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Improvement of the sensitivity for the measurement of copper concentrations in soil by microwave-assisted laser-induced breakdown spectroscopy

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ABSTRACT

This study shows a 23 fold improvement of the sensitivity in the determination of copper in soil samples when using Microwave Assisted Laser Induced Breakdown Spectroscopy (MA LIBS) compared with our conventional LIBS. This comparison between MA LIBS and LIBS was performed with identical ablation conditions and detection geometry. The signal enhancement obtained with MA LIBS allowed for the detection of spectral lines related to concentration values as low as 30 mg kg⁻¹ for copper and 23.3 mg kg⁻¹ for silver, which were not detected by LIBS.

1. Introduction

The monitoring of concentration of metallic elements in soil is of great importance to environmental research, agriculture, and public health [1–3]. Mobile toxic metals in the soil (Cu, Pb, Cd, Cr, ...) can accumulate in the human body through the food chain [3,4] or prolonged exposure to trace amounts of contaminated aerosols [5]. The so called heavy metals in the soil, whether naturally concentrated or from the discharge of industrial or civilian waste, are harmful to the health of human beings, animals and plants. Overdose of metal salts (Na, Ca, and Mg) in the soil results in salinization [1], which can reduce the productivity of farmland and have serious consequences on food production.

An element of interest is copper. The copper concentration in soil determines if it should be considered as a nutrient for plants or a toxic metallic pollutant. As a nutrient, copper is absorbed by plants and involved in photosynthesis and respiration [6]. However, a high concentration of copper can lead to growth reduction and other issues [7]. For human beings, both copper deficiency and excess can cause health problems [8]. For ecological preservation, 61 mg kg⁻¹ is set as the soil screening level (SSL) for copper by the Environmental Protection Agency (EPA), which is the level that triggers further ecological risk assessment [9].

Major environmental hazards can be contained or prevented by monitoring the elemental composition of the soil. With the data obtained, necessary warnings can be given and remedial action can be taken. Laser induced breakdown spectroscopy (LIBS) is a technique

attracting increasing attention from both researchers and end users for environmental monitoring. In LIBS, focused laser radiation is used to ablate and excite the sample material simultaneously. The plasma created from the sample material provides elemental information about the sample via the optical emission [10,11]. Compared with several elemental analysis methods for environmental monitoring such as X ray fluorescence, inductively coupled plasma mass spectrometry (ICP MS) or optical emission spectroscopy (ICP OES), and atomic absorption spectroscopy, LIBS can achieve multi element analysis with reduced time and labor costs, since no or minimal sample preparation is required [12]. With the development of lasers and improved detection techniques, LIBS has been applied to complex environmental samples such as soils and rocks in recent years for both qualitative and quantitative analyses [13–18].

To measure the concentration of metals in soil, calibration curves are usually used. The slope of this curve defines the sensitivity of the analytical method according to the IUPAC definition [19]. Assuming similar precision, higher sensitivity would allow for better discrimination between two close values of concentration [20] and helps regulators to achieve conclusive and accurate decision making. Although LIBS has made progress towards applications in environmental analysis, its sensitivity still needs to be improved compared to other standard techniques [12,21]. LIBS signal enhancement through microwave heating is a new method studied recently [22–24]. As reported in Ref. [22], the microwave plasma coupling extends the plasma emission lifetime to milliseconds, from tens of microseconds in conventional LIBS. As a consequence, the line intensity can be strengthened several tens of times. This study presents the improvement of the sensitivity of LIBS for the determination of copper in soil samples using Microwave Assisted LIBS as

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Table 1
Concentration of Cu and major elements in soil samples referred to as S1–S4.

	Cu (mg kg ⁻¹)	Al ₂ O ₃ (%)	Fe ₂ O ₃ (%)	SiO ₂ (%)
S1	1232	16.3	11	55.5
S2	738	12.4	6.8	60.3
S3	544	16.5	10.7	52.3
S4	30	11.2	6.5	68.9

well as for the detection of silver and copper at concentrations not detected with our conventional LIBS system.

2. Experimental

2.1. LIBS and MA LIBS

The experimental setup of LIBS and MA LIBS was similar to the one in Ref. [22]. The nanosecond laser (Brilliant, Quantel), the microwave system (Envimetrics), the spectrometer (2300i, Princeton Instruments Acton) and the ICCD camera (PIMAX, Princeton Instruments) were used as the basic components of the LIBS and MA LIBS setups. The key differences between this study and Ref. [22] were the laser energy and focusing conditions, as well as the spectral acquisition parameters. Laser pulses with 10 mJ energy and 5 ns duration were focused inside the sample, forming a 160 μm diameter spot on the sample surface. This spot size was optimized for the maximum LIBS signal and minimum signal fluctuation. For MA LIBS, the same ablation condition was used. The plasma emission was collected from the side by a UV transmissive fiber at about 70° from the laser direction without additional focusing lenses. The position of the fiber was optimized to obtain the maximum LIBS signal. The gate delay was set at 500 ns to eliminate the initial continuum emission, and a 20 ms or a 10 μs gate width was applied respectively when the microwave generator was either activated or not. Each spectrum was obtained by adding ten accumulations at the same spot, and 5 spectra from different locations were averaged to obtain the final spectra.

2.2. Samples

The four soil samples were a subset of the samples used in Ref. [18]. The copper concentrations, measured by ICP OES, were evaluated at

1232, 738, 544, and 30 mg kg⁻¹ in order to measure the sensitivity over a wide range. In the following discussions the samples are labeled as S1–S4 with S1 having the highest concentration and S4 the lowest. These samples were natural soil samples from different locations rather than matrix matched soils made in the laboratory, considering a linear calibration curve may have been difficult to obtain due to matrix effects in the latter case [17,18]. In order to reduce these effects, the above samples were chosen to contain relatively similar concentrations of major elements like Fe, Si, and Al (Table 1). The soils samples were prepared in the pellet form. Details of the sample preparation and ICP OES measurements can be found in Ref. [18].

3. Results and discussion

For the detection of copper as a trace element in the soil matrices, the 324.75 nm line from the 4s²S_{1/2} 4p²P_{1/2} doublet was used. The spectra of S1 from both MA LIBS and LIBS measurements are shown in Fig. 1 respectively on the left and the right. The intensity of the line was measured, after background subtraction, by fitting the peak by a Lorentzian profile and integrating its area. In the LIBS spectrum, the Cu line was on a broad background structure in the spectrum. Due to the high level of noise, precise identification of each individual peak was not achieved. The Cu peaks in the MA LIBS spectrum are much more defined than those in the LIBS spectrum due to the signal and signal to noise enhancement. In Fig. 1, the integrated line intensity of the 324.75 nm Cu line from the MA LIBS spectrum was 14 times higher than that of the LIBS spectrum, with a 10 fold improvement of the signal to noise ratio (SNR). Additionally, a few lines from other elements were observed, thanks to the improved SNR. Among them, the line at 328.07 nm was identified as the resonant Ag I emission line from the 5s²S_{1/2} 5p²P_{3/2} transition. It should be emphasized that the concentration of silver was reported to be 23.3 mg kg⁻¹ in S1 according to the ICP OES measurement and was not detected with our LIBS measurement. Consequently, MA LIBS offered in this case better performances than LIBS for the detection of these specific trace elements. It has to be noted that each LIBS experiment has its own performance depending on the experimental conditions and consequently these values comparing MA LIBS to LIBS are not to be considered absolute ones.

The calibration curves for copper are plotted in Fig. 2 for both LIBS (circles) and MA LIBS (squares). The data for each concentration

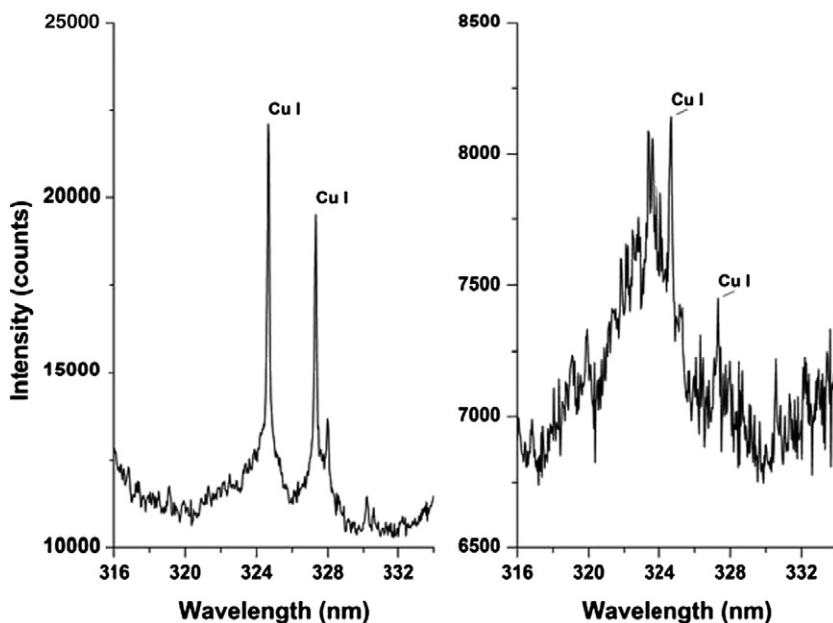


Fig. 1. Spectra of the soil sample S1 containing 1232 mg kg⁻¹ of Cu with MA-LIBS (left) and LIBS (right).

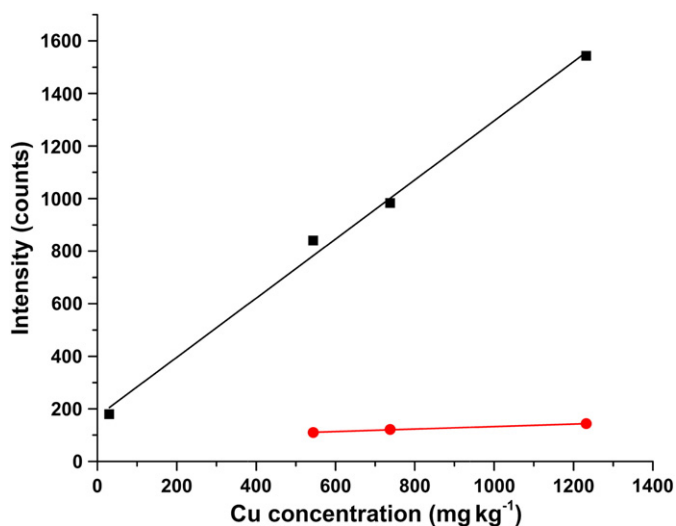


Fig. 2. Calibration curves of Cu for MA-LIBS (black squares) and the traditional LIBS (red circles).

consisted of five single spectra acquired at five different locations on the pellet. The mean values of the intensities were linearly correlated with the concentration of copper. The fitting results are listed in Table 2. In the case of our LIBS experiment, the sensitivity was 0.048 counts/mg kg⁻¹, while in MA LIBS, it increased to 1.12 counts/mg kg⁻¹, which represents a 23 fold increase. The improvement of the sensitivity is by definition beneficial for an analytical method since it is one of the most important factors for discriminating between two close values of concentration. MA LIBS can thus potentially offer advantages over LIBS in deciding if a soil sample has a concentration of a given pollutant below or above a fixed threshold.

Due to intrinsic large sample inhomogeneity of the soil samples, signal fluctuations (in the range of several tens of percent) were observed from one spot to another, for both LIBS and MA LIBS data. Such signal fluctuation is not specific to LIBS or MA LIBS but is common for any micro analysis method on inhomogeneous samples. Indeed, even if the soil samples were prepared and homogenized as much as possible, they are still heterogeneous at the scale of the laser beam size and the observed variations are really related to local composition of the samples. Without going deeper in this discussion of sampling, one can understand that in this case of heterogeneous sample, the variance from point to point has no statistical meaning and that only the average value is representative of the macroscopic sample. This is why error bars are not displayed in Fig. 2. Nevertheless, a second set of measurements was performed in this study to confirm the reproducibility of the previous result. Similar fluctuations due to the sample heterogeneity were observed, but again, the mean values of the intensity obtained for each concentration were linearly correlated with the concentrations (Table 2). The experimental points (average values) obtained during this second experiment were overlapped with the previous ones and consequently not displayed in Fig. 2 for clarity. Sensitivity improved by 20× for the second set of data, which is comparable to the 23× obtained with the first set. This confirms that, despite of the large heterogeneity of the soil samples, not discussed here, the results about the

Table 2
Summary of the fitting results for two sets of experiments.

	Experiment 1		Experiment 2	
	Slope	R ²	Slope	R ²
LIBS	0.048	0.99232	0.06	0.99872
MA-LIBS	1.125	0.99296	1.221	0.99804

sensitivity enhancement by MA LIBS were found to be reproducible, based on the analysis of the mean values.

In addition to the enhancement of the sensitivity, MA LIBS extended the range of analysis for copper, for the experimental conditions reported here. The calibration curve built with our LIBS system covered the range from 544 to 1232 mg kg⁻¹, while MA LIBS extended this range down to 30 mg kg⁻¹. For the same series of soil samples, the lowest detected copper concentration reported in Ref. [18] was 80 mg kg⁻¹ using another typical LIBS setup. Moreover, under our experimental conditions, silver has been detected only by MA LIBS, which makes this technique very promising for the detection of trace elements in soil.

4. Conclusion

In this paper, calibration curves of copper in soil samples were built by both LIBS and Microwave Assisted Laser Induced Breakdown Spectroscopy (MA LIBS). The MA LIBS signal for copper at 324.75 nm in soil samples was found to be linearly correlated to the concentration. A comparison with our LIBS data was conducted and an enhancement of sensitivity of more than 20 times was observed with MA LIBS. This improvement of sensitivity could have a significant positive impact on the monitoring of soil samples. Indeed, the ability of sorting soil samples based on their concentration of a pollutant with respect to a given threshold value could be highly enhanced. As a consequence, quick decision could potentially be taken with a higher level of confidence by MA LIBS than LIBS. However, this promising result will hold only if the signal fluctuations with MA LIBS are in the same order of magnitude as the one observed with LIBS. Future work should consequently be focused on the study of the precision in both LIBS and MA LIBS.

In addition, for soil samples, concentrations as low as 30 mg kg⁻¹ of Cu and 23.3 mg kg⁻¹ of Ag were detected by MA LIBS while not by LIBS, under the experimental condition reported here. Consequently, MA LIBS can potentially give access to spectral lines not detected by LIBS, which can be one of the major ways for detecting trace elements. Future work should address this important topic of improving the detection of trace elements with MA LIBS.

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