



Double pulse laser induced breakdown spectroscopy: A potential tool for the analysis of contaminants and macro/micronutrients in organic mineral fertilizers



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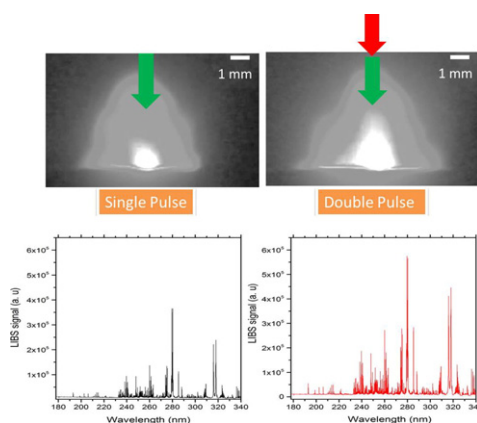
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HIGHLIGHTS

- DP LIBS is a potential tool to detect contaminants in fertilizer samples.
- DP LIBS optimization using different emission lines has been performed.
- LOD values obtained by DP LIBS increased up to seven times compared to SP LIBS.
- DP LIBS is applied for the first time to estimate LOD in fertilizers.

GRAPHICAL ABSTRACT



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ABSTRACT

Organic fertilizers are obtained from waste of plant or animal origin. One of the advantages of organic fertilizers is that, from the composting, it recycles waste-organic of urban and agriculture origin, whose disposal would cause environmental impacts. Fast and accurate analysis of both major and minor/trace elements contained in organic mineral and inorganic fertilizers of new generation have promoted the application of modern analytical techniques. In particular, laser induced breakdown spectroscopy (LIBS) is showing to be a very promising, quick and practical technique to detect and measure contaminants and nutrients in fertilizers. Although, this technique presents some limitations, such as a low sensitivity, if compared to other spectroscopic techniques, the use of double pulse (DP) LIBS is an alternative to the conventional LIBS in single pulse (SP). The macronutrients (Ca, Mg, K, P), micronutrients (Cu, Fe, Na, Mn, Zn) and contaminant (Cr) in fertilizer using LIBS in SP and DP configurations were evaluated. A comparative study for both configurations was performed using optimized key parameters for improving LIBS performance. The limit of detection (LOD) values obtained by DP LIBS increased up to seven times as compared to SP LIBS. In general, the marked improvement obtained when using DP system

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in the simultaneous LIBS quantitative determination for fertilizers analysis could be ascribed to the larger ablated mass of the sample. The results presented in this study show the promising potential of the DP LIBS technique for a qualitative analysis in fertilizers, without requiring sample preparation with chemical reagents.

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1. Introduction

In recent years the need to increase agricultural productivity to keep up with population growth has caused a substantial use of fertilizers aiming to replenish soil with the major nutrients necessary for plant growth, i.e. nitrogen, phosphorus and potassium. However, any fertilizer also contains, and introduce into soil, a number of trace elements, either micronutrients or micropollutants, the presence and concentration of which is very often not requested to be declared by the manufacturer. The contents of beneficial and adverse trace element in commercial fertilizers and the evaluation of their inputs to soil have been studied for decades (Senesi et al., 1979; Senesi et al., 1983; Senesi et al., 1988; Volokh et al., 1990; Singh et al., 1995; Haro et al., 2010).

More recently, the need to obtain fast and accurate analysis of both major and minor/trace elements contained in organic mineral and inorganic fertilizers of new generation has promoted the application of modern analytical techniques. In particular, laser induced breakdown spectroscopy (LIBS) is showing to be a very promising, quick and practical technique to detect and measure phosphorus and a number of minor/trace nutrients in fertilizers (Groisman and Gaft, 2010; Díaz et al., 2012; Farooq et al., 2012; Dong et al., 2013; Nunes et al., 2014; Marangoni et al., 2016). Although, this technique presents some limitations, such as a low sensitivity, if compared to other spectroscopic techniques (Hahn and Omenetto, 2012), the use of double pulse (DP) LIBS, as an alternative to single pulse (SP) LIBS, has been shown to improve the analytical performance of LIBS by allowing a higher flexibility in the choice of wavelength, pulse width and pulse sequence (St-Onge et al., 2002; Colao et al., 2002; De Giacomo et al., 2004; Gautier et al., 2005; Cristoforetti et al., 2005; Scaffidi et al., 2006; Piscitelli et al., 2009; Burakov et al., 2009; Rashid et al., 2011; Cristoforetti and

Palleschi, 2011; Diwakar et al., 2013; Tognoni and Cristoforetti, 2014; Nicolodelli et al., 2015). DP LIBS can be used in two configurations, i.e. two main laser beam geometries, collinear and orthogonal. In particular, the collinear configuration, in which both pulses have the same axis of propagation, i.e. are directed orthogonal to the sample surface, has been applied successfully to the analysis of various types of materials both in the liquid and solid forms, and of solid targets in liquids (Goujon et al., 2008; Piscitelli et al., 2009; Burakov et al., 2009; Rashid et al., 2011; Cristoforetti and Palleschi, 2011; Diwakar et al., 2013; Tognoni and Cristoforetti, 2014; Nicolodelli et al., 2015). Further, DP experiments in collinear geometry can be performed either using a single laser or two lasers. Although the use of a single laser can avoid alignment problems, the use of two lasers allows a higher flexibility in the choice of parameters such as laser pulse energy and delay between the two laser pulses (Nicolodelli et al., 2015).

Compared to the commonly used analytical technique of inductively coupled plasma - optical emission spectroscopy (ICP-OES) (Souza et al., 2014), SP and DP LIBS feature relatively high limits of detection (LOD). However, LIBS represents a good alternative to ICP-OES due to its several advantages that include no requirement for sample preparation and the possibility to use portable systems allowing to perform in situ measurements (Goujon et al., 2008).

To the best of our knowledge, no papers have been published in the scientific literature on the results obtained applying a DP LIBS set-up to fertilizer LOD analysis. Thus the aim of this work was to explore comparatively the analytical performance of conventional SP and DP LIBS systems when applied to the quantitative analysis of some macronutrients (Ca, Mg, K, P), micronutrients (Cu, Fe, Na, Mn, Zn) and contaminant (Cr) in a set of organic mineral and inorganic fertilizers. The LOD was determined comparatively using the SP and DP LIBS approaches and

Table 1
Elemental composition of inorganic and organic mineral fertilizer samples examined.

Samples	Class	Composed	Analyte concentration by ICP-OES										
			Al (ppm)	Ca (ppm)	Cr (ppm)	Cu (ppm)	Fe (ppm)	K (ppm)	Mg (ppm)	Mn (ppm)	Na (ppm)	Zn (ppm)	P (%)
Arad	Inorganic	Phosphate rock	535	32.12	113.28	24.31	569	2005	1094	31.24	5932	5869	26.23
Argélia	Inorganic	Phosphate rock	2504	29.02	157.15	6.89	2183	1411	11,389	10.7	9705	1484	21.5
Bayovar	Inorganic	Phosphate rock	4513	24.72	140.13	97.71	5126	2488	2977	266.4	14,437	2455	23.37
Gafsa	Inorganic	Phosphate rock	2671	29.64	131.09	6.4	1807	859	3234	15	11,613	1977	23.32
Itafós	Inorganic	Phosphate rock	17,219	23.28	22.55	24.86	13,315	5584	2630	808.0	0	3752	17.97
O-A	Organics	Fresh poultry litter + CMF ^a	3771	4.06	8.52	48.18	4960	69,633	3809	286.0	3329	2514	12.12
OB	Organics	Composed poultry litter + CMF	4273	5.01	23.14	50.78	8019	22,172	3809	349	3127	2889	20.07
OC	Organics	Fresh poultry litter + CMF	1945	25.84	121.96	24.9	5244	1245	7638	81.8	7276	1605	25.97
OD	Organics	fresh poultry litter + PR ^b	7719	17.16	76.01	90.78	11,045	17,612	5149	438.4	8049	4169	12.43
OE	Organics	Fresh poultry litter + CMF	7154	3.22	25.74	43.36	10,364	14,230	3286	347.1	2851	2537	18.29
OF	Organics	Composed poultry litter + CMF	2777	3.97	28.53	59.89	10,261	17,963	4638	420	3559	3568	20.13
OG	Organics	Fresh poultry litter + CMF	4843	2.56	22.57	44.98	6240	16,709	3565	344.8	3393	2893	12.72
OH	Organics	Fresh poultry litter + CMF	4614	1.84	15.76	42.23	5898	15,348	3210	329.1	3327	2702	16.96
OI	Organics	Composed poultry litter + CMF	8230	7.48	35.95	66.16	12,293	13,911	5095	463.4	3960	4118	18.56
OJ	Organics	Fresh poultry litter + CMF + S	3313	1.49	8.5	19.33	2947	13,870	3921	158.8	2551	730	16.12
OK	Organics	Fresh poultry litter + CMF + S	6855	3.19	20.31	42.18	9647	13,505	3170	347.8	2866	2461	18.05
OL	Organics	Fresh poultry litter + CMF + S	6287	2.93	20.79	40.64	9257	13,286	3101	337.8	2828	2382	18.332
OM	Organics	Fresh poultry litter + CMF + S	4028	1.96	21.5	38.58	6671	12,219	2929	320.7	2572	2276	17.03
ON	Organics	Fresh poultry litter + CMF + S	6039	1.76	23.59	36.76	6015	11,720	2793	309.3	2456	2170	15.93
OO	Organics	fresh poultry litter + PR	8253	14.95	33.72	39.33	10,247	11,799	3927	495	2512	2790	6.66
OP	Organics	Composed poultry litter + PR	4943	11.83	51.52	63.67	16,224	16,615	5775	637.2	3338	4517	7.77
OQ	Organics	fresh poultry litter + PR	14,507	15.19	75.6	68.69	5457	10,603	3673	281.2	8040	2678	11.71
OR	Organics	Composed poultry litter + PR	8591	20.16	93.52	91.93	12,923	17,071	5178	434.01	8617	4150	11.53

^a CMF: commercial mineral fertilizer.

^b PR: phosphate rock.

ICP-OES as the reference technique, with the main objective of quantifying the possible improvement of DP LIBS over SP LIBS in the elemental analysis of fertilizers.

2. Materials and methods

2.1. Samples

Twenty three fertilizer samples of approximately cylindrical shape of about 2 mm in diameter were used in the experiment: 5 inorganic fertilizers consisting of various phosphate rocks containing from 8 to 12% of phosphorus (P), and 18 organic mineral fertilizers consisting of mixtures of 60% fresh or composted poultry litter and 40% commercial mineral fertilizer (Table 1). To ensure homogeneity, samples were ground and sieved through a 100 mesh sieve. For the comparative LIBS analysis, each sample pellet was prepared by applying a pressure of 10 ton for 30 s.

2.2. DP and SP LIBS setups and experimental procedure

The schematic and detailed description of the experimental SP and DP LIBS setups used in this study can be found in a previous publication (Marangoni et al., 2016). Briefly, the LIBS system used was composed of two Nd:YAG lasers operating at different wavelengths, the one at 1064 nm (IR) and the other at 532 nm (VIS). The IR pulse of maximum energy of 75 mJ and width of 6 ns was generated by a Nd:YAG Q-switch Ultra (Quantel), whereas the VIS pulse of maximum energy of 180 mJ and width of 4 ns was generated by a Nd:YAG Q-switch Brilliant (Quantel) coupled with a second harmonic generator module. A 400-Butterfly Aryelle system was used to detect and select the wavelengths. The spectrometer operated in two spectral bands, 175–330 nm and 275–750 nm, with a spectral resolution of 13–24 pm and 29–80 pm, respectively, and was provided with an intensified charge-coupled device (ICCD) camera with 1024×1024 pixels.

The waist beams before the focal lens for each laser were determined by *knife edge method* (Suzaki and Tachibana, 1975) and were estimated

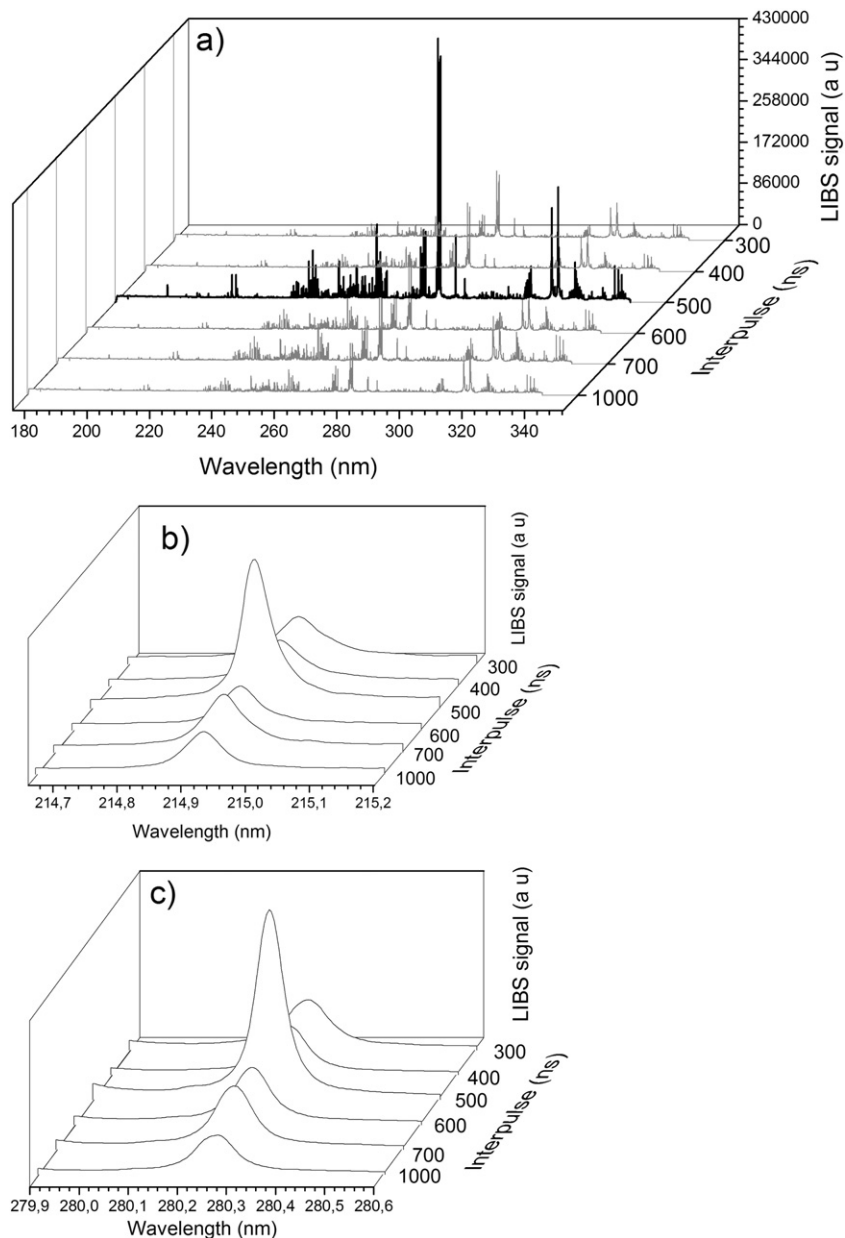


Fig. 1. DP LIBS spectra in the UV range (a), P I range (b), and Mg II range (c), at six different interpulse delays.

in the focal position. The laser energy close to the focal lens was measured using an energy meter (Coherent, FieldMax II) and the power density on focal position was estimated for them. Two laser beams with total power density (Laser VIS + Laser IR) of approximately $2.3 \pm 0.1 \times 10^{12} \text{ W cm}^{-2}$ were used for the acquisition of DP LIBS spectra in the collinear geometry assembly. The beams were focused and aligned by dichroic mirrors to hit the target sample in the overlapping mode with a delay between them. The variations of delay time and interpulse delay (from 300 to 1000 ns) were investigated by performing ten measurements on the surface for each parameter of each sample at different position, and each value was obtained from five accumulated pulses at a width gate time fixed at $10 \mu\text{s}$. For the efficient collection of emitted plasma two silica lenses were placed between the sample and the tip of the fiber, and used at the optical position. The sample support was placed in a micro-controlled xy stage for an easy and fast scanning of the laser beam impinging on it.

The SP LIBS spectra were acquired using the VIS green laser beam at the wavelength of 532 nm and at a total power density of approximately $2.3 \pm 0.1 \times 10^{12} \text{ W cm}^{-2}$. The temporal parameters, delay time (0.5, 1,

2.5 and $2 \mu\text{s}$) and width gate (from 1 to $20 \mu\text{s}$), used in this setup were optimized for the best signal-to-noise ratio, the best values found were at a delay time of 1 μs and at a width gate of $10 \mu\text{s}$.

The comparative SP LIBS and DP LIBS study was performed on 20 measurements with the SP LIBS and 20 with DP LIBS on each face of each pellet. The background of the LIBS spectra was corrected by subtracting the average noise region near the element emission line. Results were based on the areas obtained from the Lorentzian fit for one peak emission in each spectrum and then by averaging the areas.

2.3. SEM and ICP-OES analysis

The images of the craters generated on the pellets by different settings of the laser system were analysed by scanning electron microscopy (SEM) (JSM-6510/JEOL, Thermo Scientific).

An ICP-OES model OPTIMA 3000 (Perkin Elmer) was used for the analysis of P in solutions obtained by digestion of 1 g of each fertilizer sample in 20 mL of nitric acid and 5 mL of chloridric acid at the boiling temperature. The analysis of Ca, Cr, Cu, Fe, K, Mg, Mn, Na and Zn were

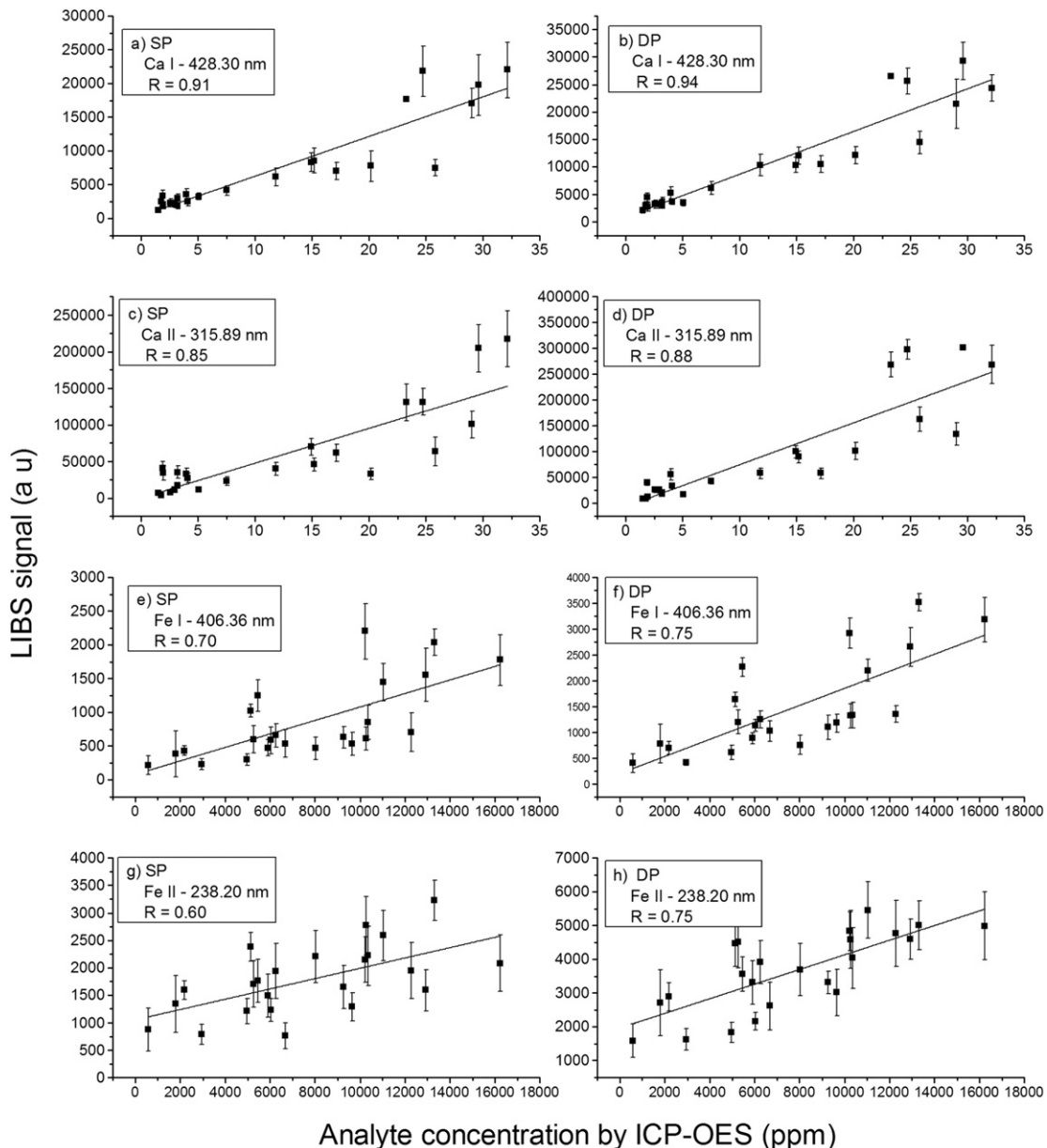


Fig. 2. Calibration curves for Fe I, Fe II, Ca I and Ca II obtained by SP and DP.

performed by an ICP-OES model Vista PROCCD (Varian) with a digestion step at a temperature 110–120 °C on solutions of 1 g of each fertilizer sample in 20 mL of aqua regia (HNO₃ + 3HCl).

2.4. Estimation of mass ablated and plasma volume

The diameter and depth of the craters were measured by a confocal microscope (LSN 780, Zeiss). The microscope was coupled with a micrometer stage on x-y-z axes that allowed the estimations. Craters were approximated as cylindrical or bulk-conical shape to estimate the volumes. The ablated mass was estimated from the ablated volume and sample density.

The images of the plasma plume were obtained from a camera (Sony Cyber Shot, Alpha 55) and a set of appropriate filters and lenses was used to filter the scattered light and expand the image of the plasma. The plasma generations, for DP and SP setup, were filmed for 1 s and the overall images were integrated in 100 ms.

2.5. Limit of detection (LOD)

The limit of detection (LOD) was calculated according to the following equations (Currie, 1968):

$$\text{LOD} = 3.3\sigma/b \quad (1)$$

where “ σ ” is the standard deviation of the background emission of the air spectrum and “ b ” the slope of the calibration curve.

3. Results and discussion

Temporal parameters of the emission lines of interest were optimized for both SP and DP setups. Fig. 1a shows the DP LIBS spectrum in the UV range of a representative organic mineral fertilizer sample recorded at a fixed delay time of 500 ns and at six different interpulse delays using the IR laser as the second pulse, i.e. with the sequence 532 and 1064 nm. It is well known in literature (Piscitelli et al., 2009 and Coons et al., 2012; Nicolodelli et al., 2015) that the IR (1064 nm) laser is more suitable for re-heating plasma when used as a second laser in the sequence.

Fig. 1b and c clearly show that for two chosen macronutrients (P and Mg) the optimal interpulse delay value results to be at 500 ns. The effect

Table 2
R and LOD values obtained by SP- and DP-LIBS.

Element	Wavelength (nm)	R		LOD (ppm)	
		SP	DP	SP	DP
<i>Macronutrients</i>					
P I	214.91	0.84	0.91	4007 ± 561	1430 ± 138
P I	213.61	0.82	0.92	2386 ± 367	922 ± 86
P I	255.33	0.82	0.95	5430 ± 821	1320 ± 99
Mg II	280.27	0.62	0.84	38 ± 7	5 ± 0.8
Mg I	285.17	0.77	0.92	84 ± 17	15 ± 2
Ca II	315.89	0.85	0.88	0.04 ± 0.005	0.02 ± 0.002
Ca I	428.30	0.91	0.94	0.68 ± 0.06	0.34 ± 0.05
Ca I	643.91	0.93	0.94	0.42 ± 0.02	0.20 ± 0.03
K I	769.90	0.96	0.96	196 ± 26	128 ± 16
<i>Micronutrients</i>					
Zn II	206.20	0.74	0.82	960 ± 181	323 ± 48
Cu II	224.69	0.52	0.93	^a	112 ± 28
Fe II	238.20	0.60	0.75	^a	310 ± 57
Fe I	406.36	0.70	0.75	4900 ± 970	2103 ± 405
Mn II	259.37	0.87	0.92	46 ± 6	9.8 ± 0.9
Na I	589.99	0.93	0.94	101 ± 8	38 ± 3
<i>Contaminants elements</i>					
Cr II	205.56	0.57	0.97	^a	54 ± 3
Cr I	520.84	0.87	0.95	78 ± 10	28 ± 2

^a No LOD estimated.

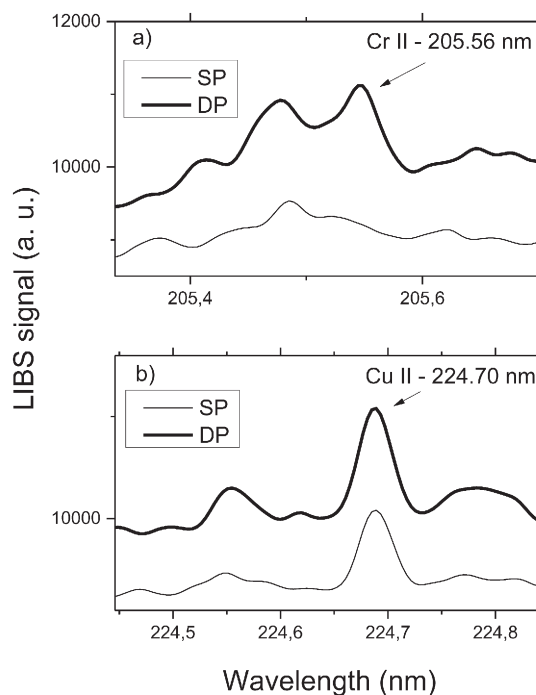


Fig. 3. Cr and Cu ionic emission lines detected at 205.56 and 224.7 nm in SP and DP LIBS spectra from O4 sample with a Cr concentration of 9.44 ppm and Cu concentration of 90.78 ppm.

of the interpulse value on the intensity of the LIBS signal is related to the temporal evolution of the shock wave (SW), since the SW may affect the amount of ablated mass of material due to a shielding effect (Hussein et al., 2013).

After selection of the optimal parameters, the LIBS spectra were recorded in the two configurations, SP and DP. Then, the calibration curves, i.e. the correlations between the areas of the LIBS emission lines and the corresponding concentration values obtained by ICP-OES, were calculated for all macro- and micro-nutrients studied (Ca, Cu, Fe, K, Mg, Mn, Na, P and Zn) from data obtained by both SP- and DP-LIBS on the organic mineral and inorganic fertilizer samples examined. The possible contaminant element such as Cr (205.56 nm) was also identified and quantified in the samples. The chemical concentration obtained by ICP-OES for each element was reported in Table 1. Spectral emission lines with well-defined shape and without

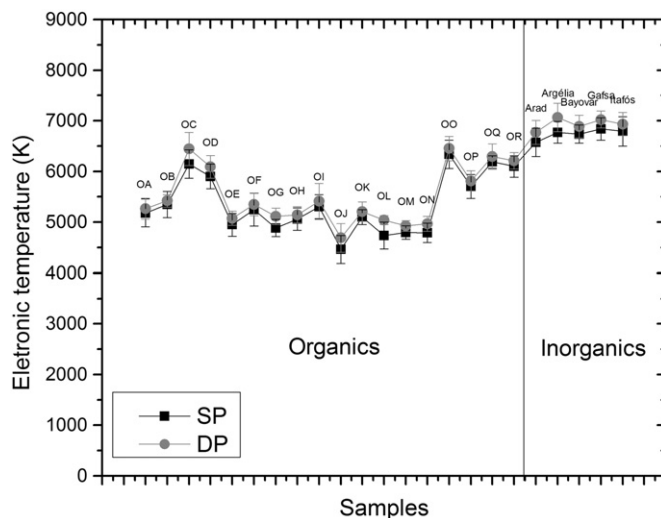


Fig. 4. Plasma temperature excitation obtained using DP and SP setups for organic mineral (left) and inorganic (right) fertilizer samples.

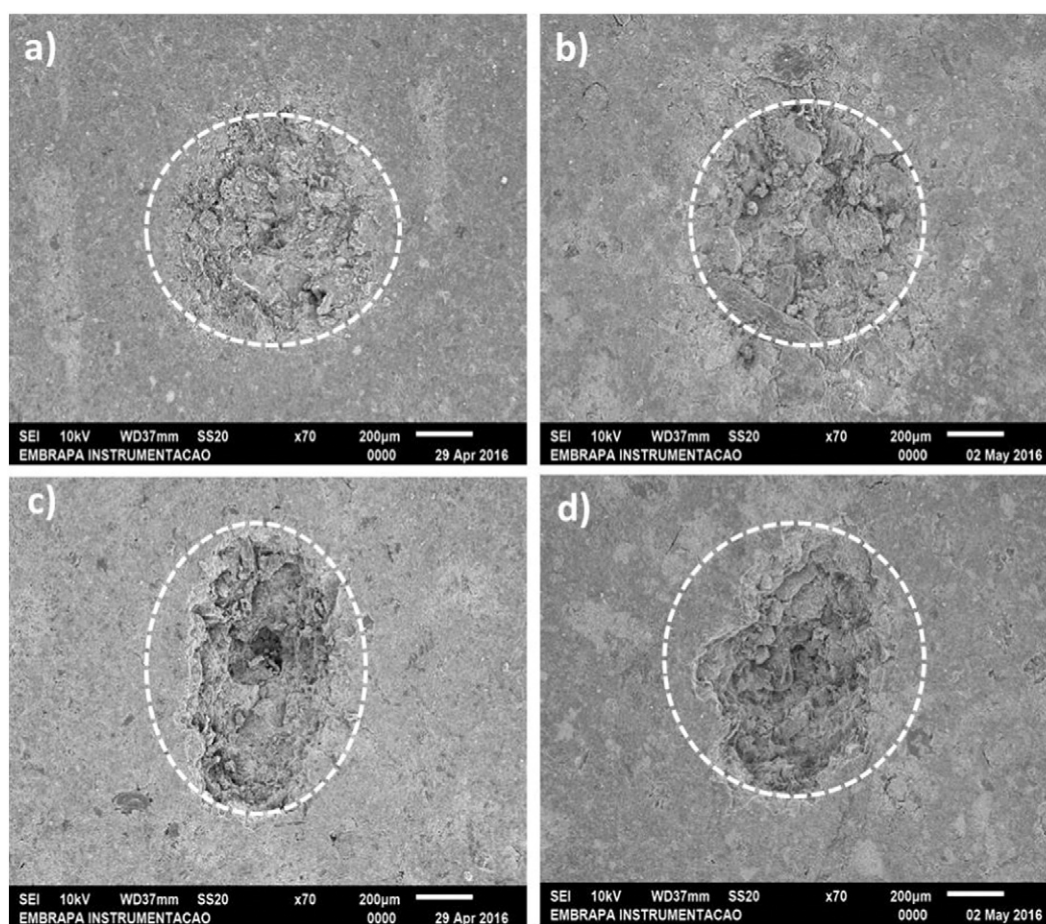


Fig. 5. SEM images of irradiated surfaces of samples O2 and O12, respectively, obtained from SP (a–b) and DP (c–d) setup.

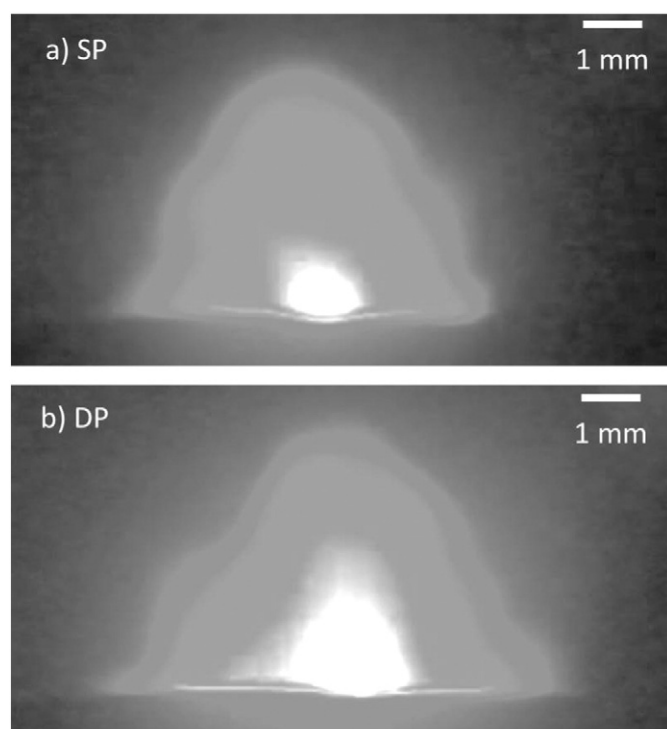


Fig. 6. Whole plasma image obtained for SP and DP setup using 100 ms of integration time.

interference of other emission lines were chosen to build the calibration curves. The calibration curves obtained for Fe I (406.36 nm), Fe II (238.20 nm), Ca I (428.30 nm) and Ca II (315.89 nm) are shown as examples in Fig. 2, for SP and DP configurations.

The LOD and R values found for all elements in SP and DP, respectively, are showed in the Table 2. Clearly, data show that, with respect to SP LIBS, DP LIBS improves markedly the correlation with the reference data and the LOD values. LOD values obtained by DP LIBS increased up to seven times (Mg II) as compared to SP LIBS, for the present setup. These improvements can be ascribed to the increased plasma temperature and/or larger ablated mass, or larger plasma volume achieved in the DP LIBS configurations (St-Onge et al., 2002; Colao et al., 2002; De Giacomo et al., 2004; Gautier et al., 2005; Cristoforetti et al., 2005; Scaffidi et al., 2006; Piscitelli et al., 2009; Burakov et al., 2009; Rashid et al., 2011; Cristoforetti and Palleschi, 2011; Diwakar et al., 2013; Tognoni and Cristoforetti, 2014; Nicolodelli et al., 2015).

Fig. 3a–b shows Cr and Cu emission lines detected at 205.56 nm and 224.70 nm, respectively, in SP and DP LIBS spectra. From the comparison spectra in SP and DP LIBS shown in Fig. 3a–b it's possible to confirm that in DP LIBS mode, an enhancement of the emission line is evident and this is fundamental to detect pollutants (Cr) or trace elements in agricultural-environmental samples. According to the MAPA's regulation (MAPA, 2006) the maximum limit of Cr amount allowed in fertilizers in Brazil is 200 ppm. This value is 7 times higher than the LOD evaluated by DP-LIBS in this study, what emphasize the applicability of the methodology. The highest amount of Cr present in these fertilizers was 157 ppm, near to the limit allowed by Brazilian's law.

The plasma temperature was calculated by using the Boltzmann method (Ohno et al., 2006) for the element Ca, which was chosen

because it showed the greatest number of resolved peaks and no interference from other lines. The emission lines used were at: 428.30, 428.94, 431.87, 585.74, 643.91, 644.98 and 646.26 nm. In general, the plasma temperature values for the 23 fertilizer samples examined feature a small, not statistically significant increase for the DP configuration with respect to the SP configuration (Fig. 4).

According to St-Onge et al. (2002), the plasma produced by DP irradiation is not much hotter than that formed after a single (first) pulse (SP). The authors suggested that the spectral intensity enhancement could be explained by a larger plasma volume, i.e. a region where the optimal temperature for emission is maintained for a longer time. This phenomenon can be ascribed by two factors: lower thermal conduction losses toward the sample and lower radiation losses toward the environment, as a consequence of the expanding plasma already present at the time of the second pulse (Tognoni and Cristoforetti, 2014; St-Onge et al., 2002).

Thus, the next step was to evaluate the variation of the ablated mass by analysing the images of the two craters formed by SP- and DP-LIBS on two representative organic mineral fertilizer samples (Fig. 5).

Apparently, the amount of ablated material is larger when DP-LIBS is used (Fig. 5c–d), compared to SP-LIBS (Fig. 5a–b). To prove the previous assumption the ablated mass was estimated using the SP and DP laser for three different samples (O2, O11 and O13). The average values calculate were, respectively, $10 \pm 2 \mu\text{g}$ using SP setup and $82 \pm 5 \mu\text{g}$ using DP setup. Therefore, an increase of the ablated mass of approximately 8 times is found when DP was used. In the DP configuration, the first pulse causes a temporary increase of the target surface temperature and the formation of a plasma plume and a shock wave that produces a transient change in the local atmospheric conditions (Tognoni and Cristoforetti, 2014). It is well known (Diwakar et al., 2013; Tognoni and Cristoforetti, 2014; Nicolodelli et al., 2015) that if a suitable value of the inter-pulse delay is chosen, these two effects cooperate to increase the coupling of the second pulse energy with the target surface, increasing the total ablated mass in DP configuration compared to SP with the same total irradiance. Benedetti et al. (2005) also ascribed the bulk of the spectral intensity enhancement to the increase of the mass removed in DP, with respect to SP, while the temperature increase was associated with the upper level energy of the transition. Further, a qualitative analysis of the plasma volume was made from a whole plasma image shown in Fig. 6.

Fig. 6 clearly shows an increase in plasma volume for DP setup when compared to SP. The core plasma (white region) is increased by around three times corroborating other evidence in literature and supporting our results.

4. Conclusion

A considerable improvement was obtained, as compared to SP LIBS, in the linear correlation between the DP LIBS signal and the element concentration measured by ICP-OES in a number of organic mineral and inorganic fertilizers. The LOD values obtained by DP LIBS increased up to seven times as compared to SP LIBS. The enhancement of elemental emission line intensity and LOD values obtained using the DP system was attributed mainly to the larger emitting volume and increased mass ablated. In general, the marked improvement in the simultaneous quantitative determination of various macro and micronutrient elements and contaminant element in fertilizers by DP LIBS overcomes the limitations usually presented by the SP-LIBS technique. Particularly, DP LIBS showed an efficient tool for Cr quantification, since its LOD is around 7 times higher than maximum allowed concentration by Brazilian's laws. This kind of tool is very important to support in the quality control of organic mineral fertilizers. Thus, LIBS can be used as an alternative, fast and ecologically clean technique to the traditional analytical methods that requires sample preparations with chemical reagents.

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