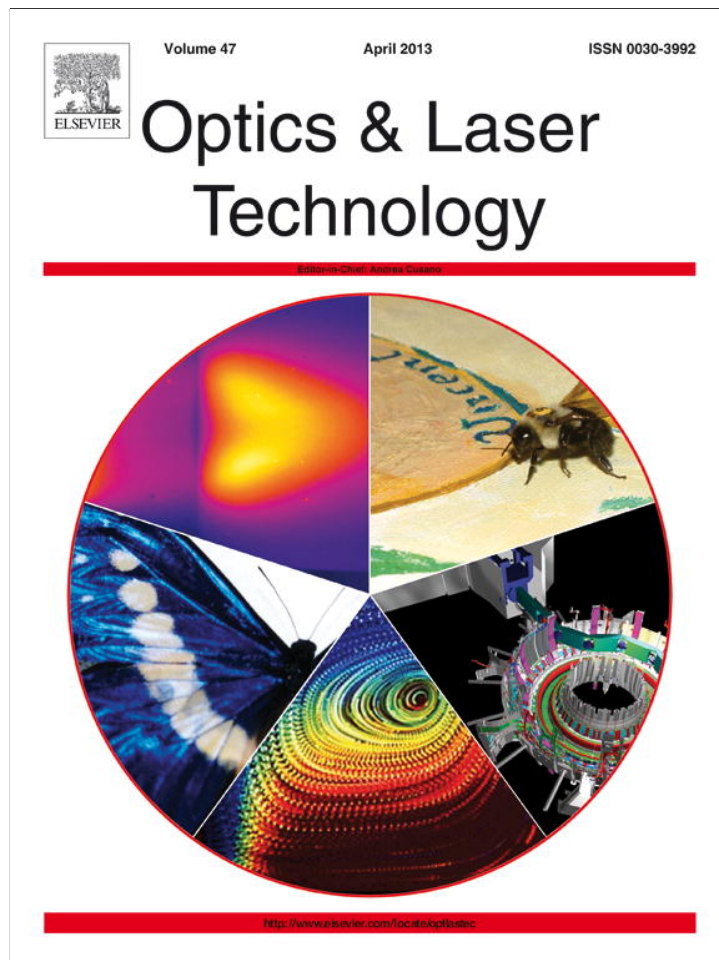


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Laser-induced breakdown spectroscopy for quantitative analysis of copper in algae

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ABSTRACT

Laser-induced breakdown spectroscopy (LIBS) has been applied for quantitative analysis of Cu in algae plants, an issue of paramount importance for environmental monitoring. For the analysis with LIBS, algae were compacted into solid pellets with powdered calcium hydroxide addition as binder and a pulsed Nd:YAG laser was employed to produce the plasmas in air at atmospheric pressure. In this approach, atomic lines from traces of Cu were detected, as well as other major and minor elements. The plasma was characterized and a calibration curve was constructed with reference samples prepared with calcium hydroxide. The results obtained demonstrated the usefulness of the method for Cu monitoring in algae plants.

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1. Introduction

Laser-induced breakdown spectroscopy (LIBS) is an analytical method based on the spectral analysis of radiation emitted by a laser-induced plasma (LIP) for the determination of the elemental composition of gases, liquids, and solids [1]. Nowadays, LIBS is a very active field of research because of its inherent advantages of rapid, in situ, multi-element measurements with a minimum of sample preparation, which are conditions not feasible with other well-established techniques. These unique features make LIBS a very promising method to be integrated to the conventional analytical methods requiring a pre-treatment of the samples; i.e., digestion, such as ICP and AAS [2]. Within a widespread range of applications in many fields, LIBS has been demonstrated as a powerful tool for the analysis of environmental samples of relevant interest for pollution monitoring [3]. Nevertheless, spectrochemical analysis by LIBS is not a straightforward task because the spectroscopic emission of the LIP is determined not only by the concentration of the analyte in the sample, but also by the properties of the plasma itself, which in turn depend on the experimental conditions; e.g., laser characteristics, time of observation, geometric setup, atmosphere gas, and other parameters [4]. Thus, a detailed analysis of the measured spectra is required in order to obtain reliable quantitative results. From an experimental point of view, the most common approach to perform quantitative LIBS

analysis relies on the construction of calibration curves employing matrix-matched standards. Nevertheless, in many practical situations reference samples are often either limited or unavailable (e.g., unique, complex, expensive or unknown samples).

Among LIBS applications for agricultural studies, the determination of essential elements in plant materials (leaves, roots and fruits) has been reported in the literature due to its importance to both monitoring nutrients and toxic metals [5]. An issue of key importance is the investigation of phytoremediation by employing plants species that absorb and gather harmful elements from the environment [6]. Between them, aquatic algae species are known to be useful bioindicators of pollution in aquatic ecosystems because they accumulate naturally toxic compounds present in the water they are immersed [7–9]. The presence of heavy metals in surface water indicates the existence of contaminant sources such as spills of wastewater, industries and/or discharges of treatment plants. Several investigations have been devoted to the research of the accumulation of different elements, including heavy metals, on vegetable samples such as plant leaves [10–13], grains [14], and potatoes [15]. However, most of them have carried out qualitative analysis and only a few works have been reported in the pertinent literature dealing with quantitative analysis [5]. This may be attributed, in part, to the lack of availability of suitable standards, and to the inherent difficulties for pellet preparation with binders in the laboratory [16–18]. Hence, it has been stressed that further efforts are required for the development of more appropriate reference materials together with the investigation of new strategies of calibration for LIBS analysis of plant materials. A suitable approach has been applied by Niu et al. [19] for the quantitative determination of Sr in two certified marine algae samples using the standard addition

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method to avoid changing the matrix of the analytical samples. Calibration curves were constructed and the results obtained showed a good accuracy.

In the present work, we applied the LIBS technique for the determination of Cu in algae samples aimed at potential environmental diagnostics. Cu is an essential micronutrient involved in many vegetable functions, including photosynthesis [20–22].

2. Experimental

2.1. Algae and reference samples preparation

Several algae and reference samples were prepared for LIBS analysis in the form of pressed pellets with binder using a similar procedure of sample preparation to that reported in a previous paper [23]. In that work, liquid samples were transformed into solid pellets of calcium hydroxide, overcoming the drawbacks of liquid analysis and accomplishing the advantages of direct interrogation of solids. Fresh algae plants free of pollution were collected from a watercourse located in the hills, distant from the city area. The algae were washed to remove dust and disposed for Cu determination by preparing five samples to perform a standard addition calibration procedure. In order to avoid disintegration of the algae pellets during laser ablation, they were mixed with a binder which provided them adequate resistance and allowed the averaging of many measurements. For each sample, we used 6 g of the algae samples and added to them standard solutions with Cu prepared by diluting appropriate volumes of a stock solution (Fluka Analytical, pure material in 2% HNO_3) with bi-distilled water. Then, we added to each sample 9 g of powdered calcium oxide (CaO , Aldrich Chemistry 99.9%) which reacted chemically with the water content to form calcium hydroxide [$\text{Ca}(\text{OH})_2$]. The mixture of algae material and $\text{Ca}(\text{OH})_2$ was well stirred to make it homogeneous and left dry at room temperature until constant weight. After that, it was finely ground and pressed in a die to form pellets of approximately 3 cm of diameter and 1 cm of thickness. The added Cu concentrations were

0, 14, 25, 68, and 129 ppm. For calibration purposes, we also prepared four pellets with a calcium hydroxide matrix with Cu concentration in the range 5–100 ppm.

2.2. Experimental setup

The experimental setup employed is shown in Fig. 1. A Nd:YAG laser (Continuum Surelite II, $\lambda = 1064$ nm, 7 ns pulse FWHM, 100 mJ/pulse, repetition rate of 2 Hz) was used to generate the plasmas in air at atmospheric pressure on the pellets. The laser beam was focused at right angle onto the surface of the samples by an antireflection coated lens of 10 cm focal length. The pellets were rotated to avoid the formation of a deep crater. The spatially integrated emission of the laser-induced plasmas was collected along the line-of-sight in a perpendicular direction to the laser beam by a fused silica quartz lens of 20 cm focal length and focused into the entrance slit (50- μm -wide) of a monochromator (Jovin Yvon Czerny–Turner configuration, resolution 0.01 nm at $\lambda = 300$ nm, focal length 1.5 m, grating of 2400 lines/mm). The detector was a photomultiplier (PM, Hamamatsu IP28, spectral response range 200–600 nm) whose signal was time resolved and averaged with a Box-Car. Finally, the spectra were recorded and processed by a PC. This experimental setup provided a good spectral resolution that allowed suitable measurements of individual line profiles, as well as detection of trace elements with concentrations of few ppm. An accurate wavelength calibration was carried out with a standard Hg pencil lamp. Craters of about 1 mm diameter were observed in the pellets.

The measurements were performed with temporal resolution using a suitable delay time of 6 μs with a gate width of 0.6 μs to discriminate the early plasma continuum from late line emissions. In such conditions, line profiles with an appropriate signal-to-noise ratio (SNR) were measured by scanning the monochromator and recording the signal with the PM. Each point of the emission profile was obtained averaging for three laser shots. Calcium could not be considered since its emission does not come from the vegetal tissue but from the $\text{Ca}(\text{OH})_2$ substrate.

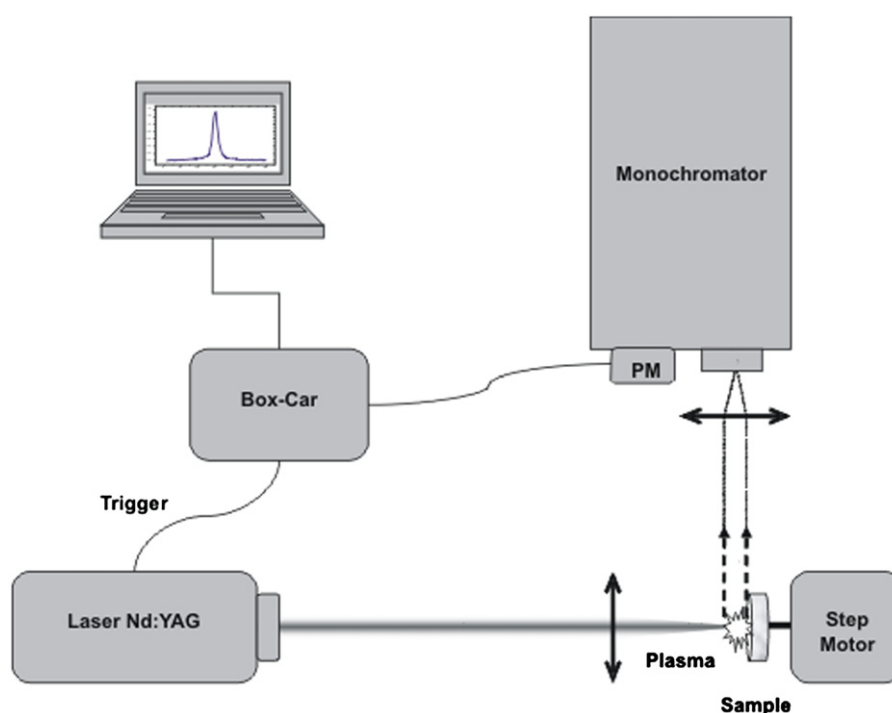


Fig. 1. Experimental setup used for LIBS measurements on algae samples.

3. Results and analysis

Firstly, the algae samples were measured to investigate their elemental composition. The spectroscopic information obtained was in the form of emission lines located at specific wavelengths which are the ‘fingerprints’ of the different species. In our experimental conditions, the detected species in the LIBS spectra included major elements: Mg, K, Na, Fe, and Si; minor elements: Mn, Ti, Al and V; and traces of heavy metals: Cu, Cr, Pb, and Zn. Some of the stronger spectral lines detected are exposed in Table 1.

Then, to obtain quantitative information about the Cu elemental content by means of a calibration curve method we must check for the equivalence of the matrices of the algae samples to be analyzed and the Cu samples proposed to be employed as references for constructing the curve. The assessment of the matrix influence on the LIPs was carried out by characterizing the plasmas produced and constructing calibration curves in both kinds of samples.

3.1. Plasma characterization

The LIPs generated on algae and Cu-calibration samples were characterized through its temperature and electron number density assuming Local Thermodynamic Equilibrium (LTE) condition. This is generally fulfilled in LIBS experiments by the relatively high electron densities achieved (10^{17} cm^{-3}). The temperature was determined using the Boltzmann plot method with the Cu I lines of Table 2 [24]. These lines are isolated and free from interferences of other elements. Their relevant spectroscopic parameters were obtained from Refs. [25,26]. The experimental line net intensities of Cu (corrected for the quantum efficiency of the PM), corresponded to

Table 1
Some of the atomic spectral lines of elements detected in algae.

| Element | Charge state | Emission line (nm) |
|---------|--------------|--|
| Al | I | 394.40 |
| Cd | I | 326.11 |
| Cr | I | 357.87 |
| Cu | I | 324.75 ^a , 327.39, 465.11, 510.55, 515.32, 521.82, 578.21 |
| Fe | I | 385.99 |
| K | I | 404.41 |
| Mg | I–II | 285.21, 279.07, 279.55, 279.80, 280.27 |
| Mn | I | 403.08 |
| Na | I | 588.99 |
| Pb | I | 405.78 |
| Si | I | 288.16, 300.67 |
| Sr | I–II | 407.77, 421.55, 460.73 |
| Ti | I–II | 332.29, 326.16, 481.11 |
| V | I | 318.39 |
| Zn | I | 481.05 |

^a Analytical line selected for quantitative determination of Cu.

Table 2
Atomic Cu lines employed for the calculation of the plasma temperature. Data from Ref. [25].

| Species | Wavelength (nm) | $A_{ji} \text{ (s}^{-1}\text{)}$ | $E_j \text{ (eV)}$ | $E_i \text{ (eV)}$ | g_j | g_i |
|---------|-----------------|----------------------------------|--------------------|--------------------|-------|-------|
| Cu I | 324.75 | 1.39×10^8 | 0.000 | 3.820 | 2 | 4 |
| Cu I | 327.39 | 1.37×10^8 | 0.000 | 3.780 | 2 | 2 |
| Cu I | 465.11 | 3.80×10^7 | 5.072 | 7.740 | 10 | 8 |
| Cu I | 510.55 | 2.00×10^6 | 1.389 | 3.817 | 6 | 4 |
| Cu I | 515.32 | 6.00×10^7 | 3.786 | 6.191 | 2 | 4 |
| Cu I | 521.82 | 7.50×10^7 | 3.817 | 6.192 | 4 | 6 |
| Cu I | 578.21 | 1.65×10^7 | 1.642 | 3.786 | 4 | 2 |

the integrated area of the line profile subtracting the baseline or background. Generally, the resonance lines are excluded from the Boltzmann plot to avoid the undesirable effects of self-absorption taking place inside the LIP, which causes a lowering of the emission intensities and leads to a consequent overestimation of the plasma temperature.

In typical LIBS experiences, Stark broadening is the predominant mechanism that determines the Lorentzian contribution to the line profile [27]. The Stark broadening is a consequence of the interactions of the electric fields near the emitter and, therefore, it is proportional to the electron number density [24], namely, $w_{\text{Stark}} = 2wN_e/10^{16}$, where $N_e \text{ (cm}^{-3}\text{)}$ is the electron density and w is the electron impact (half) width. The electron number density was determined using the experimentally measured Stark width of the Mg II line at 279.55 nm, where the necessary broadening parameter was taken from Griem’s database [28]. For an accurate determination of the electron density, isolated spectral lines with a suitable SNR and emitted in optically thin conditions have to be selected. In fact, self-absorption will have the effect of broadening the lines producing apparently larger widths and, thus, an overestimation of the electron density. As will be shown in the following, in our experiment the Mg and Cu concentrations were sufficiently low to consider self-absorption of the lines negligible.

To evaluate a possible self-absorption of Mg lines, we conducted a secondary experiment with the goal of checking the intensity ratio of the lines Mg II 279.55 nm ($A_{ji} = 2.60 \times 10^8 \text{ s}^{-1}$; $g_j = 4$) and Mg II 280.27 nm ($A_{ji} = 2.57 \times 10^8 \text{ s}^{-1}$; $g_j = 2$), belonging to the same multiplet, for different Mg concentrations. The experimental spectral lines (corrected for the quantum efficiency of the PM) were fit with Voigt profiles with a fixed Gaussian component of about 0.0049 nm at 280 nm (mainly due to the instrumental profile) to obtain their net intensities, given by the integrated area of the line profile subtracting the baseline or background, and their Stark widths.

For this pair of lines, the theoretical intensity ratio expected in optically thin conditions is $I^{279.55}/I^{280.27} = (A_{ji}^{279.55} g_j^{279.55}) / (A_{ji}^{280.27} g_j^{280.27}) \approx 2$. A reduction in the observed intensity of the strongest line in multiplet relative to the weaker one indicates that self-absorption occurs. On the other hand, if the line ratio remains constant then self-absorption is negligible [29]. We employed seven calcium hydroxide pellets with Mg concentration in the range 30–510 ppm. The CaO has a Mg concentration of 30 ppm present as impurity which was taken into account. The intensities of the Mg II doublet were measured from plasmas generated under identical conditions to the main experiment on the Mg samples and observed variations of the intensity ratio with increased concentrations. The results obtained are exposed in Fig. 2. It is observed that the experimental ratio is approximately two for concentrations less than 200 ppm and, then, it steeply decreases for higher concentrations. Therefore, the Mg II lines measured in algae samples are optically thin and may be used to calculate the electron density of the plasmas without correction for self-absorption.

We observed that the temperatures and electron densities measured in both algae and Cu-calibration samples are compatible within the experimental errors. As an example, Fig. 3 shows the Boltzmann plots obtained from the algae pellet with a concentration of 68 ppm together with that from the Cu-calibration sample with a concentration of 50 ppm. The temperatures were $kT^{(\text{Algae})} = (0.9 \pm 0.2) \text{ eV}$ and $kT^{(\text{Calib})} = (1.2 \pm 0.2) \text{ eV}$, respectively. The experimental errors were derived from the standard deviations of the slopes of the linear fittings. The corresponding electron number densities were $N_e^{(\text{Algae})} = (7.3 \pm 0.1) \times 10^{17} \text{ cm}^{-3}$ and $N_e^{(\text{Calib})} = (5.5 \pm 0.1) \times 10^{17} \text{ cm}^{-3}$. The errors were estimated from the propagation of the uncertainties of the Stark widths and the electron impact parameter.

From the results obtained from plasma characterization, we deduce that the effects of the plasma parameters on the analytical results for the algae and calibration samples are negligible.

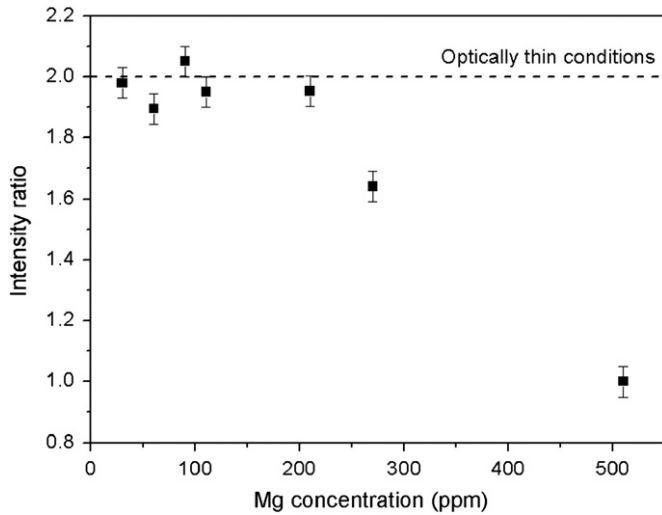


Fig. 2. Intensity ratio of Mg II line 279.55 nm respect to Mg II line 280.27 nm calculated from plasmas generated on reference samples with an increasing Mg concentration. The dashed line indicates the theoretical ratio expected in optically thin conditions.

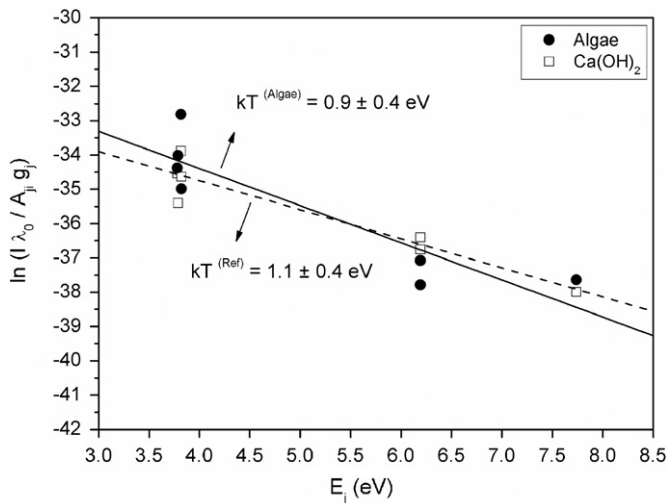


Fig. 3. Boltzmann plots obtained with Cu I lines for the determination of temperatures of laser-induced plasmas generated from (a) algae pellets with 68 ppm of Cu and (b) Cu-calibration samples of calcium hydroxide with 50 ppm of Cu. The temperatures deduced from the slopes of the linear fittings are indicated.

Thus, the matrix-matched calcium hydroxide samples can be employed to calibrate the Cu content in the algae pellets, carried out in the following section.

3.2. Calibration curves

The strong resonance Cu I line at 324.75 nm was selected as a suitable analytical line for direct elemental analysis in algae samples. Calibration curves of the net intensity (integrated area minus background) of Cu I line at 324.75 nm versus the corresponding concentration were constructed using both Cu-calibration and algae pellets, as shown in Fig. 4. It can be seen that the two sets of measurements show linear trends for Cu concentrations less than 130 ppm. The data were well fit with parallel straight lines, indicating similar ablation conditions for trace Cu concentrations. For Cu concentrations higher than 130 ppm, self-absorption effect starts to be noticeable, as evidenced by the slight drop of its measured intensity respect to the linear behavior; thus, the corresponding experimental point was not included in the linear fitting. The calibration curve corresponding

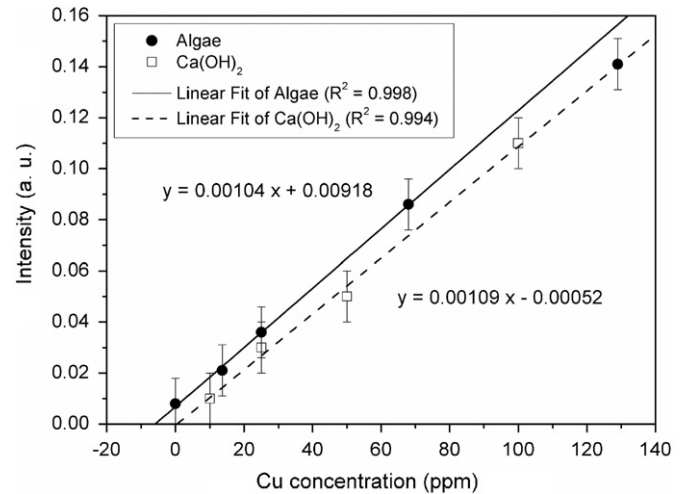


Fig. 4. Experimental calibration curves of the net intensity of Cu I line at 324.75 nm versus Cu concentration measured from algae pellets (●) and calibration samples of calcium hydroxide (□). The fitting parameters (a : slope, b : intercept) are shown.

to algae pellets has a non-zero intercept that indicates a pre-existing concentration of the analyte in the original sample ($x_0 = -a/b$, where a : slope and b : intercept). From the negative intercept of the linear-regression fitting, a Cu concentration of $x_0 = (9 \pm 2)$ ppm was estimated in the natural algae plants analyzed. This value was considered as the limit of detection (LOD), defined as the minimum detectable concentration [30]. It agrees with the values reported for such element in vegetables with LIBS [18]. Both calibration curves are the same except for an initial Cu concentration in algae (x_0), which was confirmed by the detection of the Cu I line 324.75 nm with a good SNR.

Given the linear behavior of the calibration curve of Fig. 4, we deduce that self-absorption of the Cu I line 324.75 nm is negligible in the current range of concentrations. Since that is the most intense Cu I line, we can infer that the other weaker Cu I lines of Table 1 are also emitted in optically thin conditions and may be used to calculate accurately the plasma temperature, as done in Section 3.1.

4. Conclusions

In this paper, the LIBS technique was applied for quantitative analysis of Cu in algae plants. The samples were prepared by mixing algae tissues free of pollution with powdered calcium hydroxide added as binder, then finely ground and pressed to obtain solid pellets. The algae samples had a pre-existing concentration of 9 ppm of Cu in the natural algae plants.

The feasibility of employing calibrations samples with a calcium hydroxide matrix was demonstrated for trace Cu concentrations in order to further simplify and enhance the rapidness of LIBS analysis. The proposed method is simple, fast, and provides the samples the additional advantages inherent to LIBS analysis of solid targets, e.g., repeatability and sensitivity. The procedure can be extended to the investigation of other heavy metals of environmental significance present at trace levels in natural algae samples by taking advantage of their humidity to prepare the samples for LIBS analysis by adding CaO. In addition, some drawbacks of the standard addition method are improved. In fact, the time-consuming requirements of collecting large amounts of sample material and carrying out many measurements when analyzing several samples can be overcome. Therefore, LIBS application to trace monitoring of Cu in environmental

algae plants turns out to be practical and it could be considered as a good alternative to complement the other analytical methods.

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