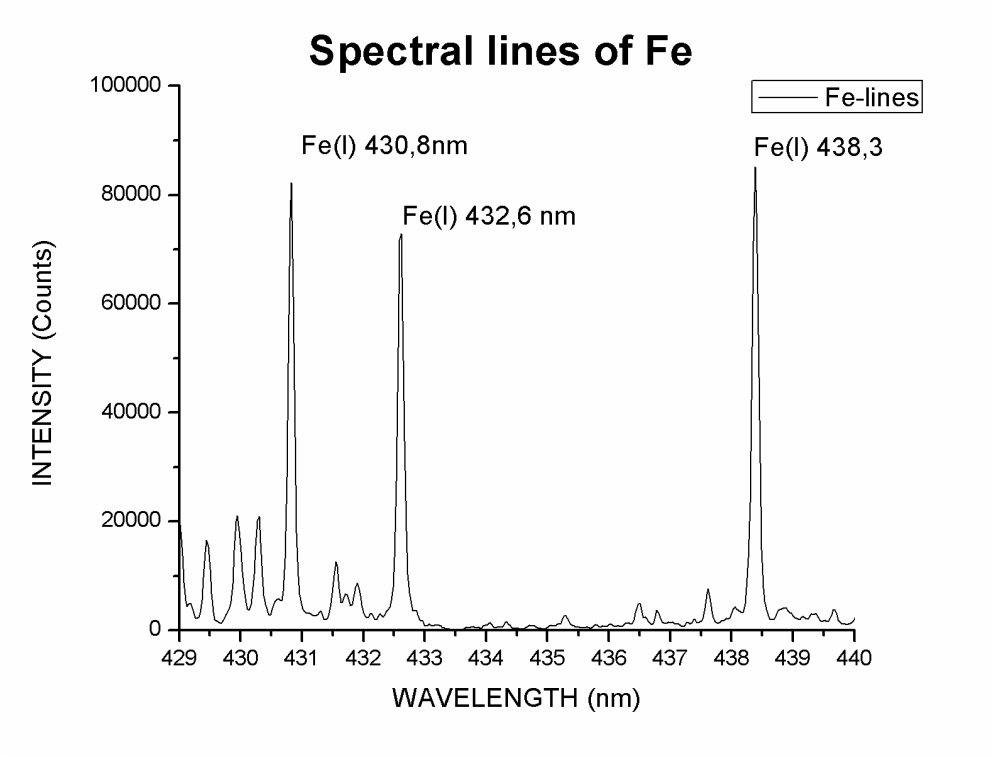

Figure 3. Spectral lines of Fe in a measure of a tablet sample for calibration curve.

All spectral lines were analyzed by peak intensity; considering just the more intensive line for meet the IUPAC[17] (International Union of Pure and Applied Chemistry) criterion of 3 times the noise[18].

Mechanical properties for both methods were evaluated at this point. Fixation method by CMC showed poor mechanical properties, fragility, incompatibilities with the copper salt (specifically, the sulfate ion of the salt) that forcing us to carry out the calibration curve with copper oxide, and a difficult handling of the samples. Also, the samples were not possible to separate from the fixation surface sometimes, situation that represented a waste of time and reagents. These results were caused by the sample dependences of the time and dry temperature, variables that need to be handle with care. On the other hand, tablet fixation showed good mechanical properties and this method has the advantage of not showing incompatibilities. For all these reasons, tablet fixation is useful for all kind of solid samples, and CMC fixation has to be carried out carefully with some samples.

Figure 4. Comparison between tablet (right) and CMC (left) samples.

3.1 Delay time and gate pulse width optimization

Delay time and gate pulse width play an important role in quantitative LIBS analysis. Since, early stages of plasma discharge are characterized by the brehmsstrahlung continuum emission, and only the subsequent stages show the characteristic line pattern, which allows for the quantitative analysis of the samples composition[19], the optimization of these parameters is necessary[20]. The signal-to-noise ratios were obtained when four tablets of known concentration of copper were analyzed by varying the delay time and setting the gate pulse width at 5μs (see Table 1), where 800 ns of delay time was better for a higher signal-to-noise ratio. The emission line of Cu(I) at 521,8 nm was chose for the analysis.

Table 1. Delay time and gate pulse width values for the optimization of the signal-to-noise ratio.

Delay time (ns)	Gate Pulse Width (μs)	S/N
500	5	3,67541006
600	5	8,87522007
700	5	10,8397349
800	5	17,0603993
800	3	12,7695104
800	4	68,0048738
800	5	11,9442172
800	6	29,8119115

Taking this into account, the delay time was set at 800 ns and the optimization of the gate pulse delay was carried out (see Figure 3). The signal-to-noise ratios of these acquisitions gave as 800 ns of delay time and 4 μs of gate pulse width as the best condition for the analysis. The signal-to-noise ratio (S/N) were calculated by:

$$\frac{S}{N} = \frac{\bar{X}}{\sigma} \qquad (1)$$

Where $\overline{X}$ is the average of the intensities of the chosen spectral line and σ is the standard deviation of the measurements.

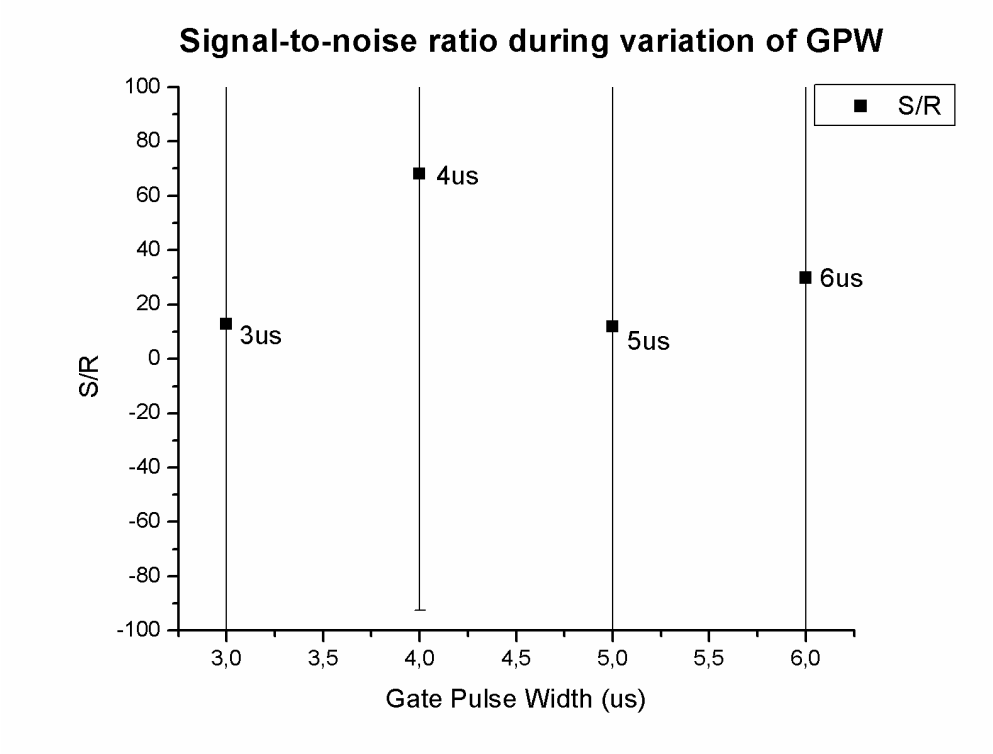

Figure 5. Plot of the S/N ratio versus gate pulse width.

3.2 Comparative analysis of tablets and CMC fixation methods

For a comparative analysis of two methods, figures of merit are calculated. The commons figures of merit used in a LIBS analysis are limits of detection, the correlation coefficients in calibration curves is a good figure of merit for a quantitative analysis and can help for comparing two different methods of fixation. Also, the repeatability and reproducibility of the analysis, and relative standard deviation (RSD in %) or standard deviation described the precision of the measurements[21, 22].

For comparative analysis in copper samples calibration curves were made for each method setting the parameters of delay time and gate pulse width calculated previously at different concentrations of Cu. Between 4 to 10 % of Cu in pressed tablets and 5 to 15% of Cu for CMC fixation. A simple linear regression of the measurements was performed and correlation coefficient was obtained for both methods (see Table 2). Calibration curves for tablets and CMC fixation are represented in Figure 4 and Figure 5. A linear correlation between intensity and concentration of Cu is showed in the range of work for tablets and CMC fixation. Also, high correlation coefficients are obtained for the calibrations curves, where some works considered an R^2>0,99 as good for quantitative analysis[21]. The correlation coefficients, slope, offset and root mean square error or mean relative error (RE%) are the major statistics for determining a good linear regression[21].

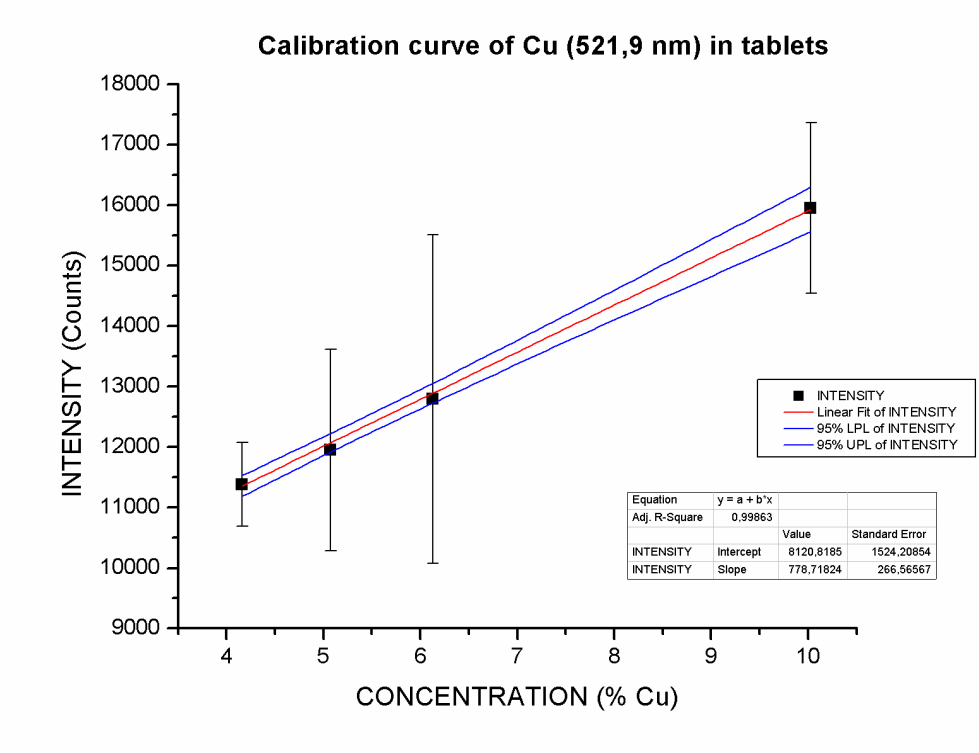

Figure 6. Calibration curve for copper samples pressed in tablets. A small slope is observed in the graph and high correlation coefficient is observed.

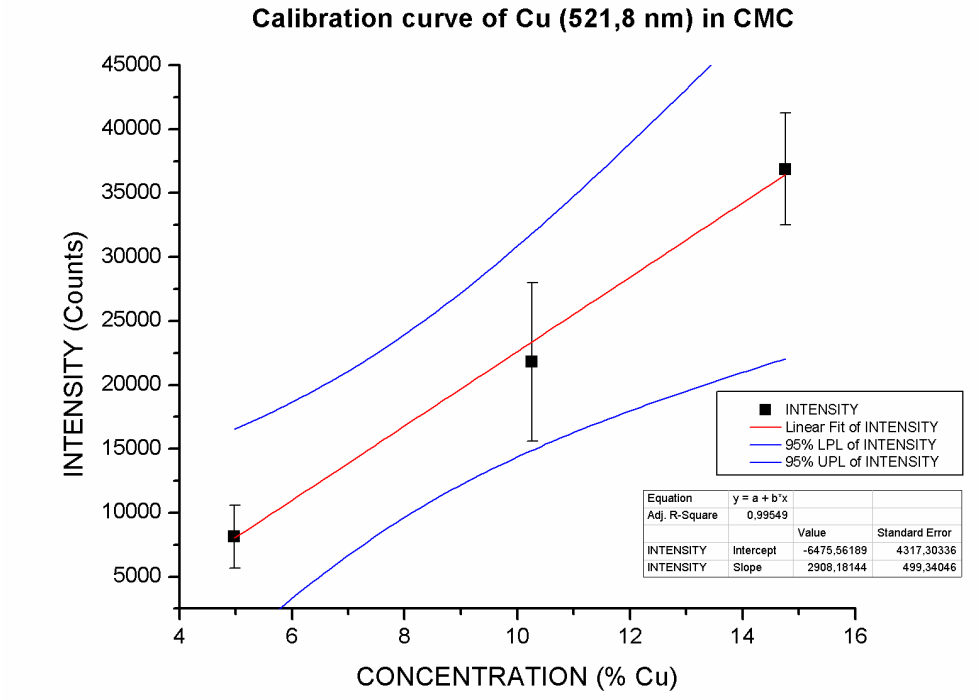

Figure 7. Calibration curve for copper samples fixed by carboxymethyl cellulose. A high correlation coefficient is observed and a large slope too.

The difference between both correlation coefficients were small and further analysis need to be performed for compared this two methods. Also, a larger slope is presented by pressed tablets in the simple linear regression analysis, which could lead to higher limit of detections.

Table 2. Correlation coefficients and slope of simple linear regression of calibration curves for pressed tablets and CMC fixation.

Method of fixation	Correlation coefficient R^2	Slope	RE%	Mean Square Error
Cu Tablets	0,99863	778,71824	34,1689375	0,00391
Cu CMC	0,99549	2908,18144	52,9935417	0,07671
Fe Tablets	0,93829	12194,22347	-	6,77689
Fe CMC	0,93219	2697,72635	-	0,51973

The same procedure was carried out for calibration curves for iron samples for both methods (see Figure 6 and Figure 7). Where a range of 5 to 15% of Fe was evaluated in pressed tablets and 3 to 12 % of Fe for CMC fixation. Correlation coefficients were too similar too in this case. However, the slope together the R^2, the pressed tablets show a better fitting model for the analysis.

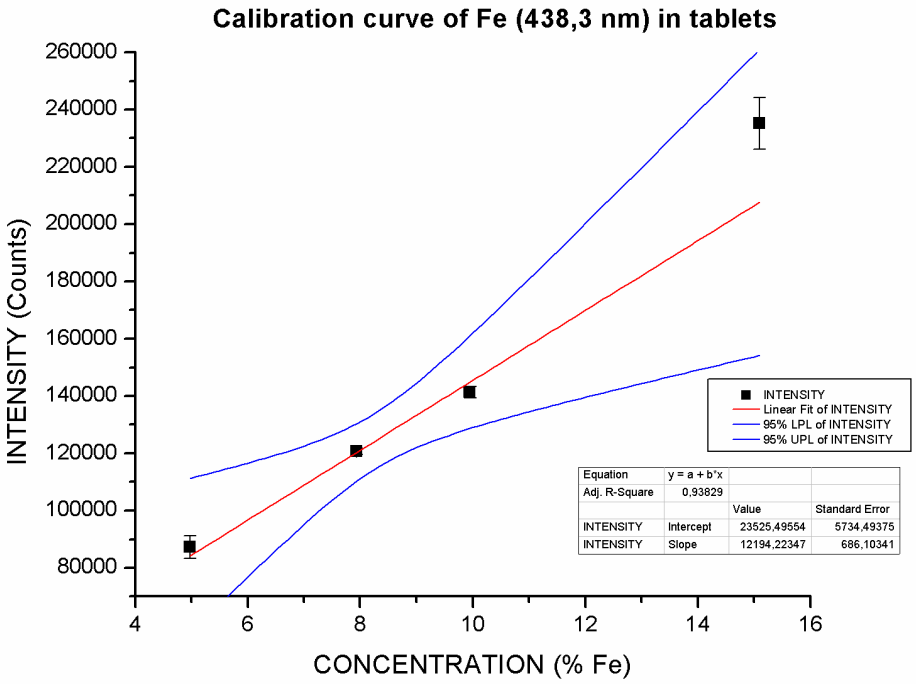

Figure 8. Calibration curve for iron samples in pressed tablets. A large slope is observed.

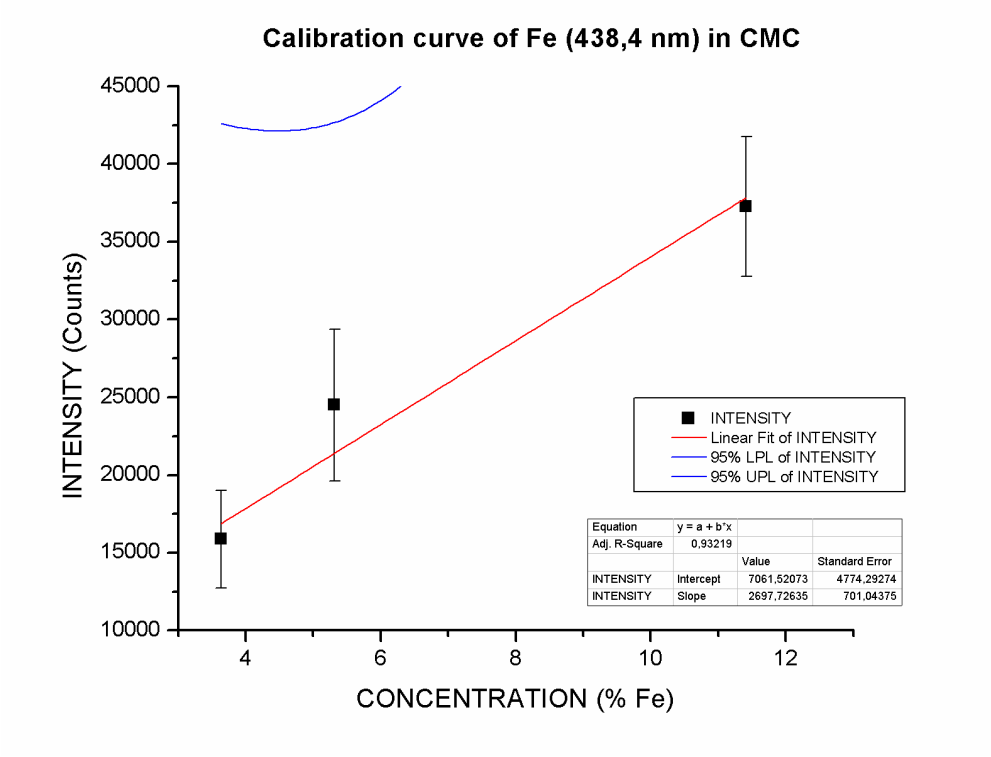

Figure 9. Calibration curve for iron samples fixed by carboxymethyl cellulose. A large slope is observed.

Limit of detection (LOD) can be calculated from the information of the simple linear regression, where the slope of the linear fit is crucial. A lot of works use the following equation for calculating the LOD[15]:

$$LOD = \frac{3\delta}{s} \qquad (2)$$

Where δ is the standard deviation of the blank or background and s is the slope of the linear regression. Given LOD are show in Table 3, where CMC fixation has better LOD than pressed tablets in the analysis of Cu; but in Fe analysis, the pressed tablets method has a better LOD.

Table 3. LOD for each method in both metals.

Method/Metal	***Tablets/Cu***	***CMC/Cu***	***Tablets/Fe***	***CMC/Fe***
LOD	16,9732	4,5448	1,0839	4,8994

3.3 Evaluation of an unknown sample of copper

Unknown samples of Silica nanoparticles doped with Cu were analyzed by LIBS. A delay time of 800ns and gate pulse width of 4μs were set for the measurements. The linear regression for both methods was used for the analysis. Obtained concentrations of Cu are show in Table 4 for the measurements of two different samples.

Table 4. Concentration of Cu in unknown samples analyzed by LIBS using pressed tablets and CMC fixation.

Method of fixation	Sample	Concentration (% Cu)	Average (% Cu)	Standard deviation
Tablets	1	4,97576	5,266485	0,411147238
	2	5,55721		
CMC	1	3,957016667	3,76051667	0,277892965
	2	3,564016667		

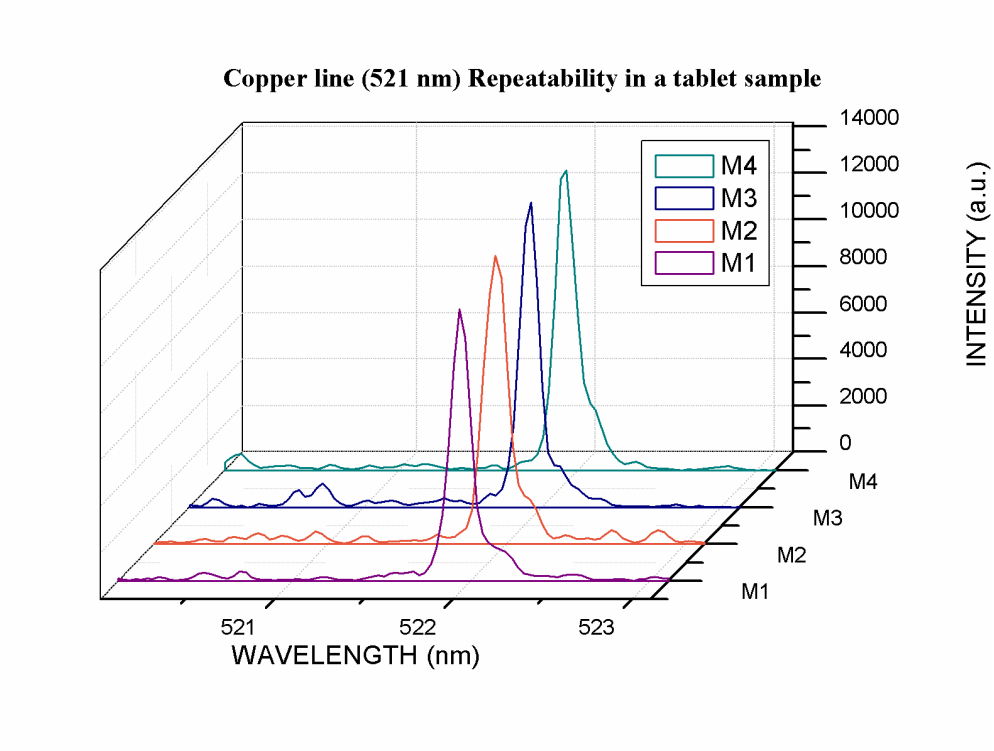

Figure 10. Plot of the different measurements over a same sample in the tablet fixation method.

A good repeatability was observed in tablet fixation method when we plotted the several analysis results over the same sample (see Figure 10), where the intensity of single measurements were similar. This repeatability is not observed with the fixation by CMC (see Figure 11). The reason of this could be that tablet samples were more homogeneous than CMC samples.

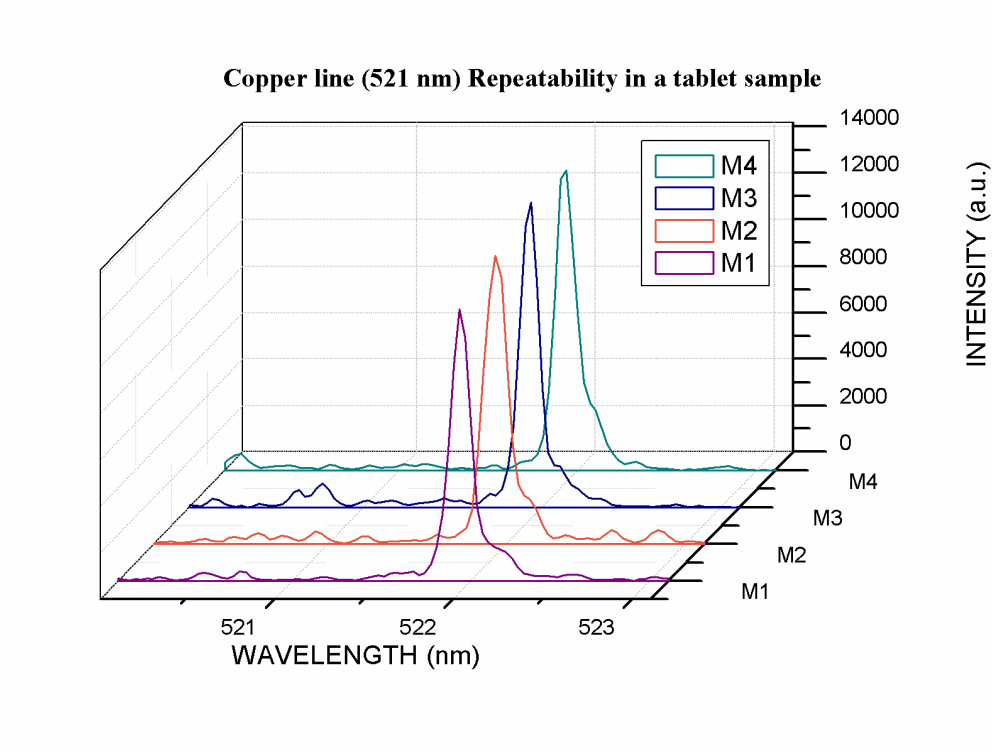

Figure 11. Plot of the different measurements over a same sample in the CMC fixation method.

The truth value of the concentration of copper in the silica nanoparticles is 8%. Considering this, the trueness of the pressed tablets is better than the one from CMC fixation. But, precision is better in CMC fixation because of his low standard deviation in comparison with the pressed tablets[23]. This shows that CMC fixation has better reproducibility. Despite that, the model of prediction can be evaluated by calculating the mean relative error[21]:

$$RE(\%) = 100\frac{1}{N}\sum_{i=1}^{N}\frac{\left|\bar{Y}_i - Y_i\right|}{\bar{Y}_i} \quad (3)$$

Where N is the number of samples, $\bar{y}_i$ is the reference value or true value and Y_i is the predicted one from the model. The RE for pressed tablets is 34,1689%, since CMC fixation has a RE of 52,9935%. The values of the RE for both methods show that pressed tablets has a better model of prediction than the CMC fixation.

The analysis of Fe in unknown samples showed that only the pressed tablets model were able to predict in a better way the concentration of Fe in the samples, since CMC fixation model exhibit negative values of concentration.

4. CONCLUSIONS

The analysis of powder by Laser-Induced Breakdown Spectroscopy had to be made applying a fixing method. The common fixing methods for powders are pressed pellets or tablets. A comparative analysis of the pressed tablets fixing

methods with CMC fixation taking in account the LOD, correlation coefficient and the mean relative error of the prediction model was carried out. In general, pressed tablets had better ability to predict the concentration of the metal in silica nanopartículas by observing the mean relative error, a better correlation coefficient than CMC fixation method and a good repeatability and reproducibility. Despite that, when the precision and LOD of both method of fixation were compared, CMC fixation had a better LOD and reproducibility for copper while Fe samples showed a better LOD by pressed tablets method.

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