Laser-induced breakdown spectroscopy determination of K in biochar-based fertilizers in the presence of easily ionizable element

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A B S T R A C T

Laser-induced breakdown spectroscopy is an optical emission technique quite suitable for the analysis of recalcitrant materials as it eliminates complex procedures of sample preparation. However, for some simple LIBS instrumentation the detection limits are still higher compared to those of consolidated spectroscopic techniques. The aim of the present work was to develop a method for the determination of K in new biochar-based fertilizer samples using a simple single pulse LIBS arrangement. Due to the low K detectability, which made impossible to obtain calibration curves, an exploratory qualitative study was performed aiming to evaluate the influence of the addition of easily ionizable elements (EIE) on the sensitivity. To this aim different salts containing EIE (K, Li and Na) and other cations (Cu and Mg) have been evaluated. Results obtained showed that salts containing EIE cations increased the spectral emission signals of some elements in samples previously submitted to charring. In particular, the strategy of using Li^+ was applied to the determination of K in biochar-based fertilizers. The addition of Li^+ allowed to develop an analytical method for K determination featuring a linear dynamic range from 0.8% to 21.56% K, and limits of detection and quantification of 0.2% and 0.8%, respectively.

1. Introduction

Laser-induced breakdown spectroscopy (LIBS) is a modern spectroanalytical technique that allows direct analysis of solid, liquid or gaseous samples [1–3]. LIBS uses laser pulses to ablate a small fraction of sample that generates a plasma where the species present are excited and emit characteristic radiations that are recorded, thus allowing the qualitative and quantitative elemental analysis of the sample [2,4].

Although this technique shows a number of attractive analytical features, depending on the instrumentation used it presents low sensitivity in comparison with classical spectrometric techniques, such as flame atomic absorption spectrometry (FAAS) and inductively coupled plasma optical emission spectrometry (ICP OES) [5]. However, some strategies have been developed [6–9] to improve the detectability of LIBS, which include the use of a spark for sample pre-ablation [10,11], spatial confinement of laser-induced plasma [12–14], use of a micro torch [15] and use of two (double-pulse) or more lasers pulses for plasma species excitation [16–20]. Some authors attribute the observed increase in sensitivity to the increment of temperature and electronic

density of the plasma, an higher sample mass ablation and plasma reheating [21–27].

Besides instrumental strategies, some chemical strategies, such as nanoparticle-enhanced (NE) LIBS, have also been evaluated to improve sensitivity. This method consists in the deposition of Au and Ag nanoparticles on the sample surface, which improves sample ablation due to the laser irradiance amplification caused by the low thermal conductivity of nanoparticles [28,29]. However, despite the various strategies mentioned above, the improvement of LIBS sensitivity when employing simple and low-cost instrumentation is still an analytical challenge.

Among several other applications, LIBS has been shown to be a promising analytical tool for biochar elemental analysis [30]. However, low emission signal intensities were obtained due to the matrix complexity (high C content) of these materials, which rendered difficult the excitation of the species of interest. In particular, the sensitivity reduction was possibly ascribed to the weakly ionized plasmas where collisional processes predominated over the radiant processes [31].

Due to the increasing interest in the use of biochars as agricultural

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fertilizers [32–34], the analysis of plant nutrients like K in these materials is very relevant. In this perspective, the objective of this work is to evaluate qualitatively the detection improvement of a simple, single pulse LIBS instrumental arrangement achieved by the addition of various easily ionizable element (EIE) cations, and to apply this strategy to the measurement of K in biochar-based fertilizers.

2. Materials and methods

2.1. Reagents and substrates

To evaluate the influence of different cations on LIBS sensitivity, the following salts were used: $CuSO_4$ (Synth, Brazil), KCl (Mallinckrodt, England), Li_2CO_3 (Vetec, Brazil), $MgSO_4$ (Synth, Brazil), NaCl (Mallinckrodt, England). The effects of salt addition on elements detectability in different matrices was evaluated for the following samples: eucalyptus biochar (produced by charring branches and leaves of eucalyptus trees); banana fiber biochar (produced by charring of pseudo stems of banana trees); rice husk biochar (produced by the charring rice husks); roasted and unroasted coffee; and orange leaves. Cellulose type 101 (Sigmacell, USA) was used as pellet binding agent.

In particular, the biochar samples were prepared according to the following procedure: the substrate materials were dried, crushed and grounded. Approximately 2.0 g of each material were accurately weighed and placed in a porcelain crucible that was closed to maintain the inside atmosphere at a low oxygen content. The crucibles were placed in a muffle oven (EDGCON 5P, Brazil) and the heating program was performed, i.e. a heating rate of $10\,°C\,min^{-1}$ was applied up to the temperature of 260 °C, at which the sample was maintained for 60 min. Then the temperature was lowered to 60 °C and the crucibles were removed. The biochar samples produced were stored in polypropylene flasks. The orange leave and unroasted coffee samples were only dried, if required, crushed, grounded and stored for further studies.

2.2. Sample preparation and experiments

Four experiments were conducted in this work: (i) the effect of different salts on LIBS signal intensities of eucalyptus biochar was evaluated on mixtures of 160 mg of eucalyptus biochar, 80 mg of cellulose and 40 mg of each salt; (ii) the effect of Li^+ on the signal intensities of all samples indicated above was evaluated in mixtures of 160 mg of each sample, 80 mg of cellulose and 40 mg of Li_2CO_3; (iii) the optimal amount of Li^+ to be used to maximize signal intensities of eucalyptus biochar was evaluated on mixtures of 160 mg of eucalyptus biochar and 80 mg of cellulose added with Li_2CO_3 to obtain increasing Li^+ concentrations, i.e. 0%; 0.17%; 0.67%; 1.33%; 2.04% and 2.72% and corn starch to reach a final mass of 280 mg; and (iv) to evaluate the effect of addition of Li_2CO_3 on K determination in biochar-based fertilizer samples were prepared by mixing 177 mg of biochar (eucalyptus, banana fiber and peanut shells), 80 mg of cellulose and 28 mg of Li_2CO_3, whereas the calibration standard pellets were prepared by

mixing 60 mg of eucalyptus biochar, 80 mg of cellulose and 28 mg of Li_2CO_3 added with variable masses of KCl to obtain K concentrations of 0.0%; 5.7%; 8.3%; 12.9%; 16.5% and 21.6% (m/m)) and corn starch to reach a final mass of 285 mg.

2.3. Instrumentation and analytical procedure

The LIBS system used was equipped with a Q-switched Nd:YAG laser emitting at 1064 nm (Quantel, Big Sky Laser, Ultra 50) and operating at 50 mJ maximum power energy with a repetition rate up to 20 Hz, a pulse duration of 20 ns and a laser spot diameter of 0.5 mm. The detection device consisted of 4 pieces of HR2000+ spectrometers (Ocean Optics, USA) that provided an optical resolution of 0.1 nm (FWHM) on a wavelength range of 199–631 nm with an integration time of 1 µs. Each sample was placed in a sampling chamber controlled by a joystick with movement in the x-y directions and equipped with a video camera for monitoring in real time the laser pulse-sample interaction. The Q-Switched delay time selected for spectra acquisition was 0.5 µs. The system was controlled by the OOLIBS software (Ocean Optics, USA).

All experiments were carried in triplicate and each sample mixture was pelletized by applying a pressure of 10 tons. For each sample sixty emission spectra were acquired by shooting 30 laser pulses on each pellet side. Each spectrum was submitted to baseline correction by deducting from the spectral region an average of intensities calculated in a window containing pure noise. Finally, an average spectrum for each pellet was calculated.

To check the accuracy of LIBS results in K determination, a contrAA 300 (Analytik Jena, Germany) high-resolution continuum source flame atomic absorption spectrometer (HR-CS FAAS) equipped with a xenon short-arc lamp operating in the "hot-spot" mode as a continuum radiation source was used. The flame was produced by mixing high-purity acetylene (99.7%) (Air Liquid, SP, Brazil) and compressed air at flow rates of 594 and $80\,L\,h^{-1}$, respectively, and the sample aspiration rate was of $5.0\,mL\,min^{-1}$. An amount of 100 mg of each sample (five replicates) was digested for 65 min at a temperature not exceeding 220 °C in 3,00 mL of HNO_3 70% (v/v), 2,00 mL of deionized water and 1,00 mL of H_2O_2 30% (v/v) in quartz flasks using a microwave oven (Multiwave, Anton Paar, Graz, Austria).

3. Results and discussion

3.1. Qualitative evaluation of salt addition on LIBS detectability

The original eucalyptus biochar sample yielded a simple LIBS spectrum with few, very weak emission lines that showed no apparent significant spectral variation when $CuSO_4$ and $MgSO_4$ were added, whereas the addition of KCl, Li_2CO_3 and NaCl yielded a variable increase of some emission line intensities (Fig. 1). In particular, the low intensity of Ca I emission lines at 428.30, 428.94, 430.25 and 431.86 nm increased with EIE cations addition.

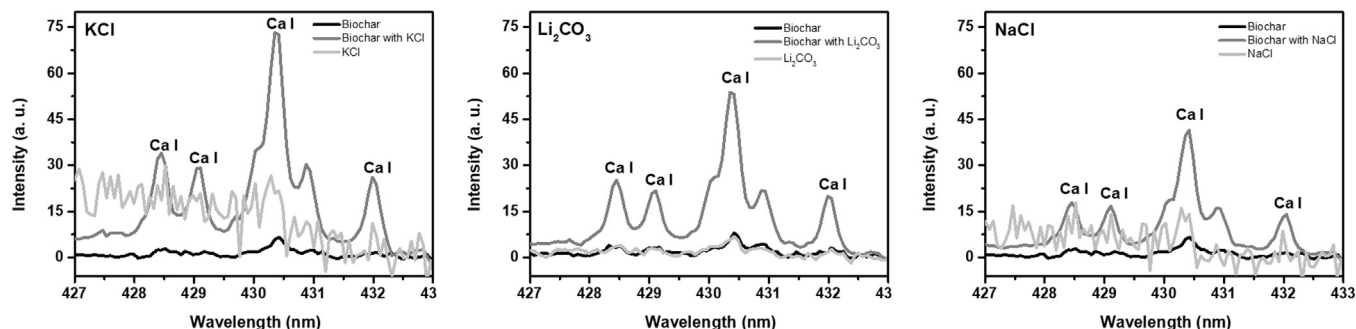As the LIBS plasma is considered a low ionized plasma with a free

Fig. 1. Average LIBS spectra (*n = 60*) of the salt and the eucalyptus biochar sample without and with salt addition.
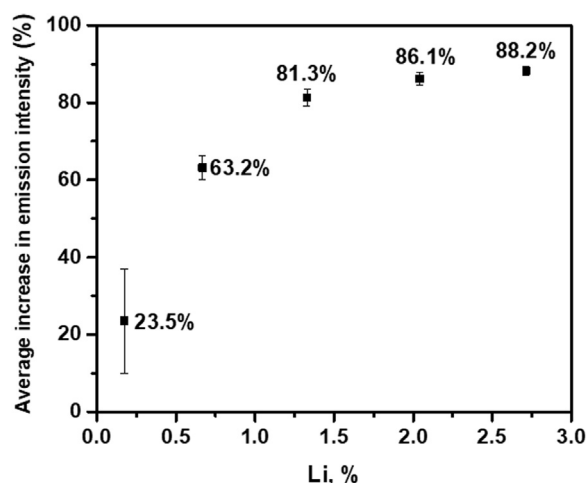
Fig. 2. Average increase of emission line intensities of the eucalyptus biochar sample as a function of Li% addition.

electron amount lower than 10% of the other species present [31], the addition of salts of EIE cations would produce an increment of plasma electron density, thus increasing the collisional probability and plasma temperature, and making more efficient the excitation processes.

Although the largest increase of signal intensities was obtained by KCl, the K^+ added would obviously affect the K analysis in biochar-based fertilizers that are also rich in Na but not in Li. Thus, Li_2CO_3, was selected for the next experiments. The effect of Li^+ addition on LIBS sensitivity was evaluated in the other samples, i.e. banana fiber biochar, rice husk biochar, roasted and unroasted coffee and orange leaves. Results showed no significant effect of Li^+ addition on LIBS signals sensitivity for unroasted coffee and orange leaves, whereas an apparent increase was observed for all biochars and roasted coffee samples. Previous thermal analysis results [30] have shown that in mixtures of eucalyptus biochar and Ca^{2+}, the thermal decomposition of $CaCO_3$ occurred at temperatures higher than those measured for the eucalyptus biochar itself, which suggested the occurrence of incorporation of Ca by the biochar, so changing its thermal properties. These results suggested that the increase of emission signals in burned samples could be explained by salt cation incorporation to biochar, which yielded the simultaneous breakdown processes for both the analyte and Li^+.

After having verified the positive effect of Li^+, its optimal concentration to be used was evaluated for eucalyptus biochar. The emission line intensities appeared to increase with increasing the amount of Li^+ added. The plot of the percentage of the average increase of emission line intensities as a function of Li^+ addition showed that no further increase was measured at Li^+ concentrations higher than 1,85% (Fig. 2). Thus, the concentration of 1.85% of Li^+ was used in the further experiment.

3.2. Determination of potassium

In attempting to use LIBS to measure the K content in commercial fertilizers, Yao et al. [35] found that the K (I) 404.41 nm emission line intensity was not linearly correlated to the analyte concentration, which was possibly due to the matrix effects caused by the large amount of other elements present in the samples. In an attempt to solve this problem the authors used a multivariate LIBS calibration approach. The same lack of correlation was observed in this work for the determination of K in biochar-based fertilizers, i.e. no significant differences of K emission lines were observed for calibration standards with different concentrations of the analyte. Thus, Li^+ at the optimal concentration of 1,85% was added to the calibration standards and fertilizer samples in the form of Li_2CO_3, which allowed to obtain satisfactory differences of K signals in the spectra of calibration standards containing different K
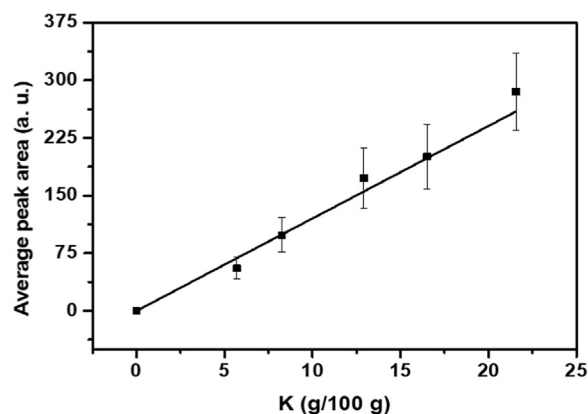

Fig. 3. Average peak area of the K I line at 404.64 nm as a function of K % in biochar-based fertilizers.

concentration.

The calibration model so constructed (Fig. 3) showed the existence of a strong linear correlation (R = 0.993) between K concentration and the average peak area of the K (I) line at 404.64 nm as fitted by the Lorentzian function in the calibration standards. The calibration model was then applied to measure the concentration of K in eucalyptus, peanut shells and banana fiber biochar fertilizers, which yielded K% of 0.82 ± 0.02, 1.82 ± 0.12 and 8.23 ± 0.11, respectively. These values were in good agreement (paired *t*-test at a 95% confidence level) with the reference values of 0.81 ± 0.01, 1.79 ± 0.13, 8.29 ± 0.18, respectively, obtained by HR-CS FAAS. Further, the LIBS method featured a linear dynamic range of 0.8–21.56% K, and limits of detection and quantification of 0.2% and 0,8% respectively.

4. Conclusion

Materials, such as biochar-based fertilizers, which are able to incorporate EIE cations showed an improvement of analyte detectability when using a simple single pulse LIBS instrument. This effect was feasibly due to the salt cations contribution to the plasma electronic density, which was apparently indispensable for K determination in biochar-based fertilizers. The method developed incorporated all the advantages of the LIBS technique, including simple sample preparation consisting only in mixing Li_2CO_3 and cellulose with the sample. Differently, any other analytical technique would require the application of drastic conditions for solubilization of such recalcitrant samples.

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