

# Comparison Study of Two Commercial Spectrometers for Heavy Metal Analysis of Laser Induced Breakdown Spectroscopy (LIBS)

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**Abstract:** The purpose of this paper is to compare the performance of two spectrometers that are manufactured from the same company. In this work, heavy metals like lead Pb and copper Cu in the KBr matrix were analyzed using the laser induced breakdown spectroscopic technique. A Q-switched Nd:YAG laser with 90 mJ per pulse operating at the fundamental wavelength of 1064 nm and pulse duration of 10 ns was used to generate plasma at the focal region. The important experimental parameters such as the laser energy, integration time, distance between the lens and sample, distance and angle of the optical fiber from the target were optimized. Two spectrometers manufactured by Ocean Optics namely as Maya2000Pro and USB 4000 were employed for analyzing the spectral lines. The experimental setup and conditions were remained the same for both experiments. The production of spectral lines from each of the interested elements was analyzed and compared with the NIST (National Institute of Standards and Technology) database. The sensitivity, repeatability and limit of detection for each of the systems are discussed in detail.

**Keywords:** Heavy metal, spectrometer, LIBS, LOD

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## 1. Introduction

Laser induced breakdown spectroscopy (LIBS) is a prominent technique for detection and analysis of chemical, biological, explosive, and hazardous materials. The LIBS involves interaction of a target with an intense laser pulse which generates plasma. The spectral emission from the plasma contains the specific signature of atoms of the material [1, 2]. The LIBS is, in principle, a straightforward and simple analytical technique that can be employed even by non specialist users. It is a quick and portable measurement technique providing results

practically instantaneously after analysis. Also, it is applicable *in situ* — that is, on the object itself and under certain conditions are nearly nondestructive [3].

The basic principle behind the LIBS is as follows. The output of a pulsed laser is focused onto the target material so that a luminous micro plasma or spark is produced on the surface, the optical emission of which is characterized of the target material. A fraction of the micro plasma light is collected and analyzed by an optical spectrometer, and the results of the measurement are displayed on

the computer screen as signals within a few seconds [4]. The LIBS offers several advantages compared to other spectroscopic techniques including (1) short time for sample preparation, (2) simultaneous multiple element analysis for almost all the elements in nature, (3) real-time response, (4) applicability to all states of the sample i.e., — solid, liquid or gas, (5) only need for little amount of the sample, and (6) high sensitivity [5].

The LIBS technique has now been widely used to study various materials like metals, alloys, biological samples, polymers, soil, environmental pollutants, land mines, and explosive materials [6, 7]. For elemental analysis by the LIBS, the appropriate choice for the experimentalist is based on the type of the spectrometer, which requires a balance among the wavelength coverage, spectral resolution, read time, dynamic range, and detection limit.

The type of the spectrometer is an important factor to be considered in optical emission spectroscopy (OES) for any plasma characterization or analytical spectrochemistry experiment [8, 9]. The ideal spectrometer depends on several parameters to get a good spectrum leading to the elements in the sample like: (a) a high resolution to resolve more lines of interest and avoid overlapping, (b) wide wavelength coverage, typically from 200 nm to 800 nm to be able to detect simultaneously several elements, and (c) high sensitivity and a linear response to radiation. Furthermore, for rapid analysis, the readout and data acquisition time should be shorter [10]. Currently, these factors can be obtained by using different types of spectrometers. In this work, a comparison study between two commercial spectrometers, USB4000-UV-VIS with Toshiba TCD1304AP detector and Maya2000 Pro with Hamamatsu S10420 detector, was performed. The lead (Pb) and copper (Cu) in the KBr mixture were analyzed at the atmospheric pressure. Both spectrometers were conducted in the range of UV-visible. The KBr powder with the high purity (99%) was chosen as a

matrix for Pb and Cu powders because it can produce strong signals and clear spectrum lines. The aim of this research was to select the suitable spectrometer to give us the best limit of detection for heavy metal analysis and determine the sensitivity of our LIBS system.

## 2. Experimental setup

In this work, a Q-switched Nd:YAG laser (AL-14 FP6000) with the wavelength of 1064 nm and pulse duration of 10 ns was employed. The laser was operating in the repetition mode with the rate of 1 Hz, and the energy remained constant as 90 mJ per pulse. The laser pulse was focused by a lens with the focal length of 8 cm. The beam diameter was 2 mm on the sample, and the distance between the laser aperture and sample was fixed at 10 cm. Hence, the energy density delivered on the target was estimated to be as  $2.3 \text{ J/cm}^2$ . Potassium bromide (KBr), lead (Pb) powder and copper (Cu) with the purity of more than 99.5% were used as the target sample. KBr was used as a reference sample, and the following with the mixture of KBr with Pb and Cu of different concentrations varied from 0.01 g to 1 g.

Two commercial spectrometers namely USB4000 and Maya2000 Pro manufactured from Ocean Optics were utilized as the spectral analyzer. The specifications for both spectrometers are summarized in Table 1. In order to investigate the performance for both systems in the LIBS analysis, the experimental conditions and setup were remained the same. Initially, all the powders were heated in an electrical furnace at  $60 \text{ }^\circ\text{C}$  for 2 hours. The powders were then weighed accurately by a digital balance (Precisa-XT 220 A) and mixed in an appropriate ratio to make samples of desired concentration prior to be palletized by an electrical pelletizing press (Herzog – Germany) with a pressure 50 kN for 5 minutes. Each of prepared pellets of KBr+Pb and KBr+Cu had the same dimension of 5 mm in thickness, 40 mm in diameter, and 10 g of the weight. Finally, all the pellets were

heated at 60 °C for 2 hours before executing the LIBS analysis. The plasma radiation was collected via a collimating lens prior to passing through a 2-m long optical fiber of the 600- $\mu\text{m}$  (pure silica) core diameter coated with dopped-flourine silica. The fiber optic cable passed the collected radiation to the spectrograph through an entrance slit of the 5- $\mu\text{m}$

width. The spectrograph dispersed the radiation into its constituent wavelengths, and a charge coupled device (CCD) detector recorded them as a spectrum graph during an integration time of 100 ms. Figure1 shows the experimental setup of the LIBS system. Both spectrometers were used in the same experimental setup.

Table 1 Specifications of USB4000 and Maya2000Pro spectrometers.

Specification	USB4000 spectrometer	Maya2000 Pro spectrometer
Manufacturer	Ocean Optics	Ocean optics
Type of detector	Toshiba TCD1304AP linear CCD array	Hamamatsu S10420 detector
Spectral range (nm)	200 – 1100	165 – 1100
Optical resolution	0.1 – 10.0 nm FWHM (grating dependent)	0.035–10 depending on grating groove density and slit size
Entrance aperture	Slit-5 (5- $\mu\text{m}$ width $\times$ 1-mm height)	Slit-5 (5- $\mu\text{m}$ width $\times$ 1-mm height)
Signal to noise ratio	At full signal about 300:1	At full signal about 450:1
Integration time	3.8 – 10 seconds	6.0 – 5 seconds

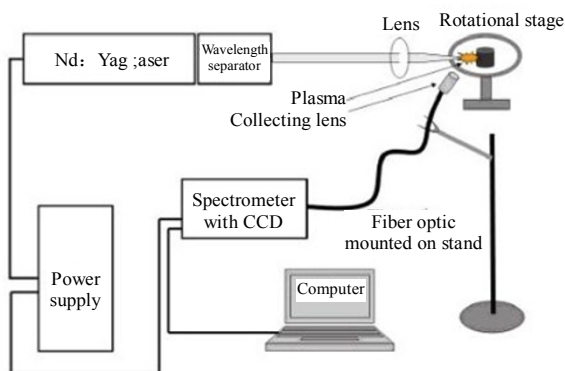


Fig.1 Experimental setup of the LIBS system.

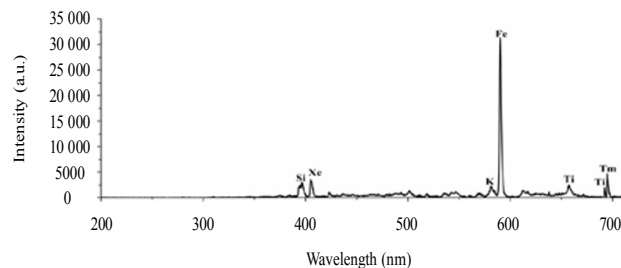
### 3. Results and discussion

Typical results of the spectral analysis of the KBr pellet are shown in Figs. 2(a) and 2(b), which illustrate the detailed LIBS spectra obtained from USB4000 and Maya2000Pro spectrometers, respectively. In both cases, the spectral range of study is 200 nm – 700 nm.

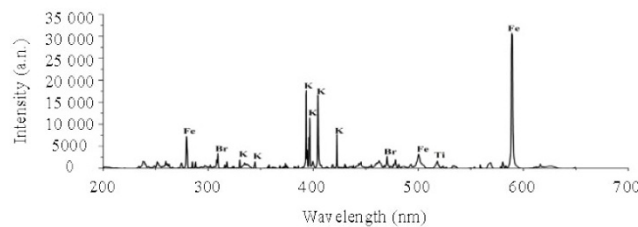
In Fig. 2(a), no lines of K are observed, except at 581.21 nm. That is overlapping with neighboring lines, while Fig. 2(b) shows clear lines of K and Br in the spectrum obtained from the same KBr pellet.

The spectral analysis of the (KBr + Pb) pellet is shown in Fig. 3. Two lines of lead appeared from

USB4000 spectrometer at 368.93 nm and 406.21 nm, respectively. The Maya spectrometer has displayed many spectral lines of lead which were obtained from the same pellet in the spectral range of 200 nm – 700 nm. The difference between the spectral lines produced from different spectrometers is shown in Figs. 3(a) and 3(b).



(a)



(b)

Fig. 2 LIBS spectra of the KBr pellet sample with (a) USB4000 spectrometer and (b) Maya2000 Pro spectrometer.

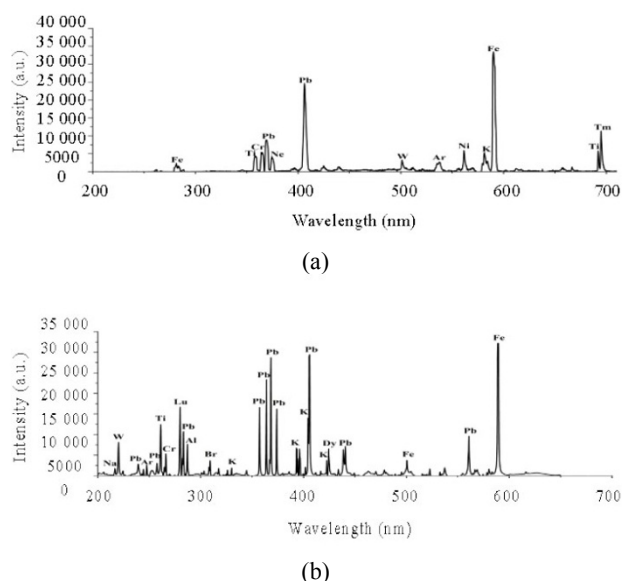


Fig. 3 LIBS spectra of the KBr + Pb pellet sample with (a) USB4000 spectrometer and (b) Maya 2000Pro spectrometer.

The spectral analysis of the (KBr + Cu) pellet is shown in Figs. 4(a) and 4(b). Two lines of copper were observed in the spectrum using the USB4000 spectrometer at 324.75 nm and 374.47 nm. Similarly, the Maya spectrometer has shown many spectral lines of copper produced from the same pellet in the same spectral range of 200 nm – 700 nm.

LIBS spectra by the USB4000 spectrometer for the pellets were recorded, and the data of K line appeared only at 581.21 nm, but the spectral line at 581.21 nm was overlapped with a nearby Fe I line. Pb lines were observed only at wavelengths of 368.93 nm and 406.21 nm, for Cu lines only at wavelengths of 324.75 nm and 374.47 nm. With the second spectrometer Maya2000Pro for the pellets in the same spectral range 200 nm – 700 nm, the lines of K appeared at wavelengths of 330.16 nm, 344.63 nm, 393.43 nm, 396.67 nm, 404.41 nm, and 422.56 nm, and Pb lines were observed at 239.37 nm, 257.72 nm, 283.3 nm, 357.27 nm, 363.95 nm, 368.34 nm, 373.99 nm, 405.78 nm, 438.64 nm, and 560.88 nm, for Cu at wavelengths of 203.58 nm, 222.77 nm, 236.81 nm, 279.17 nm, 324.75 nm, 390.31 nm, 406.81 nm, 435.52 nm, and 453.07 nm.

We also observed some clear lines representing

emission from gases of the atmosphere such as Ar, Ne, and Xe. The wavelength data in spectra indicated the peaks exclusive for Pb and Cu spectral lines, and we noticed the difference with the number of those lines appeared from two spectrometers. All the spectral lines were compared with the NIST (National Institute of Standards and Technology) database [11].

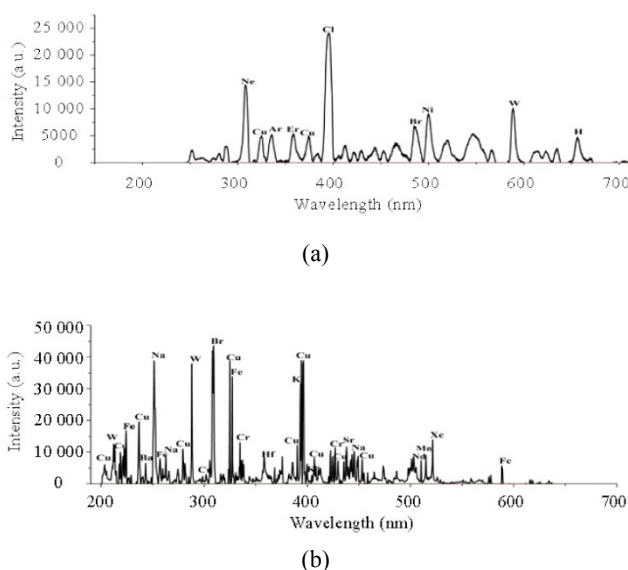


Fig. 4 LIBS spectra of the KBr + Cu pellet sample with (a) USB4000 spectrometer and (b) Maya2000 Pro spectrometer.

The accuracy of calibration curves between the two spectrometers' strongest lines of Pb was selected at 406.21 nm for the USB4000 spectrometer and 373.99 nm for the Maya2000Pro spectrometer. The Pb content in the KBr samples varied from 0.01 g to 1 g. As shown in the Fig. 5, the two curves were reasonably linear and comparable in terms of the sensitivity (slope) and repeatability. In the first calibration curve for this system PbI 406.21 nm emission line was employed, and the correlation coefficient ( $R^2 = 0.956$ ) was obtained, while in the second calibration curve at PbI 373.99 nm, we acquired the correlation coefficient ( $R^2 = 0.987$ ).

The strongest lines of Cu element were selected at 374.47 nm for the USB4000 spectrometer and 236.81 nm for the Maya2000Pro spectrometer. In

this study, the Cu content in the KBr samples varied from 0.01 g to 1 g. The two curves were reasonably linear and comparable in terms of the sensitivity (slope) and the repeatability. In the first calibration curve in this system, Cu 374.47 nm emission line was employed, and the correlation coefficient was obtained as  $R^2 = 0.9$ .

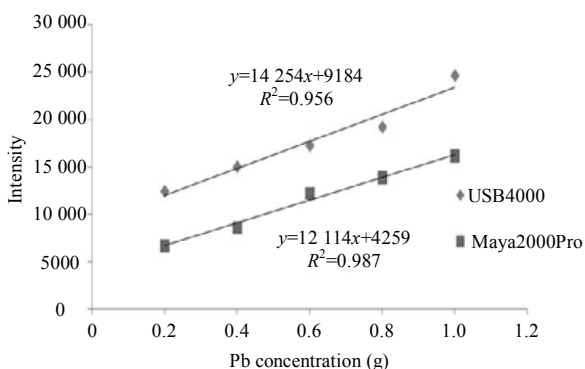


Fig. 5 Calibration curve for the concentration of Pb in the KBr matrix by using USB4000 at 406.21 nm and Maya 2000Pro at 373.99 nm.

However, in the second calibration curve, the Cu at 236.81 nm had the correlation coefficient of  $R^2 = 0.983$  as shown in Fig. 6.

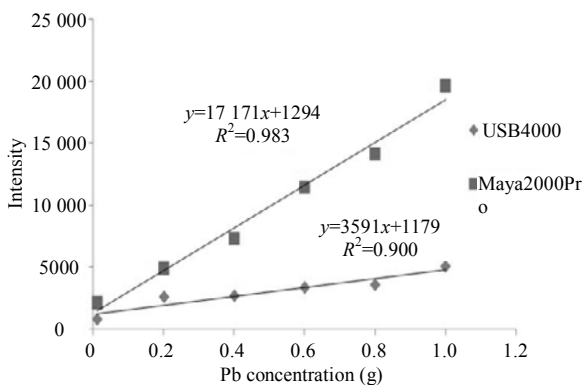


Fig. 6 Calibration curve for the concentration of Cu in the KBr matrix by using USB4000 at 374.47 nm and Maya 2000Pro at 236.81 nm.

The limit of detection (LOD) calculation is based on the  $3\sigma$  IUPAC (International Union of Pure and Applied Chemistry) definition [12, 13]:

$$LOD = \frac{3\sigma}{S} \tag{1}$$

where  $\sigma$  is the standard deviation of the background, and  $S$  is the slope of the calibration curve.

The limit of detection of each element in the

KBr matrix calculated by using (1), the standard deviation (SD), and LOD for both spectrometers are listed in Table 2. The LOD of the two elements Pb and Cu in the KBr matrix by using the USB4000 spectrometer is not as good as their LOD values when using the Maya spectrometer. Poor LOD i.e. 116 ppm was obtained with PbI 406.21 nm line recorded by the USB4000 spectrometer while the best LOD i.e., 67 ppm was obtained with PbI 373.99 nm line recorded by the Maya Pro spectrometer. Copper lines produced by USB4000 have the LOD of 63 ppm with emission line CuI 374.47 nm which from Maya was about 37 ppm at the wavelength of 236.81 nm. Thus, the LOD of the studied elements in the same matrix mainly depended on the type of the deployed spectrometer.

Table 2 Limit of detection for various elements in the same KBr matrix obtained by two spectrometers.

Element	Wavelength (nm)	Standard deviation	LOD (ppm)	
			USB4000	Maya2000Pro
PbI	406.21	7293	116	
	373.99	3040		67
CuI	374.47	2981	63	
	236.81	2166		37

It should be highlighted that the sensitivity and the limit of detection of a system depend on the type of the spectrograph as well as its detector. The capability of a spectroscopic detection system is deduced from the combination of the components making up the system, specifically dispersing element (i.e., grating or prism) and the detector. In this case, the dispersing element was grating with 600 grooves/mm in both spectrometers. Also, the entrance slit had the same dimensions i.e.,  $5\mu\text{m} \times 1\text{mm}$ . Therefore, there was a higher possibility that the differences resulted in our spectra were the consequence of different detector types used by these spectrometers. A detector may even respond differently in different spectral regions due to its variable quantum efficiency. In addition, the pixel size of the detector does matter in resolving power

of the spectrum. Better resolution is obtained with smaller pixels. It is clear from Figs. 2 – 4 that the detector with bigger pixels ( $8\ \mu\text{m} \times 200\ \mu\text{m}$ ) i.e., Toshiba TCD1304AP detector (in USB4000) generates low resolution spectra as compared to Hamamatsu S9840 detector (in Maya pro) that has significantly smaller pixels (i.e.,  $14\ \mu\text{m} \times 14\ \mu\text{m}$ ). Therefore, the LIBS detection system that can produce rich and well resolved spectra, is said to be a good detection system and can provide a good amount of information. Such a system would be more appropriate for the application. Other parameters to be considered are the spectral range and resolution power, which present some limits related to the well of the CCD detector of the spectrometer.

#### 4. Conclusions

A comparative study has been carried out between two commercial spectrometers using the LIBS technique. Spectral lines of Pb and Cu in the KBr matrix were analyzed. The two spectrometers were running under the same experimental conditions and observed within the same range of 200 nm – 700 nm. Some differences in the production of spectral lines attributed via Pb and Cu were realized. The Maya system has shown better performance since it has lower LOD and higher repeatability  $R^2$  in the calibration curves for both heavy metals Pb and Cu as compared to the USB4000 system. In the future studies, the delay time parameter in the LIBS setup will be considered for achieving a suitable strategy in identification of heavy elements.

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