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6th Ibero-American Conference on Optics (RIAO)
and the
9th Latin-American Meeting on Optics, Lasers and Applications (OPTILAS)

Campinas, São Paulo, Brazil 21 – 26 October 2007

EDITORS
Niklaus Ursus Wetter
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AMERICAN INSTITUTE OF PHYSICS

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Niklaus Ursus Wetter

Institute for Nuclear and Energetic Research
São Paulo, Brazil

Jaime Frejlich

IFGW-UNICAMP
Campinas, Brazil

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Editors:

Niklaus Ursus Wetter
Institute for Nuclear and Energetic Research
R. Lineu Prestes 2242
Cid. Universit.
05508-000 São Paulo - SP
Brazil

E-mail: nuwetter@ipen.br

Jaime Frejlich
Laboratório de Óptica
IFGW-UNICAMP
Caixa Postal 6165
13083-970 Campinas - SP
Brazil

E-mail: frejlich@ifi.unicamp.br

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PREFACE

These Proceedings contains papers presented at the "6th. Ibero-American Conference on Optics and 9th. Latin-American Meeting on Optics, Lasers and Applications" (acronym: "RIAO/OPTILAS'07") that was held in Campinas, São Paulo State, Brazil, between the 21st. and 26th. of October 2007.

The RIAO/OPTILAS conferences are held each three years in Latino-American and Iberian countries and are focused on senior and young researchers as well as students working in all areas of Optics, mainly in these countries, but warmly welcoming participants from all over the world.

The present RIAO/OPTILAS'07 follows the one held in Venezuela in 2004 and will preced the next one already appointed to be held in Peru in 2010. The most active countries in the area like Argentine, Brazil, Mexico, Spain, Colombia and Venezuela have registered a large number of participants but other countries in the area like Chile, Cuba, Ecuador, Peru, Portugal and Uruguay have also sent a representative number of participants. About 7% of the registered participants came from Europe, USA and Middle-East. It was very stimulating to realize that about 44% of the accepted registered participants were students. An international committee was in charge of selecting the best student posters and thus ten students were awarded with prizes offered by organizations (SPIE, Wiley & Sons) and individuals.

There were 7 plenary invited talks by high quality researcher from Argentine, Germany, Israel, Italy, Mexico and Ukraine and 12 invited contributions from Brazil, Finland, Italy, Spain, UK and Uruguay.. The Book of Abstracts recorded 471 communications divided into 15 different topics with 160 oral communications in three parallel sessions and 311 posters in two special sessions.

We are particularly grateful to SPIE, OSA and ICTP that have provided us with important financial support mainly devoted to support the participation of students in this conference.

We also acknowledge the financial and organizational support from federal (CNPq, CAPES) and state (FAPESP, UNICAMP) national brazilian organizations and institutions as well as scientific national (SBFisica, CePOF) and international (ICO, EOS) organizations that have enabled the successful development of this conference.

We warmly acknowledge the efficient work of all members of the national and international committees that have participated in the organization of the conference and the reviewing of papers.

We are particularly grateful to all those that have made their best to delight us with their interesting and high quality scientific communications.

We also acknowledge the American Institute of Physics (AIP) for offering to us the opportunity to present these Proceedings containing a selection of the most of interesting papers presented in RIAO/OPTILAS’07.

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Micro-Crater Laser Induced Breakdown Spectroscopy - an Analytical approach in metals samples.

Vincent Piscitelli[a,b], Jhanis Gonzalez[b], Xianglei Mao[b], Alberto Fernandez[a], and Richard Russo[b]

a UCV- Laboratorio de Espectroscopia Láser, Caracas, Venezuela
b Lawrence Berkeley National laboratory, Berkeley, US

Abstract. The laser ablation has been increasing its popularity like as technique of chemical analysis. This is due to its great potentiality in the analysis of solid samples. On the way to contributing to the development of the technique, we in this work studied the laser induced breakdown spectroscopy (LIBS) in conditions of micro ablation for future studies of coverings and micro crates analysis. Craters between 2 and 7 micrometers of diameter were made using an Nd-YAG nanosecond laser in their fundamental emission of 1064 nm. In order to create these craters we use an objective lens of long distance work and 0.45 of numerical aperture. The atomic emission versus the energy of the laser and its effect on the size of craters was study. We found that below 3 micrometers although there was evidence of material removal by the formation of a crater, it was no detectable atomic emission for our instruments. In order to try to understand this, curves of size of crater versus plasma temperature using the Boltzmann distribution graphs taking the Copper emission lines in the visible region were made. In addition calibration curves for Copper and aluminum were made in two different matrices; one of it was a Cu/Zn alloy and the other a Zinc Matrix. The atomic lines Cu I (521.78 nm) and Al I (396.15 nm) was used. From the Calibration curve the analytical limit of detection and other analytical parameters were obtained.

Keywords: Laser Ablation, Laser induced Breakdown spectroscopy, Micro- craters.
PACS: 52.50.Jm, 52.38.–r, 42.62.Fi

INTRODUCTION

Laser induced breakdown spectroscopy (LIBS) is an atomic emission spectroscopy technique that has the capability to detect, identify and quantify the chemical composition of many material. LIBS utilize a pulsed laser focused on a spot (typically >20μm) to create a plasma on the sample surface. The resulting light emission is collected to produce spectrum containing emission lines from the atomic, ionic, and molecular fragments created by the plasma. By properly manipulation of these spectra, elemental chemical analysis both qualitative and quantitative of a wide range of materials can be accomplished [1-4].

LIBS analysis performance depends greatly on the plasma properties and lifetime. In general, to assure adequate plasma lifetime and strong emission intensity, most LIBS setups involve the use of a high energy pulsed laser (>30mJ, depending on the type of laser and wavelength), and large spot sizes (>20μm) [4,5]. However, these experimental conditions restrict the spatial resolution (lateral and depth resolution) necessary to access smaller information domains (nanoanalysis and monolayer analysis).

Attempts are being made to push this technology towards miniaturization of the instrumentation; these efforts are mainly driven by the necessity of portable analytical systems rather than improving spatial resolution. However, as is explain below, spot sizes down to less than 10μm are used in these miniature systems.

The miniaturization of LIBS systems to compact systems ideal for field deployment have been possible due to the development of small spectrometers, fiber optics, and microchip lasers capable of delivering peak pulses powers up to megawatts [6,7] . Such systems have been used for chemical interrogation of different materials, obtaining analytical figures of merit (precision, accuracy, limit of detection, etc) comparable with the most commonly used LIBS systems, such as those that use high energy Nd:YAG lasers. However, even though there are many advantages by miniaturizing these systems, they also present some drawbacks. For example, microchip lasers can only be

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operating at high repetition rates (>kHz), reason for which is required to rotate or scan the samples while they are being ablated, limiting lateral resolution.

In addition, microchip lasers have short pulse widths, in the range of hundreds of picoseconds and they can only deliver pulse energies between 10-50μJ. Dependency on the pulse widths have been well documented [2,4,8,9], in these papers have been reported that shorter the pulse width shorter the plasma lifetime. Therefore, signal acquisition closer in time to the ablation pulse is required, for which ungated detectors could be used at the risk of increasing the background signal intensity.

Finally, due to the low energy provide by these microchip lasers tight focusing conditions are required to reach breakdown thresholds. And although the small spot size required, theoretically will improve lateral and depth resolution, in fact can introduce new problems. For example, short working distance and shallow focusing depth to such an extent that small changes in the sample surface will move the sample out of focus.

Driven by the increased need of development techniques for nano and monolayer analysis, in this paper is presented a LIBS system in which the crater size can be change between 7-14 μm using the 1064nm wavelength of a Nd:YAG laser. Signal detection and quantitative chemical analysis is shown. Also a study of plasma emission as a function of the crater size and laser energy is also presented.

EXPERIMENTAL

The first part of this study consisted on making an experimental setup that allow us to create the smallest possible crater permitted by diffraction limitations. For this purpose, the system build works in the focal plane of the objective lens, instead of the image plane which is commonly used in LIBS systems. Working on the focal plane will permit to create craters down close to the optical diffraction limit. Figure 1 show the experimental setup schematics.

A Q-switched Nd:YAG laser (τ=4ns), operating at its fundamental wavelength (1064 nm) was used to initiate the ablation. The pulse energy was precisely controlled by beam attenuation. The laser beam was directed to the sample using dicroic mirror. Then it was focused using an objective lens (Edmund Optics EO M PLAN HR OBJECTIVE 10X) with a focal length of 19 mm and numerical aperture (NA) of 0.45 and conditioned by a couple of quartz lens. A XYZ motorized stage (Thorlabs RB13S) was used for positioning the sample. Images of the sample were acquired by a camera (Canon PowerShot G7).

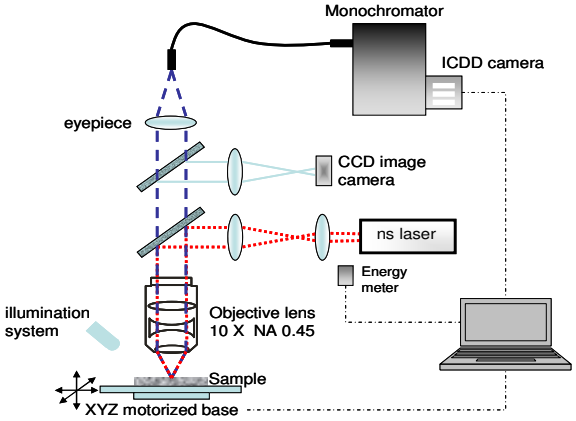


FIGURE 1: EXPERIMENTAL SETUP.

The samples were a series of standard reference materials from the National Institute of Standards and Technology (NIST zinc-base alloys 626-630) and Glen Spectra Inc. (Cu-Zn binary alloys). Table # 1 shows the SRM's compositions. The samples were cutting to an appropriate size and polish even 0.05 μm alumina powder, cleaned with acetone and storage in a dry cabinet.

The system build for these experiments resembles an optical microscope, even though the focal plane is used instead of the image plane, and the objective lens is used to focusing the laser beam.

The next step was to determine the minimum spot size (energy) from which a reliable signal distinguishable from the background is achievable. For this study the energy was also varied from 1 to 100 μJ and the emission intensity of aluminum (λ= 396.15 nm) and copper (λ=521.8 nm) were monitored.

TABLE 1. Compositions of the Standard Reference materials.

SRM	Cu	Al	Mg	Fe	Pb	Cd	Sn	Cr	Mn	Ni	Si	~Zn
625	0.034	3.06	0.07	0.036	0.0014	0.0007	6E-04	0.0128	0.031	0.0184	0.017	96.7181
626	0.056	3.56	0.02	0.103	0.0022	0.0016	0.001	0.0395	0.048	0.047	0.042	96.0795
627	0.132	3.88	0.03	0.023	0.0082	0.0051	0.004	0.0038	0.014	0.0029	0.021	95.8758
628	0.611	4.59	0.0094	0.066	0.0045	0.004	0.002	0.0087	0.0091	0.03	0.008	94.6576
629	1.5	5.15	0.094	0.017	0.0135	0.0155	0.012	0.0008	0.0017	0.0075	0.078	93.1100
630	0.976	4.3	0.03	0.023	0.0083	0.0048	0.004	0.0031	0.0106	0.0027	0.022	94.6155

#	Cu	Zn	Zn/Cu
2	55.6	44.4	0.80
4	65.2	34.8	0.53
5	69.5	30.5	0.44
7	82.5	17.5	0.21
9	89.5	10.5	0.12

The last part of this study consisted in building calibration curves using the two series of reference standard materials. Two conditions were set to meet the requirements of this study, improve spatial resolution. These conditions were the used of the smallest spot size from which reliable signal-to-background ratio was obtained (7μm diameter at 41μJ) and one pulse per sample location (10 different locations were ablated to monitor precision). Others optimized parameters used for these experiments were; Gate 300ns, and acquisition delay time 200ns. To collect the emission a 600 μm fiber multimode fiber optics was used. The end part of this fiber was focused into a 15 cm spectrometer with 600 groves/mm gratings and Princeton iCCD as a detector.

RESULT AND DISCUSSION:

Paraxial resolution

The paraxial wave equation that relates laser spot size, numerical aperture and beam quality was used to calculate the minimum spot size permitted by diffraction limits under these experimental conditions. This equation was:

$$S = 2M^2 \frac{\lambda}{\pi NA^{obj}}$$

where S is the spot size diameter, NA^{obj} is the numerical aperture of the objective lens, M^2 is the beam quality, and λ is the wavelength of the laser radiation. The theoretically spot size for our experimental conditions (NA= 0.45, λ=1064 nm and assuming M^2=1), is 1.5 μm and the size of the spot have no dependence with the energy of the laser. However, the crater size could not be experimentally reached since the intensity profile of the spot is strongly dependent on the intensity profile of the radiation, as well as the sample properties. For this reason, the dependency of the crater size with the pulsed laser energy was studied, in order to get the best relation between small crater and detectable emission light for the elements that we was chosen for the studied.

The energy was varied from 1 to 100 μJ. Sample NIST628 was used for this experiment. This sample was chose because the certificated amount of copper is enough to get a strong emission signal and low to avoid the auto-adsorption effects. The importance of the copper lines was based in the fact that whit these emission lines we can calculated the temperature of the plasma using the Boltzmann Plot. In this part of the experiment we fixed the Z sample position to the focal plane of the objective lens, and we vary the laser energy 100 μJ to 1 μJ and collect 20 spectra per energy all of them in different Y sample position. The smallest crater obtained was the 1.7 μm in diameter and 0.5 μm in depth, at laser energy of 1 μJ. this crater is close enough to the theoretical crater predicted using the paraxial wave equation. And as expected, there was a clear correlation (linear) between the pulsed laser energy and the crater size in which, higher the laser energy larger the crater size, figure 2-A. The same tendency was observed for the crater depth, figure 2a insert in figure 2-A shows the crater diameters versus crater depths. It is also important to mention that, in general, if the intensity profile is uniform the spot takes on the Airy disc intensity profile but if the intensity profile is Gaussian, as in this case, the result is an spot of Gaussian profile, as shown in figure 2-B.

Crater size versus emission

The relations between the crater size and the intensity of emission were studied using the sample 628. Figure 4, shows the integrated signals intensities versus laser energy. In this plot it is indicated the energy for which the signal intensity reaches at least three times de background level (3σ). It is also shown the total volume ablated (measured using a white light interferometer microscope (Zygo 200)) at these energies. As is expected, for aluminum (higher concentration) the requirement set for these experiments for the signal level (3σ background) is reached at lower energy than for copper. A minimum energy of 10μJ (spot size of 5.3μm) and 27μJ (spot size of 7μm) for aluminum and copper, respectively, are necessary to obtain the minimum signal set in this study for chemical analysis.

In order to understand why there was not copper emission measurable when the energy and the crater were less than 27 μJ and 7 μm, respectively. We calculated the excitation temperature from the plasmas form using energies ≥40μJ; the Boltzmann plot method was used.

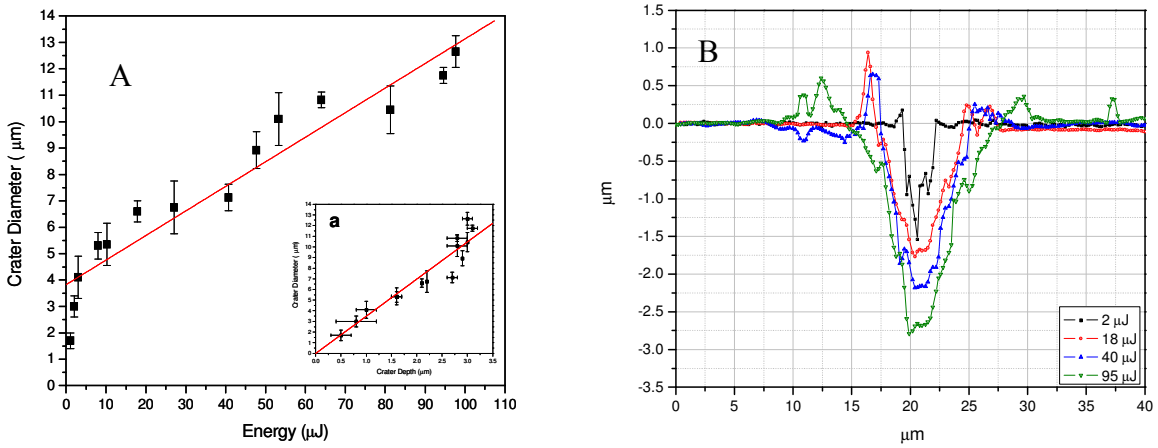


FIGURE 2: 2-A. CRATER SIZE VS LASER ENERGY: NIST 628, 2-B. CRATER PROFILES AT DIFFERENT LASER ENERGIES: NIST 628.

The Cu I emission lines centered at 427.51, 510.55 and 521.8nm were used [10]. The results are showed in figure 5. This figure shows the relation between the plasma excitation temperature and the energy. The plasma excitation temperature decrease when the laser energy decreases. This maybe is due because the amount of material that was removal is lower when the energy of the laser is lower. But also maybe is due that the plasma is so small, that it cold down so fast and no enough thermal energy is available to excite the atoms and promoted its emission. We do have not enough evidence but make sense that a combination of both of this effect is the cause of no emission where the crater size is smaller than 3 μm.

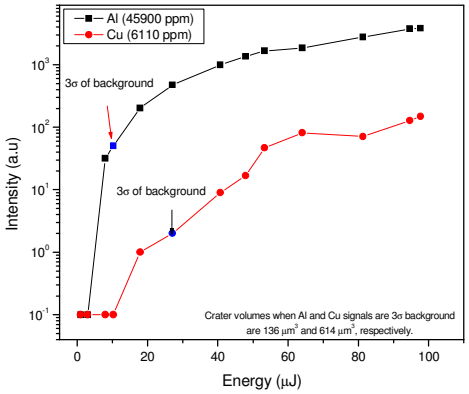


FIGURE 4: SIGNAL INTENSITIES AT DIFFERENT LASER ENERGIES: NIST 628.

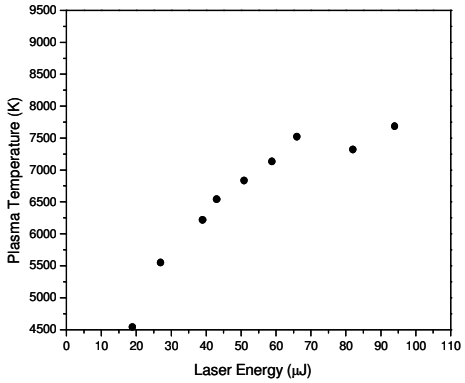


FIGURE 5: PLASMA TEMPERATURE VS. LASER ENERGY: NIST 628.

Calibration Curves

The second part of this work was building the calibration curves for Cu in order to get the analytical merits of the instrument to know which the L.O.D when micro-crater is are used instead the bigger crater.

The calibration curve obtained for NIST 627-630 using these conditions is show in figure 6. The linear regression data in figure 6 gave a correlation coefficient of 0.970 and a limit of detection of 0.1% for Cu. Samples NIST 625 and 626 were not include since they did not meet the requirement of signal-to-background ratio. The calibration curves was made using the area belong the emission peak instead the high of the peak. The 0.1 L.O.D obtained in this work is similar to the L.O.D. obtained by Winefordner et al [6] for similar crater size with the advantage that in this work we can made single crater analysis.

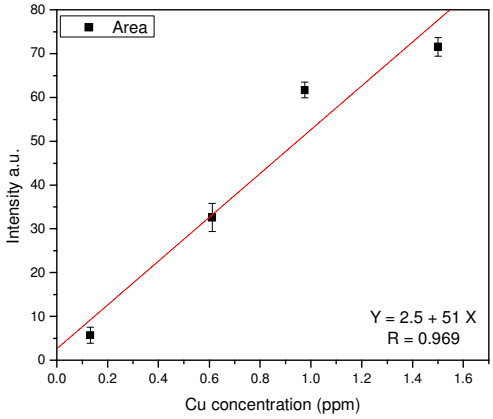
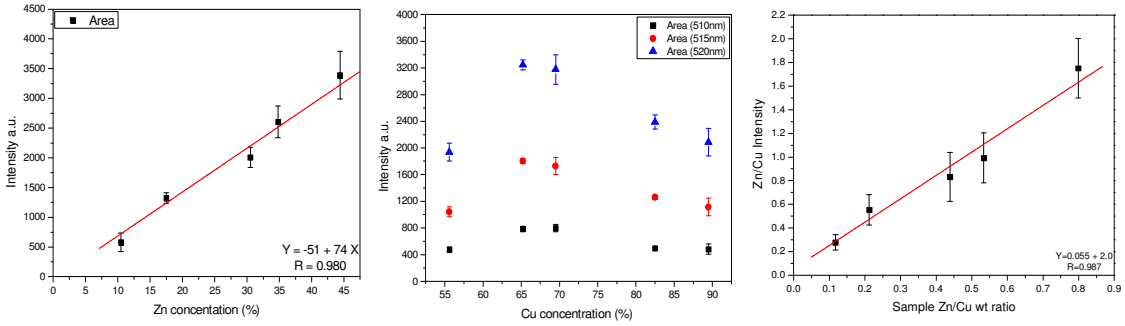


FIGURE 6: CU 520 CALIBRATION CURVE (NIST 625-630 SERIES).

. On the other hand, figure 7, in the same experimental condition the Brass series was study. For those the Cu I (521.8 nm) and the Zn I (481.5 nm) was chose. The first thing that we observed is that for Cu no linear relations was found when we made the graph concentration of Copper versus intensity. Similar effect was observed by Russo et al [11]. The reason of this effect is not well established, but the true is that the seam effect was observed in two different experimental conditions in the same series of sample. In Order to get a better calibration curve for Cu, we made the Zn/Cu ratio in concentration and intensity and the linear square relation obtained was 0.987 and 7 % of LOD for the Copper.



L.O.D.= 7%

FIGURE 7: ZN AND CU CALIBRATION CURVE (BRASS).

CONCLUTIONS

We found in this work, that it is possible to make craters near the limit of diffraction if we used the suitable optics. But these small craters are not able to emit radiation. Possibly to connect this system to a more sensible detector as a mass detector would allow the observation of the elements contained in the target. The smaller crater with emission sufficient to acquire a good spectrum that we could obtain was of 7 µm. the limit of detection as well as the other figures of merits are good enough if we consider the amount of energy provided in this experiment. This type of work opens the door to new experiments on the way to which the microanalysis of samples by means of the laser ablation and in specific of LIBS can be a reality, since they allow knowing the weaknesses and strengths the technique.

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