

Development of a portable, low-cost LIBS system

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ABSTRACT

This article reports the construction of a portable, low-cost LIBS (Light Induced Breakdown Spectroscopy) system for use in the Bolivian mining industry for the qualitative and quantitative analysis of the composition of mineral samples. The device consists of a portable laser, a medium-resolution spectrometer and an optomechanical light collection system. The laser developed for the device is a YAG:Nd⁺⁺⁺ with an estimated power output of 10 MW/cm². Weighing approximately 3 kg and powered by lithium ion batteries, it is easily carried and can be used in remote locations. The spectrometer has a resolution of 0.3 nm allowing the detection fine spectral features, while its range of 80 nm is broad enough to simultaneously show many of the principal spectral lines of the element of interest. A monochromatic CCD camera was used as the detector of the spectrometer and was fitted with an external trigger to coordinate the camera frames with the firing of the laser. The light emitted by the plasma is collected with a photographic objective and is transmitted to the spectrometer via a fiber optics cable. A mechanical system was incorporated to make, both the laser beam and the receptor positionable. In the preliminary tests of the prototype, a LIBS spectrum of a Bolivian copper coin was obtained. Analysis showed that the spectral lines obtained coincide with those of a copper reference spectrum and demonstrate the capacity of the device to perform qualitative analysis of materials.

Keywords: LIBS, Spectroscopy, Pulsed lasers

1. INTRODUCTION

LASER, which is the acronym for Light Amplification by Stimulated Emission of Radiation, it's a light source other than conventional ones by its physical properties: it is coherent, which implies mono-chromaticity, frequency stability, directionality and the possibility to focus a beam in very small areas getting amazing emission intensities.

It is because of these characteristics that lasers became a very important tool in different areas, such as medicine, telecommunications, industry, civil engineering, scientific research and other areas. The first built laser in the optical diapason was designed by T. H. Maiman at Hughes Research Laboratories in 1960, "ruby laser"^{1, 2}.

Various types of lasers exist based on the material of manufacture. A YAG:Nd⁺⁺⁺ type of laser uses doping of neodymium ions in yttrium aluminum oxide crystals (Nd:Y₃Al₅O₁₂) as a solid active medium. The first works in this direction were taken by Snitser³ who in 1961 fired the first laser activated with Nd⁺⁺⁺ ions. Laser radiation has a wavelength of 1064 nm, belonging to near infrared. Typical emission powers of this type of pulsed lasers are of the order of MW/cm² in the mode of Q-switch and of the order of GW/cm² in synchronization mode of the laser resonator modes.^{4, 5}

Laser Induced Breakdown Spectroscopy (LIBS) is a spectro-chemical technique which consists in the quantitative analysis of the materials composition, regardless of their physical state^{6, 7}. The laser is a fundamental tool for this technology that produces the induced plasma from which information of the material composition is obtained, through its atomic emission spectrum, which is caught by an optical system and directed to a spectrometer.

This methodology for measuring and analyzing samples has several advantages over others:

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- Non-invasive technique
- Portable, can be transported to the field,
- No need to prepare the samples prior to the analysis

LIBS can be applied in various fields such as mining, archeology, paintings analysis, analysis of components of different planets, analysis of the inclusions of steel, the slag analysis in secondary metallurgy and others. With the miniaturization of components and development of portable systems with low power consumption, this technology is being used by groups such as ESA, the NASA Mars exploration missions⁸, and other military applications.

This research project reports the design and construction of a portable, low-cost LIBS (Light Induced Breakdown Spectroscopy) system for its use in the Bolivian mining industry for the qualitative (as the first instance) and quantitative analysis of the composition of mineral samples. The device consists of a portable laser, a medium-resolution spectrometer and an optomechanical light collection system. The laser and the spectrometer were designed and assembled at the Centro de Investigaciones Opticas at the Universidad Privada Boliviana.

2. DESIGN AND CONSTRUCTION OF A PORTABLE PULSED YAG:ND+++ LASER

2.1 YAG:Nd+++ Laser

The YAG:ND+++ laser type responds to a pumping scheme of 4 energetic levels, for the inversion of population of the active medium, this type of solid lasers may be optically pumped by laser diodes or flash lamps. Optical pumping through flash lamps is possible thanks to the absorption in the spectral region near the 800 nm and the characteristics of the 4 level scheme. The most common emission wavelength of the YAG:Nd is the 1064 nm, from this wavelength, different harmonics can be obtained (532, 355 and 266 nm) through doubling, tripling or quadrupling of the frequency, using non-linear crystals of KDP or DKDP type. Other emission lines of the active medium are characterized by the following wavelengths 946, 1123, 1319, 1338 and 1444 nm⁹. In the case of the 946 nm transition, the system behaves as a system of 3 energetic levels, requiring higher optical pumping intensities. Some of these lines are very weak, such as 1123nm, making the laser generation efficiency very difficult to obtain.

Typical doping concentration of the YAG crystals with Nd ions is around 1%, high doping concentrations, may bring several advantages such as reducing the optical pumping length, however high concentrations can affect the lifetime of the higher energetic levels⁹.

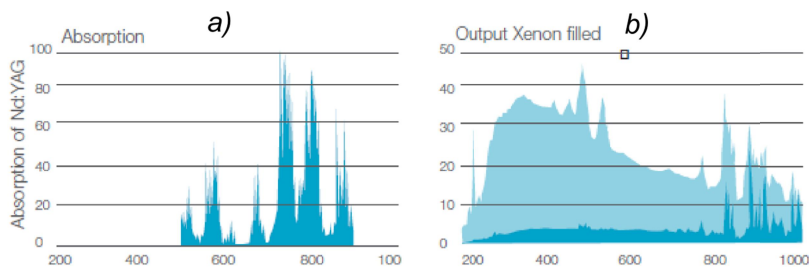


Figure 1. Absorption spectra of the YAG:Nd+++ active medium (a) and xenon lamp emission (b).

In the case of the use of flash lamps for optical pumping for the excitation of higher levels, xenon and krypton lamps are commonly used, because their emission peaks coincide with the absorption peaks of the crystal. In the specific case of the presented work, a xenon lamp was used, Figure 1 shows the emission spectra of the xenon lamp and the absorption peaks of the active medium¹⁰.

2.2 Laser Development

Figure 2 shows a detailed scheme of the 4 important blocks that were developed, this block diagram exhibits a sequence powered by batteries, the system inverter that converts DC to AC power, then the transformation of this current, raising the voltage needed to energize the power block. There is also the control block based on a PIC microcontroller and finally the laser head.

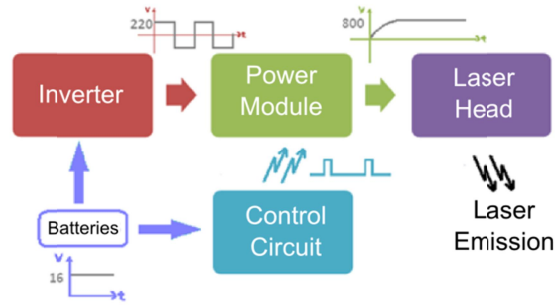


Figure 2. Block diagram of components of the developed laser system

The laser head consists of a metallic structure that contains the glass, flash lamp, reflective ceramic element for optimal use of the pump radiation of the lamp, a LiF type crystal for the passive Q-switch working mode and dielectric mirrors (R_1 -100%, R_2 -20%) for $\lambda = 1064$ nm.

A digital control system was developed, which used a PIC 16F877A microcontroller.

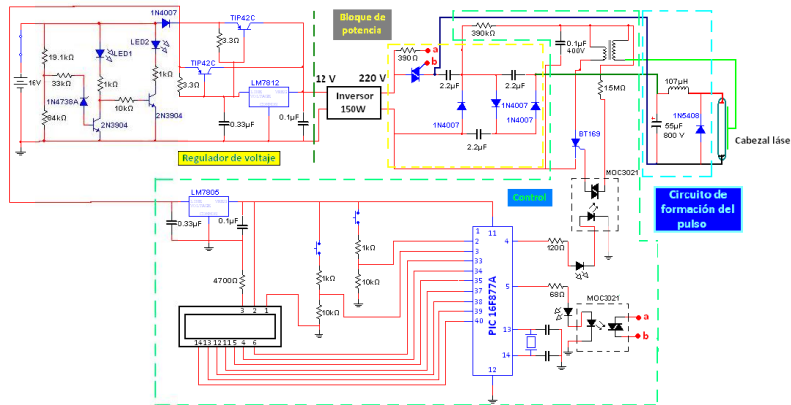


Figure 3. Electronic circuit of the portable laser system of the YAG:Nd+++ type.

An important physical phenomenon to analyze at the time of occurrence of the triggering of the lamp, as the impedance decreases drastically to 1 Ω orders; it acts almost as a short circuit, generating high peaks of current to the source side. When handling large energy to trigger the lamp, this situation is critical because it can damage different electronic components, which is why you can see the need to disconnect the power source at the time of the flash lamp triggering.

Using the mentioned PIC microcontroller also gives us the ease to control the energy directed towards the lamp at the time of shooting, to vary the energy, you can directly modify the value of the voltage or capacitance. In this work it was decided to vary the voltage, so we worked on the charging time of the capacitors, using a digital control of connection and disconnection of the power supply.

Thus, the PIC microcontroller function is summarized in the output of two signals, one that controls the trigger and the other one which controls the connection and disconnection of the power supply to the power circuit¹¹.

Figure 3 shows the complete circuit for the power supplying and controlling of the xenon flash lamp, through which the laser head emits coherent radiation of high intensity in the passive Q-switch mode.

All blocks were arranged inside a solid metallic box thereby forming the pulsed and portable YAG:Nd+++ laser, the dimensions of the equipment are 20x24x10 cm with an estimated weight of 3 kg. The laser system also has the following sings:

- Green LED as an ON/OFF state indicator of the equipment
- Red LED as a low battery indicator. This required adding a small circuit at the regulator before the inverter. This lights when battery voltage is lower than 15.3 V.

- Purple LED as an indicator when power capacitors are in charge, this is when the triac enables power to the tripler.
- Turquoise green LED as an indicator of the trigger signal. As laser fires, this LED lights.

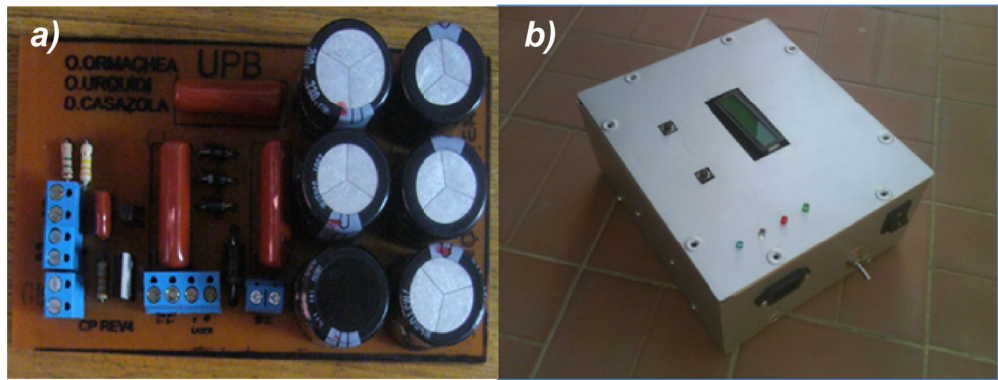


Figure 4. Photographs of one of the Printed Circuit Boards (a) and from the portable YAG:Nd+++ laser (b).

3. DEVELOPMENT OF A MEDIUM RESOLUTION VISIBLE SPECTROMETER

3.1 Classical spectrometer optical design

For the design process of the spectrometer we defined the resolution as 0.3 nm on the 500 nm region of the spectrum, enough to be able to resolve large part of the spectral lines of the elements under study in the visible portion of the spectrum. A CCD monochrome CCD camera was used as a detector for the spectrometer, the sensor used by the camera was the Sony ICX445AL. The spectral range of the CCD was in the 300 – 1000 nm region, having its maximum sensitivity in the visible portion of the spectrum.

The spectrometer design was based on a diffraction grating of 25x25 mm and 1200 lines/mm. The angles of incidence and diffraction were calculated using the grating line density and the 500 nm central reference wavelength. The total diffraction angle was determined by the physical limitations of the system, resulting in 38° ($\alpha + \beta$). Using the diffraction grating equation, the angles α and β were calculated, resulting in 37.5° and 0.5° respectively. The following equation corresponds to the diffraction grating equation, where m is the diffraction order, λ is the wavelength, d is the distance between grooves, α and β are the angles of incidence and diffraction¹².

$$m\lambda = d(\sin\alpha + \sin\beta) \quad (1)$$

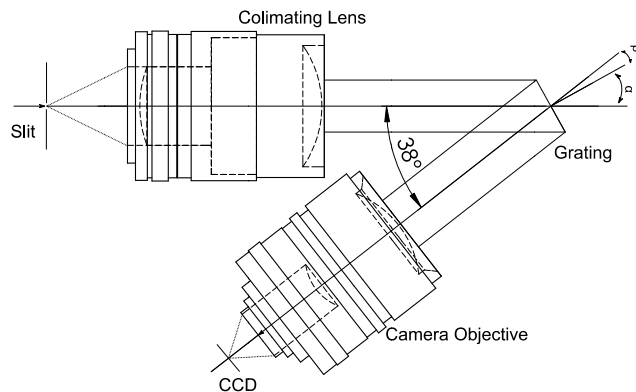


Figure 5. Optical design of the spectrometer, based on a reflection diffraction grating, commercial optical elements and a CCD camera.

A 50 mm, f/1.4 standard camera lens was used as the camera objective. This lens was selected by calculating the minimum focal length needed to obtain the required resolution. For this purpose, a FWHM of 15 μm was used, the

approximated value of the circle of confusion of this type of lens. The spectral resolving power was defined as 1666, approximately 0.3 nm of resolution in the 500 nm region.

$$R = \frac{rf_2}{FWHM} \left(\text{tg} \alpha + \frac{\text{sen} \beta}{\cos \alpha} \right) \quad (2)$$

$$r = \frac{\cos \beta}{\text{sen} \alpha} \quad (3)$$

The above equations were used to calculate the focal length of the camera objective¹³. The result showed that in order to obtain a spectral resolving power equal or greater than 1666, and objective of 38 mm or greater was needed.

A 135 mm f/2.8 photographic lens was selected as the collimating lens. This lens was selected by following two basic design principles: that its focal length needed to be greater than the camera lens focal length and that the focal ratio needed to allow the collimated beam to full illuminate de grating area.

$$SW = \left(10^7 \frac{p \cos \beta}{m f_2} \right) X \quad (4)$$

The spectral width was calculated as 80 nm using the above equation. Where f2 is the camera objective focal length, n is the grating groove density, X is the horizontal dimension of the CCD in pixels, p is the width of each pixel and β is the diffraction angle¹⁴.

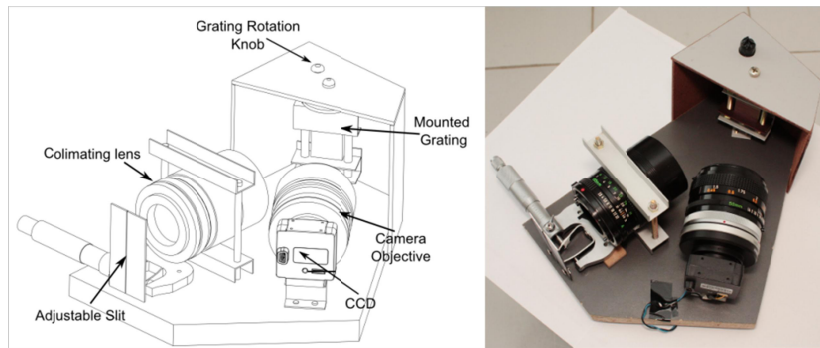


Figure 6. Designed an assembled spectrometer composed by a diffraction grating, a collimating lens, a camera objective, a CCD camera and an adjustable slit.

3.2 Wavelength Calibration

The following method is the most commonly used to perform wavelength calibration of a spectrometers¹⁵. It is based on the adjustment of an equation to the position of known spectral lines. The simplest way is to use a polynomial equation like the following.

$$\lambda(n) = A + Bn + Cn^2 + Dn^3 + \dots \quad (5)$$

Due to the capacity of the spectrometer to change the observed region of the spectrum, it was necessary to include a reference spectrum of a mercury lamp to calibrate the spectrometer. The limited spectral width of approximately 80 nm required the development of a calibration algorithm for different regions of the spectrum where just some mercury lines are observed. Using this algorithm, the developed software was able to calibrate de spectrometer using any line of the

spectrum and not always a fixed number of them. In all of the cases, the calibration was performed with a polynomial curve fitting technique.

4. DEVELOPMENT OF THE LIBS SYSTEM

4.1 Optomechanical assembly

For the LIBS system, a system to deliver the laser light and collect the plasma light was developed. This system was based on a laser focusing lens to create the plasma over a very narrow area and a light-collecting lens that was used to send the plasma light to the spectrometer through an optical fiber. The system was based on a 10 MW/cm², portable Nd:YAG laser, a spectrometer with 0.3 nm resolution and 80 nm of spectral width, a simple electronic coordination system and the processing and analysis software. The weight and dimensions of the developed laser and spectrometer, as well as the possibility to separate the spectrometer from the other elements of the system with an optical fiber, show the portability of the system for its use in the field.

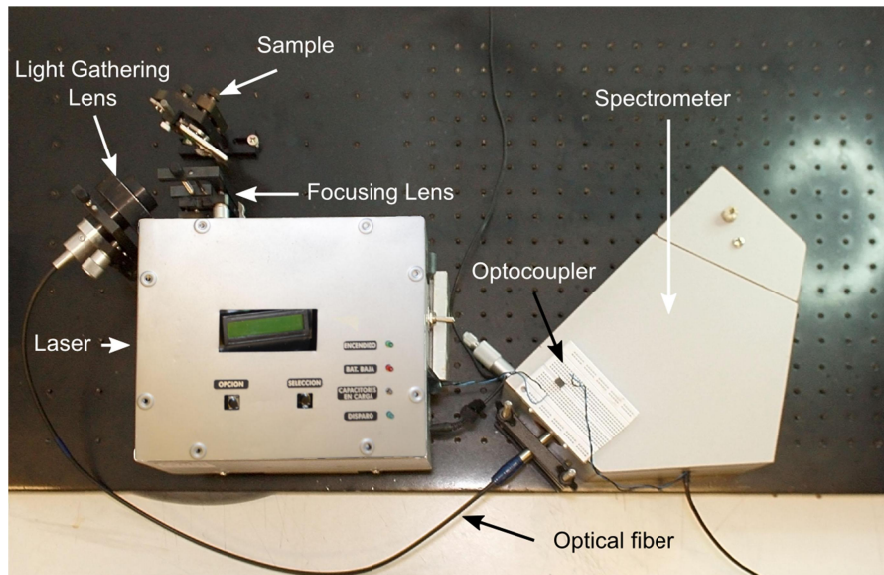


Figure 7. Mounted operational LIBS system

4.2 Detection of Cu in a Bolivian coin

The sample used for this analysis was a 10 cent Bolivian coin, this type of coins are made of Cu. The following image shows the 10 cent coin with a mark produced by the laser ablation process. The mark points the analyzed zone.

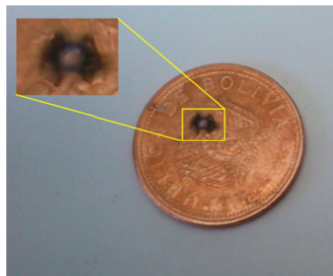


Figure 8. 10 cent Bolivian coin with a mark produced by laser ablation process.

After obtaining the spectrums and perform the calibration, the developed analysis software was used to compare the spectrum of a Cu pattern obtained from the LIBS spectra database of the Delaware State University¹⁶. A comparison between both spectrums showed coincidence in the principal lines of Cu (510.6, 513.3 y 521.8 nm), as well as in other secondary lines, showing the presence of Cu in the analyzed sample. It is important to note that the differences in intensities between both spectrums are due to differences in the sample and experimental setup. The non linear response of the CCD and the energy and duration of the laser pulse, generate these variations in the intensity of the lines and background trends.

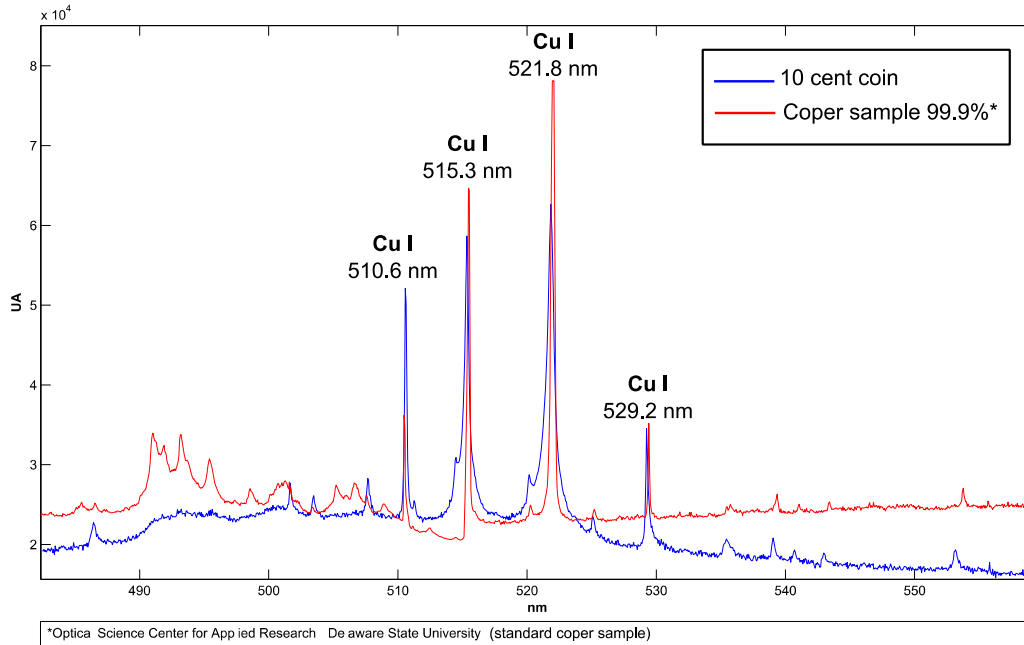


Figure 9. Comparison of 10 cent Bolivian coin LIBS spectrum and Cu pattern LIBS spectrum and centavos (482-559nm zone)

5. CONCLUSIONS

A portable, battery powered (Li-ion), Nd:YAG+++ laser ($\lambda = 1064$ nm) was designed and assembled. The laser had an estimated power output of 10 MW/cm² a weight of 3 kg and external dimensions of 20x24x10 cm. Also, a medium resolution (0.3nm) spectrometer was developed, based on a CCD monochromatic camera, reflection diffraction grating and commercial optical elements. The spectrometer had a weight of approximately 2 kg and external dimensions of 26 x 21 x 11 cm.

The LIBS system was satisfactorily developed, composed by the developed spectrometer, Nd:YAG+++ laser, and the different optical, computational and electronic systems that bond them together. Satisfactory results were obtained in the experimentation and validation process, the Cu lines of a Bolivian 10 cent coin where clearly identified. These results proved the validity of the system to perform chemical qualitative analysis of solid state samples. The whole system weight was of approximately 7 kg, fitting in a case, the developed LIBS system showed its portability for its future application in the field.

The system is in the first stage of development. The next logical step is the development of quantitative analysis methodology.

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