

Green-Synthesized Silver Nanoparticles for Nanoparticle-Enhanced Laser Induced Breakdown Spectroscopy (NELIBS) using a Mobile Instrument

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Abstract

When compared to other analytical techniques, LIBS shows relatively low precision and, generally, high Limits of Detection (LODs). Until recently, the attempts in improving the LIBS performances have been based on the use of more stable/powerful lasers, high sensitivity detectors or controlled environmental parameters. This can hinder the competitiveness of LIBS by increasing the instrumental setup cost and the difficulty of operation. Sample treatment has proved to be a viable and simple way to increase the LIBS signal; in particular, the Nanoparticle-Enhanced Laser Induced Breakdown Spectroscopy (NELIBS) methodology uses a deposition of metal nanoparticles on the sample to greatly increase the emission of the LIBS plasma. In this work, we used a simple, fast, “green” and low-cost method to synthesize silver nanoparticles by using coffee extract as reducing agents for a silver nitrate solution. This allowed us to obtain nanoparticles of about 25 nm in diameter. We then explored the application of such nanoparticles to the NELIBS analysis of metallic samples with a mobile LIBS instrument. By adjusting the laser parameters and optimizing the sample preparation procedure, we obtained a NELIBS signal that is 4 times the LIBS one. This showed the potential of green-synthesized nanoparticle for NELIBS applications and suggests the possibility of an *in-situ* application of the technique.

Keywords

LIBS; Nanoparticle Enhanced LIBS; Silver Nanoparticles; Green Chemistry

1 Introduction

2 Laser Induced Breakdown Spectroscopy (LIBS) is an atomic emission spectroscopy technique [1-
3 3] of growing popularity. The technique is widely used in both industrial applications and research
4 laboratories, and several reviews have been published, showing the versatility of LIBS in multiple
5 fields [4-8].

6 LIBS has the main advantage of the atomic spectroscopy techniques, namely the fast and
7 simultaneous determination of almost all elements, it is easy to operate and can be used to
8 analyze virtually any sample with little to no preparation required. On the other hand, quantitative
9 analysis with LIBS is not easy to perform, due to the need of matrix-matched standards and the
10 relatively low precision of the technique. The sensitivity is also low, when compared with more
11 complex atomic spectroscopy techniques such as ICP-OES. Sensitivity in LIBS is affected by the
12 laser pulse energy, the focalization setup, the type of spectrometer and the collection parameters.

13 The preferred method for improving LIBS performances has been the implementation of more
14 effective ablation procedures (e.g. multiple laser pulses, controlled atmosphere, vacuum
15 conditions, etc.) or the use of more powerful lasers and high resolution spectrometers [1-3].
16 However, this approach increases the costs of the instrumental setup and the optimization of the
17 experimental parameters requires good knowledge of both the instrumentation and the principles
18 of Laser-Induced Plasmas (LIPs) and laser-matter interaction.

19 In the recent years, several studies have explored the possibility of treating the sample in order to
20 enhance the LIBS signal. A review by De Giacomo et. al. presents the most common methods for
21 in situ treatment and the preparation of LIBS samples of different nature [9]. One of most
22 interesting methods proposed by De Giacomo et al. is the Nanoparticle-Enhanced LIBS (NELIBS)
23 technique [10-13]. This technique is being thoroughly discussed in literature and can be
24 summarized as follows. A drop of a solution containing metallic (silver or gold) nanoparticles (NPs)
25 is deposited on the sample surface and the solvent is dried. By focusing the laser pulse onto this
26 deposition, the NPs act as ignitions points for the LIP and the laser electromagnetic field couples
27 with the one induced on NPs surface plasmons, increasing the number of electrons emitted in the
28 plasma. This generates a hotter and more persistent plasma that, in turn, greatly enhances the
29 radiation emission.

30 This method seems ideal for in situ applications and for simple and fast improvement of LIBS
31 capabilities. It could also be applied in those cases where the instrumental setup cannot be
32 modified, or is not convenient to do it, for example in the case of a commercial LIBS setup. These
33 instruments usually have a set of parameters that are fixed by the manufacturer due to the intrinsic
34 limits that guarantee the portability. Also, these products, are usually intended for customers (e.g.
35 cultural heritage, geology, industry, etc.) that do not necessarily possess the knowledge to optimize
36 the instruments' parameters.

37 Suitable NP solutions are, however, usually expensive and sometimes not readily available.
38 Thanks to the relative simplicity of these methods and the growing interest for the "green
39 chemistry", the literature is rich in methods for the "green synthesis" of silver NPs, using plant
40 extracts as reducing and capping agents for the reaction with silver nitrate solutions.

41 In this work, we identified and adapted a procedure for the synthesis of a solution of silver NPs
42 suitable for NELIBS that is "green", low cost, fast and that can be realized with basic laboratory
43 equipment. We tested the performances of the synthesized NPs for NELIBS analysis with a mobile
44 LIBS system developed in our laboratory, and now produced as a commercial instrument for in
45 situ, and we compared them with the enhancement observed using commercially available silver
46 NPs. We also investigated the LODs enhancement for Zn and Cr by using NIST Standard
47 Reference Materials (SRMs).

48 **Materials and Methods**

49 **Materials**

50 Ground coffee (100% Arabica) was purchased at the local supermarket. Deionized water from an
51 Elga Purelab Option DV 35 water filtration system was used throughout the study. HPLC grade
52 ethanol (Honeywell, Chromasolv, grade $\geq 99.8\%$) was used for the preparation of the coffee extract.
53 Silver nitrate (AgNO_3 solid, for analysis) was purchased from Merck.

54 Commercially available silver nanoparticles (Silver dispersion, aqueous buffer, sodium citrate
55 stabilizer from Sigma-Aldrich) with a diameter of 20 nm were used as benchmark for the NELIBS
56 enhancement.

57 In this study, we used copper samples as their metallic and highly conductive nature is ideal for the
58 application of the NELIBS technique. Preliminary measurements and the optimization of the
59 experimental procedure were carried out using commercially available copper sheets. Standard
60 reference materials (SRM 394 Unalloyed Copper I, SRM 395 Unalloyed Copper II, SRM 398
61 Unalloyed Copper V, SRM 399 Unalloyed Copper VI, National Bureau of Standards) were used for
62 the construction of calibration curves and for the estimation of LODs improvements in NELIBS.

63 The copper sheets were cut into small pieces, thoroughly cleaned and treated with a solution of
64 HCl 1M (Titolchimica S.p.A.) in an ultrasonic bath in order to remove the superficial oxide layer.
65 After drying at 90°C for 30 minutes, the samples were prepared for NELIBS analyses. The SRMs
66 were similarly treated and air-dried before the analyses.

67 All the glassware was thoroughly washed with deionized water and acetone.

68 **Instrumentation**

69 UV-Vis measurements were performed using a Perkin Elmer Lambda 25 double beam
70 spectrophotometer. Scans were performed from 300 nm to 600 nm (scan rate 240 nm/min, 1 nm
71 slits).

72 A Zeiss Libra 120 TEM (courtesy of NEST Institute, Pisa, Italy), equipped with an OMEGA in-
73 column filter and operating at an accelerating voltage of 120 kV, was used for investigating the
74 dimensions of the synthesized nanoparticles. The solutions were deposited on carbon-coated
75 copper grids (Mesh 300).

76 LIBS and NELIBS analyses were performed using the Modi instrument [14]. Modi is equipped with
77 a Nd:YAG laser (LS2134-D, Lotis Lasers) operating at the fundamental wavelength (1064 nm) and
78 delivering two laser pulses of up to 110 mJ per pulse in 15 ns FWHM. The delay between the
79 pulses can be adjusted from 0 to 100 μs , with a maximum repetition rate of 10 Hz. The laser
80 beams are focused into an experimental chamber and the plasma emission is collected by an
81 optical fiber placed at a distance of 1 cm from the sample and at an angle of 45° with respect to the
82 laser beam. The ablation spot has a fixed diameter of about $300\mu\text{m}$. The spectra is resolved using
83 a double spectrometer (AvaSpec-2048-2, Avantes) which operates in the range of 180 nm to 450
84 nm with a resolution of 0.1 nm and from 450 nm to 900 nm with a resolution of 0,3 nm. The
85 acquisition delay can be varied from 1.26 μs up to several seconds. The acquisition gate is fixed at
86 2 ms. In this work, we chose to use the system in single pulse mode. The delay of acquisition was
87 maintained at 300 ns. The measurements were carried out with a pulse energy up to 105 mJ.

88 **Silver NPs Synthesis and Recovery**

89 The method for synthesizing the silver nanoparticle solution is a modified version of the one
90 proposed by Dhand et. al. [15].

91 The coffee extract was prepared by mixing 2.5 g of ground coffee and 50 mL of a solution 1:1 v/v
92 of ethanol and water. The solution was kept under vigorous stirring at 60°C for one hour and

93 cooled down to room temperature. The solid residue was removed by two filtration steps with
94 Whatman No.1 filter paper and the extract was stored in the dark at 4°C.

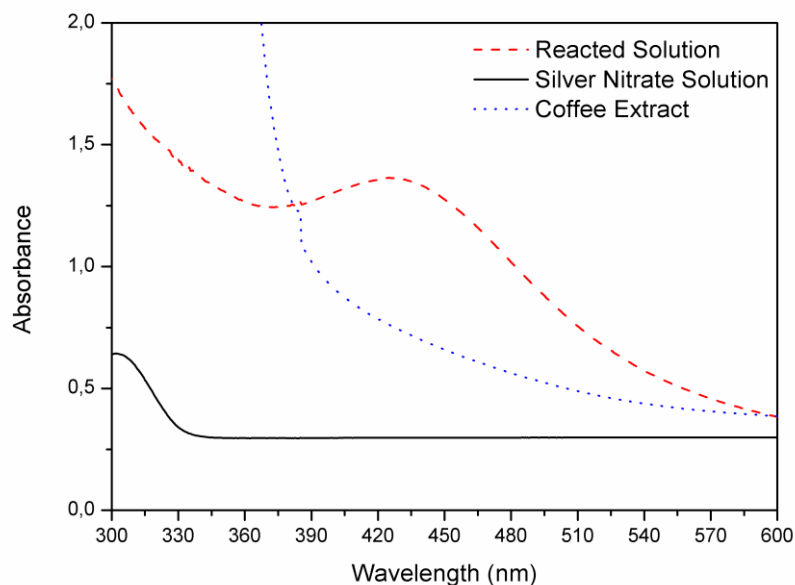
95 For the NPs synthesis, 12.5 mL of coffee extract were diluted to 25 mL with deionized water and
96 added to 100 mL of a 0.05 M solution of AgNO₃ in an ultrasonic bath at room temperature, and the
97 agitation was maintained for 15 minutes. A color change in the solution is an indication that the
98 silver nitrate has been successfully reduced to elemental silver and NPs have formed. The flask
99 was then removed from the bath and wrapped in aluminum foil in order to prevent light to interact
100 with unreacted silver nitrate. After an incubation period of two hours at room temperature, the
101 solution was centrifuged at 5600 g and washed two times with deionized water. It was then
102 transferred in screw-cap PET vials and stored in the dark at 4°C.

103 The solution was then freeze-dried and 20 mg of the solid residue were dispersed in 10 ml of
104 deionized water with an ultrasonic bath (30 min). The obtained dispersion was then used for
105 NELIBS analyzes.

106 Results and Discussion

107 Silver NPs characterization

108 In order to verify the success of the reaction and the presence of silver NPs in the solution, we
109 measured the UV-Vis absorbance of the AgNO₃ solution, the coffee extract and the yellow-orange
110 solution obtained at the end of the reaction. Samples were suitably diluted with deionized water in
111 order to avoid signal saturation.

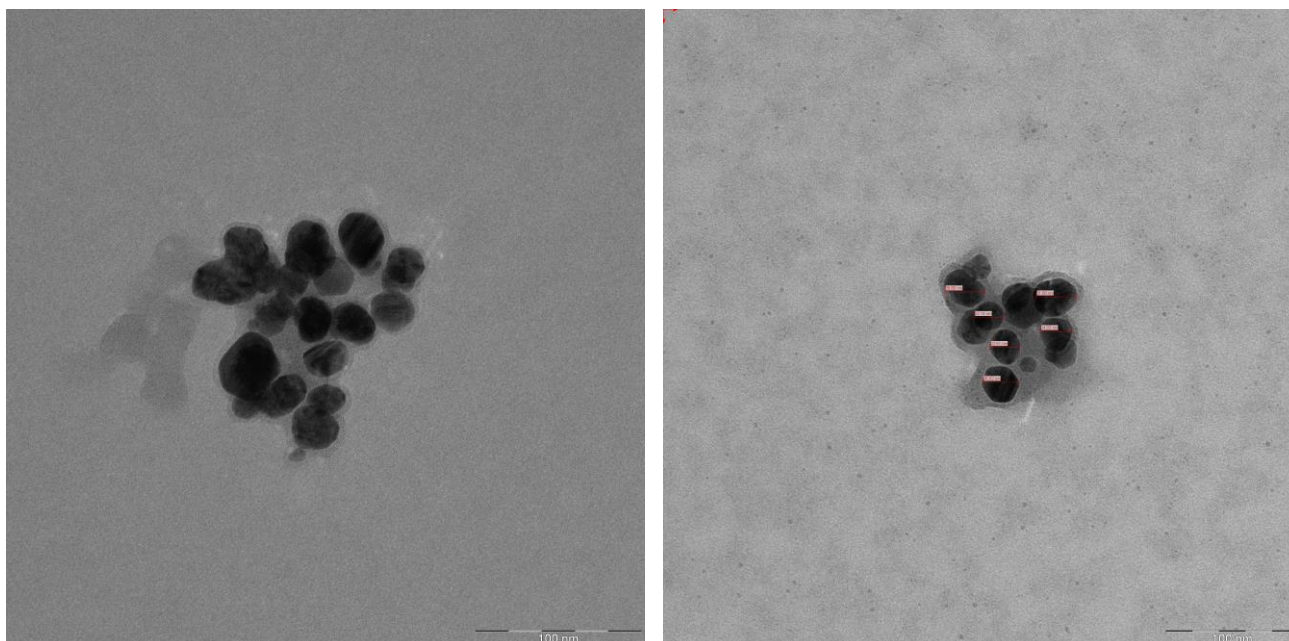


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113 *Figure 1- UV-Vis spectra of silver nitrate solution (black continuous line), coffee extract (blue dotted line) and the reacted*
114 *solution (red dashed line)*

115 In Figure 1 can be clearly seen an absorbance band around 435 nm in the spectrum relative to the
116 reacted solution, that is absent in the other spectra. This is an indication of the presence of silver
117 nanostructures as the band is caused by the surface plasmon resonance (SPR) phenomena,
118 characteristic of nanoparticle solutions. The wavelength value corresponding to the maximum
119 absorbance value in the UV-Vis spectrum could be used to estimate the size of the NPs, even
120 though it is a method prone to errors and interferences [16].

121 TEM images show the presence of spherical and spheroidal nanoparticles, grouped in clusters. We
122 could also observe the presence of seeds and areas where nanostructures are still forming. This
123 suggests that the reaction could be prolonged, even if it could lead to the formation of larger NPs,
124 which are unsuitable for NELIBS analyzes.



125 *Figure 2- TEM images of the "green"-synthesized nanoparticles. (100nm scale)*

126 From the TEM images we measured an average diameter of the synthesized nanoparticles
127 between 20 and 30 nm. As the solutions appear to be relatively diluted, we decided to prepare a
128 concentrated nanoparticle solution to test the NELIBS performances at various NP concentration.
129 The detailed results are reported in the following sections.

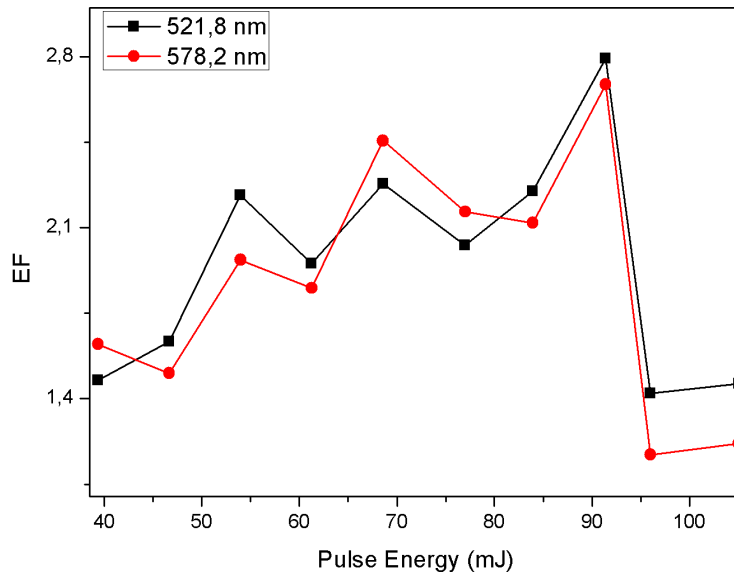
130 It is important to point out, however, some of the disadvantages related to the “green” synthesis of
131 silver nanoparticles. These methods are mostly used to produce NPs for antimicrobial applications,
132 where precise control of the geometry and the size of the nanostructures is not required and this
133 could be a problem in NELIBS. The NP dimensions can be optimized, but only after a series of
134 tests using various coffee extract or AgNO_3 concentrations, reaction times, temperatures, etc.
135 Moreover, with the use of a “green” synthesis, we obtain NPs coated with phytochemicals that can
136 hinder the laser-matter interaction and can negatively affect the enhancement of the LIBS signal.
137 There is also a risk of sample contamination if the NPs are not thoroughly and carefully washed.
138 On the other hand, this kind of approach shows several advantages over the more classical
139 methods of NPs production (i.e. chemical reduction, laser ablation, etc.). It is in line with the current
140 trends of “green chemistry” and it is a relatively inexpensive method that can yield a large quantity
141 of NPs in a short time. It doesn’t require aggressive or toxic reagents and its low complexity means
142 that it can be used by personnel with limited laboratory experience. This, coupled with the
143 possibility of using a portable LIBS instrument, makes this method potentially ideal for in situ
144 applications.

145 **LIBS and Sample Treatment Parameters Optimization**

146 Finding the optimal procedure and instrumental parameters is critical in NELIBS, in order to obtain
147 the highest enhancement possible. In this study, we investigated the effect of the laser pulse
148 energy and the air-drying time on the signal enhancement, expressed as the ratio between
149 NELIBS and LIBS integrated line intensity (EF, Enhancement Factor). For this step, five 5 μL
150 droplets of a commercially available 20 nm silver nanoparticles dispersion were deposited onto a
151 copper sheet for each different measure. Each droplet was analyzed with a single pulse and the

152 obtained spectra were averaged. We investigated the non-resonant copper emission lines at 521.8
153 nm (Cu I) and at 578.1 nm (Cu I).

154 The effect of the laser pulse energy on the signal enhancement is illustrated in Figure 3. The lower
155 limit at about 40 mJ is the lowest energy at which we could obtain reliably a measurable plasma,
156 while the upper limit at about 105 mJ is the highest energy output of the laser.



157

158

Figure 3 - 20 nm nanoparticles EF as a function of the laser pulse energy

159 We can see that the EF increases with the pulse energy. The highest enhancement was obtained
160 for a pulse energy of about 90 mJ and a sharp EF decrease was observed when using higher
161 energies. This is consistent with the work by De Giacomo [12].

162 Since LIBS performances are greatly affected by the sample surface characteristics, in NELIBS the
163 dryness of the NP deposition is crucial for achieving a good signal enhancement. From a series of
164 preliminary tests, we found that a quick drying of the copper sheets at 90°C or with hot air did not
165 yield any appreciable signal enhancement. We then analyzed the depositions after different drying
166 times at ambient temperature (about 25°C) in air. The results are showed in Figure 4.

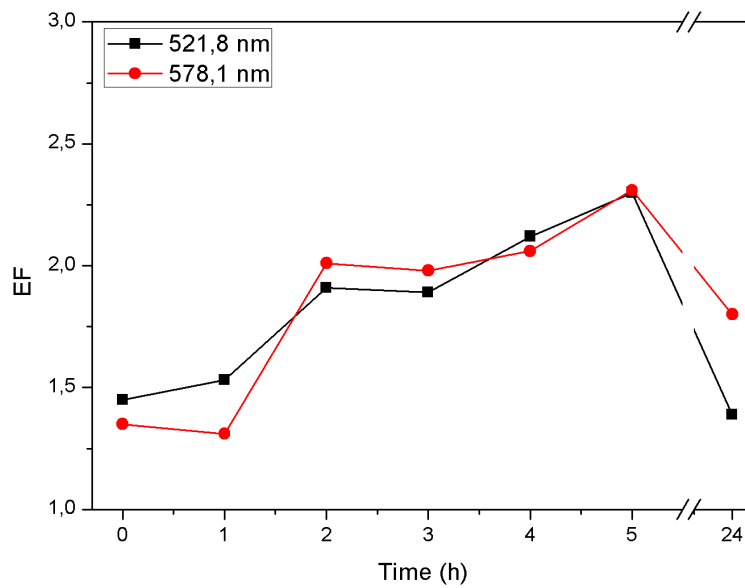


Figure 4 - 20 nm nanoparticles EF as a function of the air-drying time

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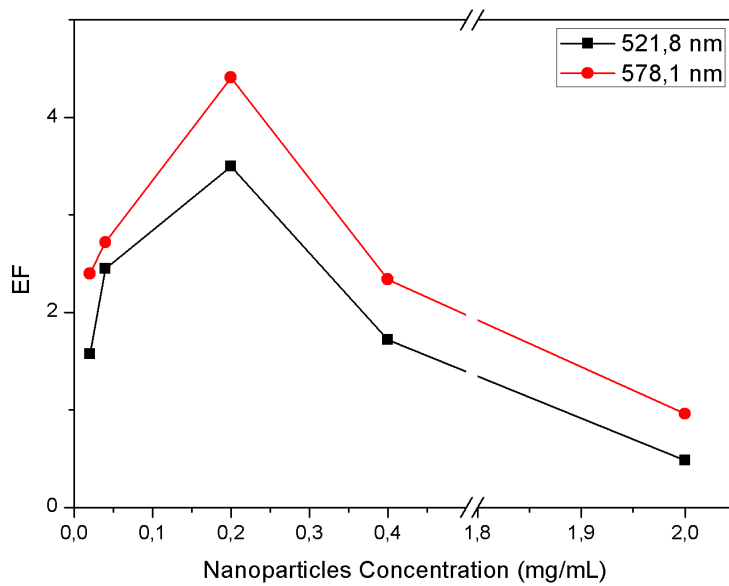
169 Similarly to what we observed for the pulse energy, the EF tends to increase with the drying time,
 170 up to a maximum at about 5 hours. After that, the EF decreases because of the oxidation of the
 171 samples, which is particularly noticeable near the nanoparticle deposition.

172 Based on these tests, we decided to use a 90 mJ pulse energy (8.5×10^{13} W/m² irradiance) and 4-5
 173 hours of air-drying for the subsequent NELIBS analyses.

174 **Green Nanoparticles NELIBS Enhancement**

175 Another critical parameter in NELIBS is the concentration of the NPs on the sample surface and,
 176 consequentially, the NPs concentration in the deposited solution. De Giacomo [12] showed the
 177 presence of a critical concentration, above which a sharp decrease in NELIBS performances
 178 occurs.

179 In our study, we prepared a dispersion of 2.0 mg/mL NPs by suspending 20 mg of freeze-dried
 180 NPs in 10 mL of deionized water. From this solution, we prepared 1:5, 1:10, 1:50 and 1:100 v/v
 181 diluted dispersions, having a NP concentration of 0.4 mg/mL, 0.2 mg/mL, 0.04 mg/mL and 0.02
 182 mg/mL respectively. The samples were then prepared and analyzed with the same procedure used
 183 for the optimization step and the results are illustrated in Figure 5.



184

185

Figure 5 - "Green" nanoparticles EF as a function of the concentration

186

The highest EF was obtained with the NPs solution at 0.2 mg/mL, resulting in a calculated surface concentration of approximately 1.4 mg/cm². Using more concentrated solutions resulted in much lower EFs.

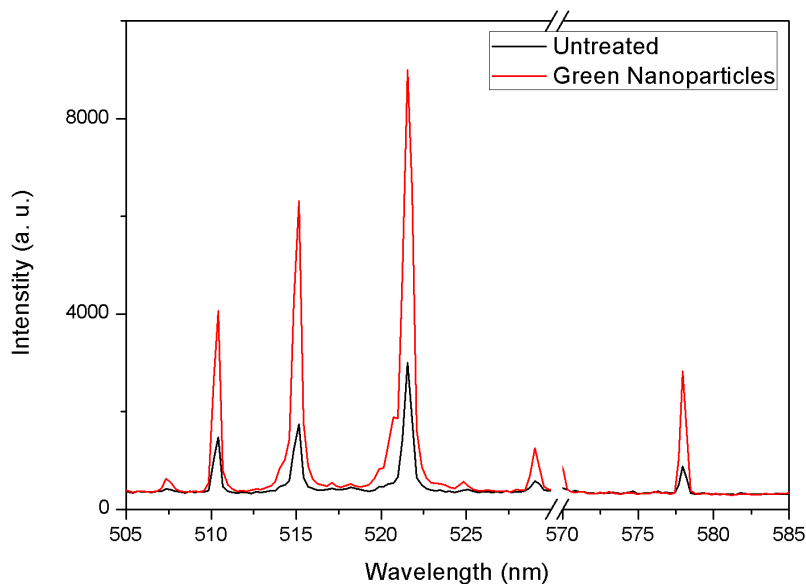
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It interesting to note how the EF registered when using the synthesized nanoparticles with the optimal procedure and instrumental parameters, is almost two times higher than the one registered when using commercially available silver NPs.

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Figure 6 - Part of the LIBS spectra obtained with 0.2 mg/mL "green" NP solution, showing the copper lines intensity enhancement

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Calibration Curves and LOD Enhancement

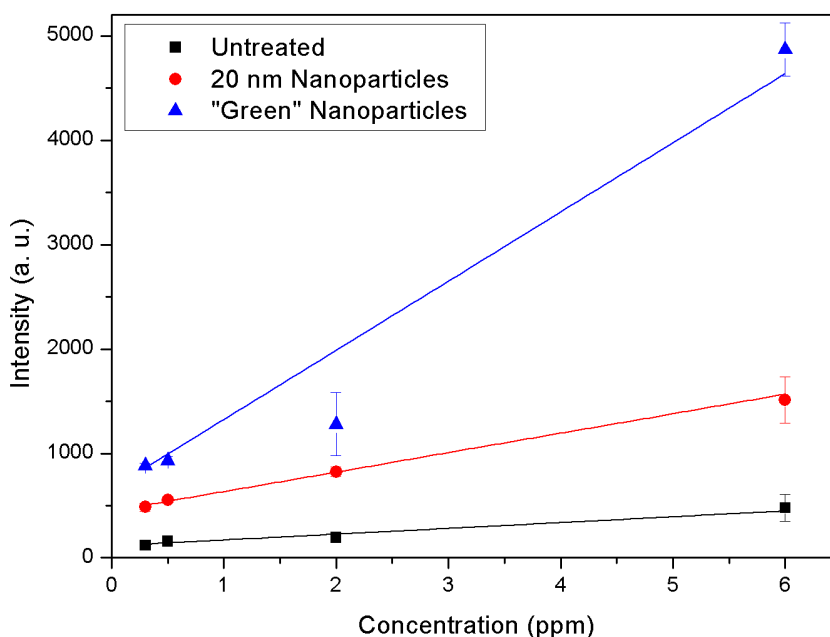
196 In order to quantify and compare the performances of the synthesized NPs with commercially
 197 available ones, we performed a calibration of our system using copper alloy SRMs. Based on
 198 preliminary tests, we chose to investigate the emission lines for Zn I (334.5 nm) and Cr I (359.4
 199 nm). The concentration values for these elements are reported in Table 1.

	Zn	Cr
SRM 394	405 ± 15	2.0 ± 0.1
SRM 395	12.2 ± 0.7	6.0 ± 0.5
SRM 398	24 ± 1	0.30 ± 0.08
SRM 399	45 ± 3	0.5 ± 0.1

200 *Table 1 - Concentrations (in ppm) for the investigated elements in the SRMs*

201 Five 5 µL droplets of both 20 nm commercially available NPs and “green” NPs (0.2 mg/mL
 202 solution) were deposited on the SRM surface and allowed to air dry before the analysis.

203 NELIBS analyses show that the EF is not the same for copper and the trace elements. This is to be
 204 expected as the signal enhancement is related to the upper level energy of the observed transition
 205 [10]. Five individual spectra were recorded for each SRM and the integrated line intensities were
 206 used to build the curves in Figures 7-8.



207 *Figure 7 – Calibration curves for Chrome*

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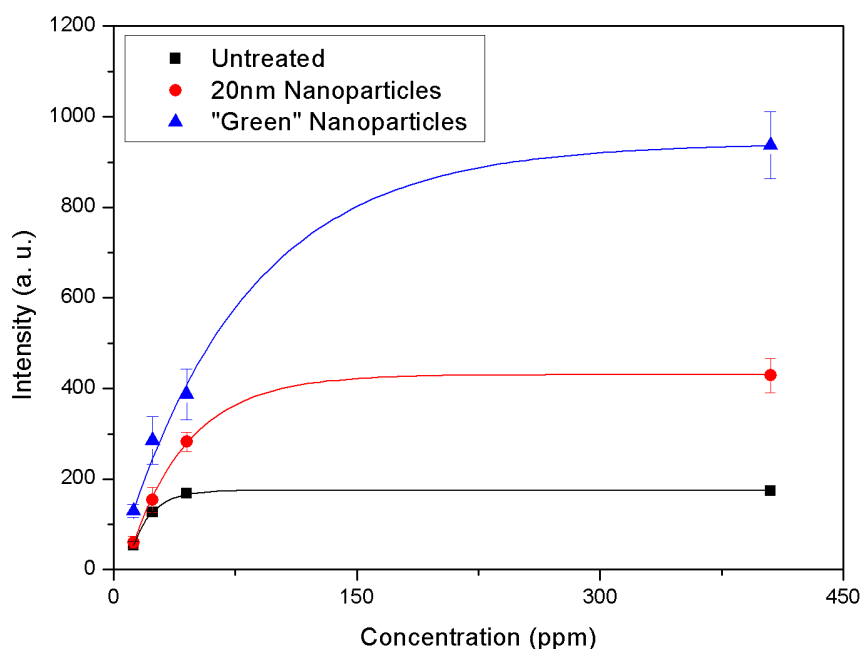


Figure 8 - Calibration curves for Zinc

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210

211 In Table 2 are reported the values of R^2 for each curve.

	R^2		
	Untreated	20 nm NPs	Green NPs
Zn	0.998	0.998	0.989
Cr	0.76	0.997	0.925

212

Table 2 – Values of R^2 for the calibration curves

213 We observed how, in the case of Chromium, that the use of NELIBS increases the quality of the
 214 calibration curves. Indeed, this is due to the increased signal intensity, which allow for a better
 215 signal to noise ratio and integration of the line intensity. In the case of Zinc, we observed a marked
 216 non-linear behavior of the emission intensity for the selected line and we decided to adopt an
 217 exponential function for the data fitting, with satisfactory results. It is necessary to point out,
 218 however, that the standard deviation values, reported in figures 7-8, are in some cases quite high
 219 (i.e. $\approx 25\%$). This is due in part to the surface dependent nature of LIBS and of the used
 220 instrumental setup, and in part to the not ideal nature of the SRMs which came in small metal
 221 chippings. This greatly hindered the NP deposition and the focalization of the laser onto the
 222 samples surface.

223 From the calibration curves, we estimated the limits of detection (LODs) that are obtainable with
 224 NELIBS. By using the relation $LOD \approx 3\sigma/Slope$ we obtained the values in Table 3.

Cr (ppm)	Untreated	20 nm NPs	Green NPs
		1.0	0.6

225

Table 3 - LOD for Chromium

226 As expected, the LODs are lower in the case of NELIBS analyses. The values also show how,
 227 generally, the performances of the "green" NPs are comparable with those of commercially
 228 available NP solutions.

229 The use of an exponential fitting for Zinc meant that this kind of LOD estimation could not be
 230 applied. Even if only 3 points are not enough for a real estimation of the LOD, we tried to use a
 231 linear fitting for the low-concentration zone of the calibration curve, in order to obtain a LOD and
 232 the results are summarized in Table 4.

	Untreated	20 nm NPs	Green NPs
LOD (ppm)	6.4	5.9	5.3
R ²	0.64	0.998	0.91

233 *Table 4 - LODs and R2 values for Zinc linear fitting*

234

235 **Conclusions**

236 In this work, we successfully adapted a simple and low-cost method for the “green synthesis” of
 237 silver nanoparticles, of comparable morphology with commercially available ones, to the
 238 preparation of silver NP solutions suitable for the NELIBS technique.

239 We were able to optimize the parameters for NELIBS analyses and we established a procedure for
 240 the preparation of nanoparticle depositions on the investigated samples.

241 We registered a signal enhancement using green-synthesized NPs that was higher than the one
 242 obtained with commercially available NP solutions. We also investigated and estimated the LODs
 243 for NELIBS using the “green” nanoparticles. We found values of ≈6 ppm for Zn and ≈0.1 ppm for
 244 Cr. We found these LODs to be comparable with those obtained when using commercially
 245 available silver NPs.

246 The results are encouraging and further studies should be carried out in order to improve the
 247 quality of the synthesized nanoparticles and obtain a more intense NELIBS signal. It is known from
 248 the literature that, in order to obtain the best enhancements in NELIBS (up to 2 orders of
 249 magnitude), the use of a laser capable of investigating a much larger area while maintaining a
 250 sufficiently high power density is necessary, as the entire NP deposition should be ablated during
 251 the laser pulse. The successful application of NELIBS to a mobile, relatively low power LIBS
 252 system is, however, an interesting result as it demonstrates the versatility of the NELIBS method,
 253 and could be a starting point for further optimization towards *in situ* NELIBS applications.

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