

DOI: <https://doi.org/10.24297/jap.v16i1.8326>**Laser Induced Breakdown Spectroscopy and PIXE for Differentiation Between Different Tungsten Alloys**

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Abstract

Tungsten is one of the hardest metals that has high melting point and high thermal conductivity. These unique properties make it suitable for many industrial applications. The increasing demand for using tungsten made the need for a fast and reliable analytical technique for tungsten to increase. In this paper we are comparing the ability of laser-induced Breakdown Spectroscopy (LIBS) as a multi-elemental analysis technique to particle-induced X-ray emission (PIXE) which is a well known established multi-elemental technique in the analysis of tungsten alloys. It is found that LIBS has the advantage over PIXE in the detection of the trace and minor elements, while PIXE is better than LIBS in the detection of major elements in the samples.

Keywords: LIBS, PIXE, Tungsten alloys, quantitative analysis.

Introduction:

Tungsten is one of the hardest metals in the periodic table; it has a high melting point (3695 K) and thermal conductivity too. This makes its alloys to be used in many applications that need highly rigid metals like metal cutting tools, bullet proof shields and many other applications. Recently, tungsten has been used in the TOKAMAKs walls [1, 2] where plasma is confined inside. Since the TOKAMAK walls are facing the plasma, some changes in the surface composition may occur and so there is a need for a reliable fast analytical technique to monitor these changes [3, 4]. Some models have been used to describe this [5, 6]. Not only TOKAMAKs but also as the applications of tungsten increase, the need for a fast reliable analytical technique also increases.

Laser-induced Breakdown Spectroscopy (LIBS) is a spectroscopic multi-element analysis technique that can be used for the analysis of all of the material phases [7, 8]. LIBS is a surface analysis as well as bulk analysis technique. The simultaneous and high data collecting rate of LIBS provide the potential to address LIBS as a fast real elemental analysis technique. These advantages make LIBS to be a promising qualitative and semi-quantitative analytical technique used in many fields [9–17].

Some previous works have been done using LIBS in the analysis of tungsten. In 2016, Mal and Khare [18], used LIBS to study the laser produced tungsten plasma in air. And they observed that the spectral lines intensities and the values of the plasma parameters increase with the increase of the laser fluence. In the same year, Nishijima et al [3], used LIBS in analyzing tungsten surfaces using nanosecond and femtosecond lasers. They found that the depth resolution is better in case of fs laser than in case of ns laser. But also they reported that the signal intensity in case of fs laser is weaker due to the smaller amount of material ablated. Again in 2018 Nishijima et al [19], used LIBS in measuring the existence of a small fraction of rhenium in bulk tungsten where they compared their results with energy-dispersive X-ray micro-analysis (EDX) for the same samples.

In the same year, Shaw et al [4], detect the He inclusion in polycrystalline tungsten that takes place after bombardment with He ions using LIBS. They observed that the LIBS depth profiling results were in good agreement with Stopping and Range of Ions in Matter (SRIM) results.

Again in 2018, Lednev et al. [20] demonstrated the ability of using LIBS in real time quantitative multi-elemental analysis during parts growth by additive manufacturing technology. This was done by following up the carbon and tungsten spectral line intensities during synthesis of high wear resistant coatings of nickel alloy reinforced with tungsten carbide.

In this work, two tungsten alloy samples are analyzed using LIBS and particle induced X-ray emission (PIXE) in order to compare the LIBS results to that of PIXE which is the well established technique in differentiating between the two samples. And determine the abilities of each technique in determining the major and minor elements in samples.

Experimental setup:

Two tungsten alloy samples are used in this study. The chemical composition of the samples was analyzed using 2.5 MeV PIXE. For the LIBS analysis, the tungsten plasma was produced through collimating Nd:YAG laser (1064 nm, 50 mJ, 6 ns) onto the surface of tungsten samples in air at atmospheric pressure using a quartz lens of focal length 10 cm. The produced plasma emission was then collected by a 600- μm quartz optical fiber.

The optical fiber was adjusted so that the emission of the plasma plume to be within the collection cone of the fiber. The light collected by the optical fiber is then fed into an Echelle spectrometer coupled to an intensified charge coupled device (ICCD) camera. This spectrometer- ICCD combination allows a spectral analysis ranges between of 200–900 nm with a constant spectral resolution $\cdot \cdot \cdot \cdot = 7500$. After examining the best gate and delay times it was found that the optimum conditions occur at a gate width of 2500 ns and delay time of 1500 ns. To enhance the spectral reproducibility, signal-to-noise ratio and reduce the sample inhomogeneity, the average of spectra from different positions was taken each spectrum is the accumulation of 5 single spectra. The data was then fed into a computer and analyzed using LIBS ++ software. The laser energy signal to signal fluctuation was measured using a Scientech power meter (model AC5001, USA). The experimental setup is shown in figure 1. The LIBS experiment was done in the ambient conditions.

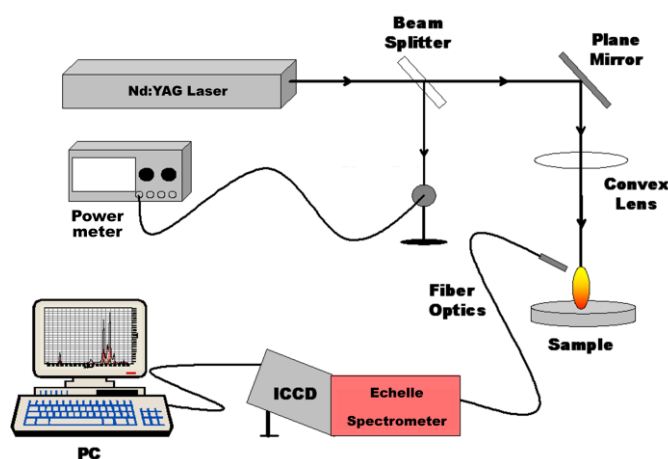


Figure 1: LIBS setup

Results and Discussion:

Two samples of commercial tungsten alloy samples with different compositions are used in this study. The samples were then sent for PIXE for analysis and the determination of some elements. Figure 2 shows the PIXE spectrum of both samples with some elements lines labeled. Ca, Ti, Fe, Co and W were chosen for this study.

PIXE was able to determine the concentration of such elements in the samples. Table 1 shows the concentration of the elements under study in the samples detected using PIXE.

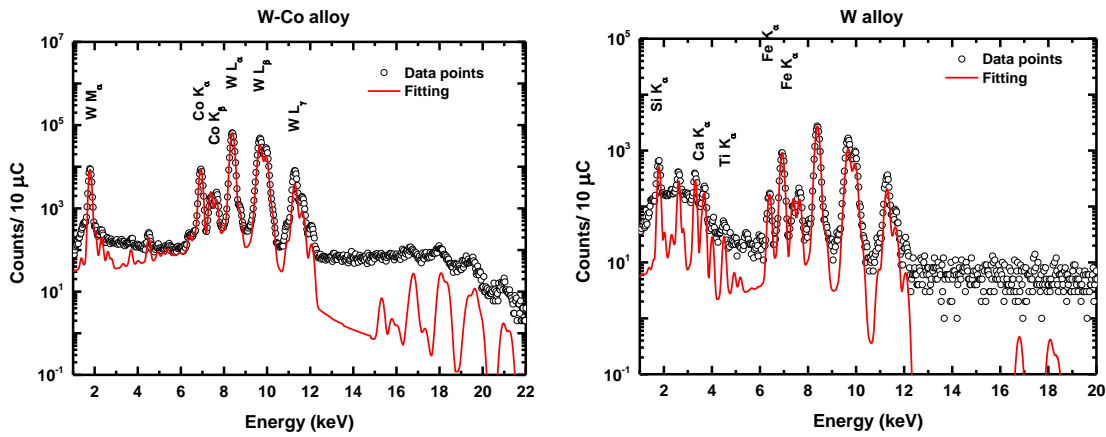


Figure 2: PIXE spectrum for the samples W-Co Alloy and W Alloy.

Table 1: The concentration of the some chosen elements in the samples under using PIXE.

Elements	W-Co-alloy	W-alloy
	ppm	ppm
Ca	159.93	297.53
Ti	311.50	50.16
Fe	387.87	350.43
Co	24277.33	2040.67
W	934612	35360.67

The samples were then analyzed using laser induced breakdown spectroscopy (LIBS). But before doing the analysis the optimum delay time should be determined. A gate width of 2500ns was chosen for performing the experiment. In order to choose the best delay time the intensity of two Ti spectral lines were followed up at different delay times. Figure 3 shows the intensity behavior of the chosen Ti lines intensities with delay. As it can be seen in the figure, the spectral lines intensities decreases exponentially with delay time. For the LIBS analysis, the best delay time was chosen to be 1500ns in order to be away from the beginning of the plasma where the intensity is so high and the plasma is out of the local thermodynamic equilibrium [21].

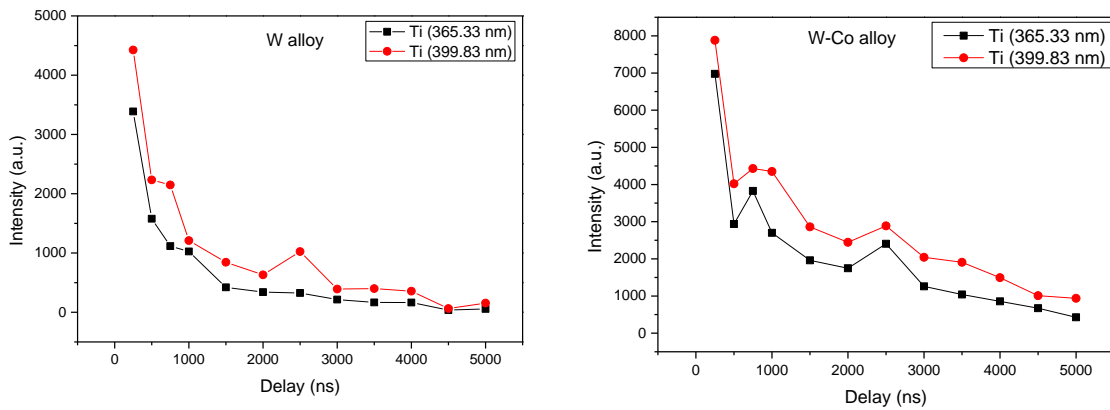


Figure 3: spectral lines intensities behavior of the Ti lines at 365.33nm and 399.83nm for the samples under study.

At the delay time 1500ns and gate width 2500ns, the LIBS spectra was recorded by recording the accumulated emission of 5 consecutive shots. In order to be sure that no inhomogeneity effect in the samples, the averaging spectra of five different positions were recorded. The spectra were then normalized by dividing the spectra on the spectral line intensity of the carbon line at 247nm to get rid of any fluctuations that may occur in the laser intensity.

The fulfillment of the local thermodynamic equilibrium (LTE) conditions has been checked using MacWhirter criterion. [22]

Figure 4 shows the LIBS normalized spectra of the two samples under study at the optimum delay time and gate width. It can be seen clearly that there are some differences between the two spectra due to the different composition of both samples.

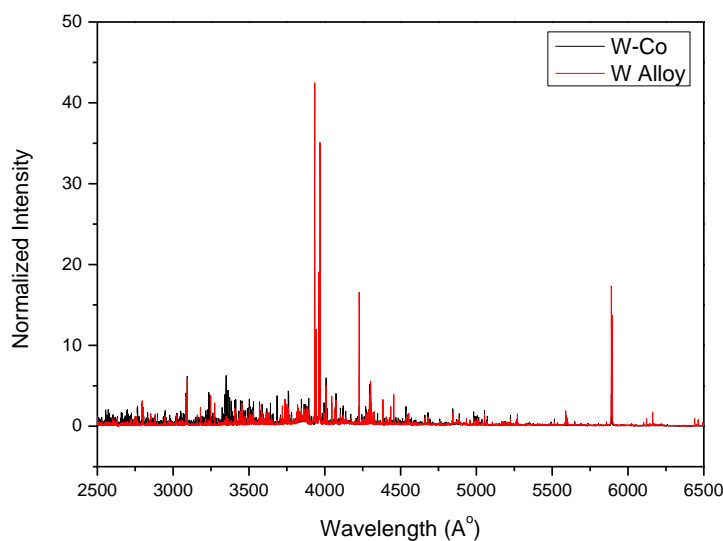


Figure 4: LIBS normalized spectra of the samples W-Co (black) and W alloy (red) at delay time 1500ns and gate width 2500ns.

For the elemental concentration comparison for the elements Ca, Ti, Fe, Co and W two lines for each element was chosen. Table 2 lists the spectral lines used and their properties.

Table: Spectral lines properties.

Element	Wavelength (nm)	ion species	E_k (cm^{-1})	A_{ki}	g_k	g_i
Ca	616.2	1	31539.49	0.477	3	5
Ca	643.9	1	35896.89	0.53	9	7
Ti	365.3	1	27750.12	0.754	11	9
Ti	399.8	1	25388.33	0.408	9	9
Fe	275.5	1	37157.56	0.2	5	3
Fe	344	1	29469.02	0.084	5	7
Co	340.5	1	32841.99	1	10	10
Co	344.3	1	33173.36	0.69	8	8
W	407.4	1	27488.11	0.1124	7	7
W	429.4	1	26229.77	0.1331	5	7

As an evaluation for LIBS as a semi-quantitative analysis technique for analyzing the tungsten alloys, the LIBS normalized intensities of the chosen elements are compared together and then compared to the results obtained by PIXE. Figure 5 and figure 6 show this comparison.

Figure 5 shows the comparison between LIBS results using two lines for each element and PIXE results in detecting some of the minor elements (Ti, Ca and Fe) in the two tungsten samples. It can be seen that there is a good resemblance between the results of both techniques in case of Ti and Ca. On the other hand, in case of Fe it can be seen that PIXE showed that the concentration is almost the same in both samples. While for LIBS it was able to detect that the iron content was higher in case of W alloy than in Co-W alloy. As it was mentioned before that the LIBS results were confirmed by making the analysis with two lines.

The comparison between LIBS and PIXE in detecting the major elements in the samples is shown in figure 6. It can be seen clearly in the results that there is a good agreement between the LIBS and PIXE results. The results showed that both tungsten and cobalt are higher in case of W-Co than in W alloy. Also it showed that the ratio between the concentrations of W and Co is higher in case of PIXE than in case of LIBS. This is due to the self absorption that may take place in the LIBS plasma [23], where the plasma reabsorbs some of the emitted spectral lines which causes lowering in these spectral lines intensities.

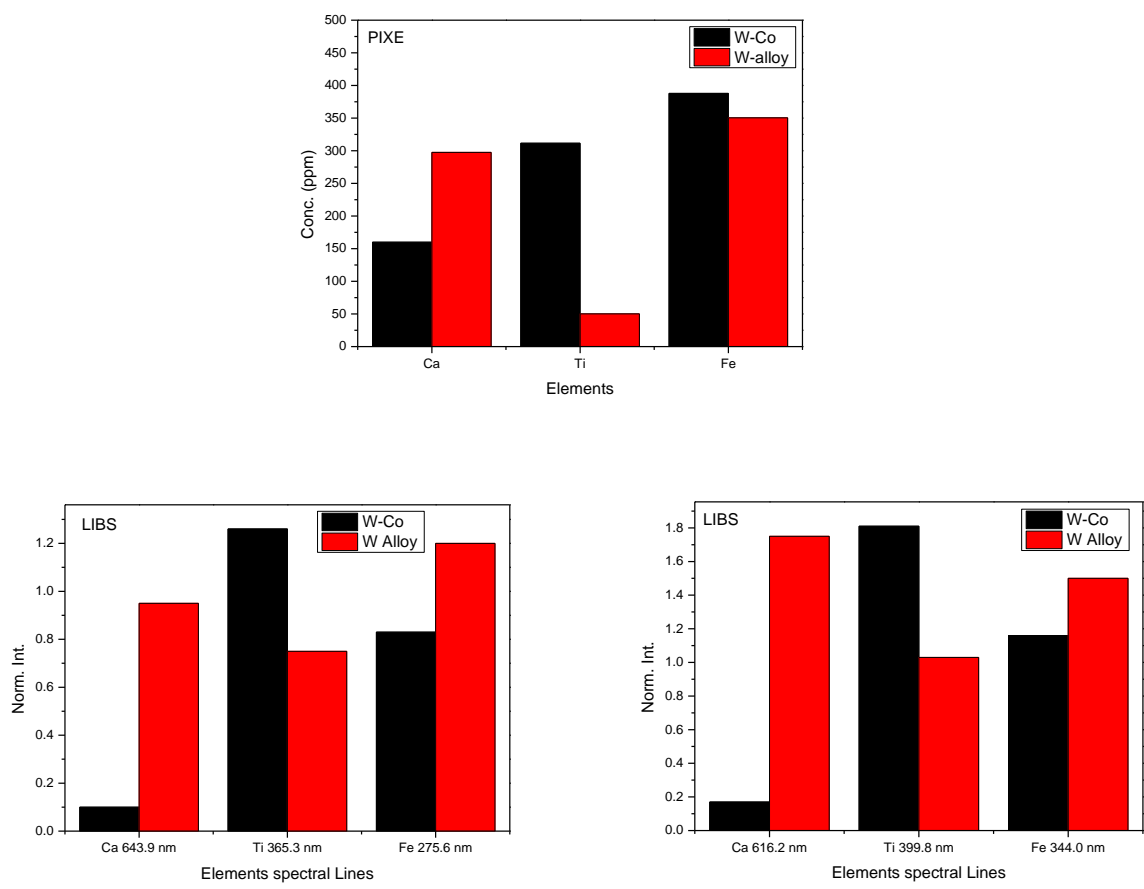


Figure 5: comparison between LIBS results using two line for each element and PIXE results in detecting some of the minor elements (Ti, Ca and Fe) in W-Co (black) and W alloy samples.

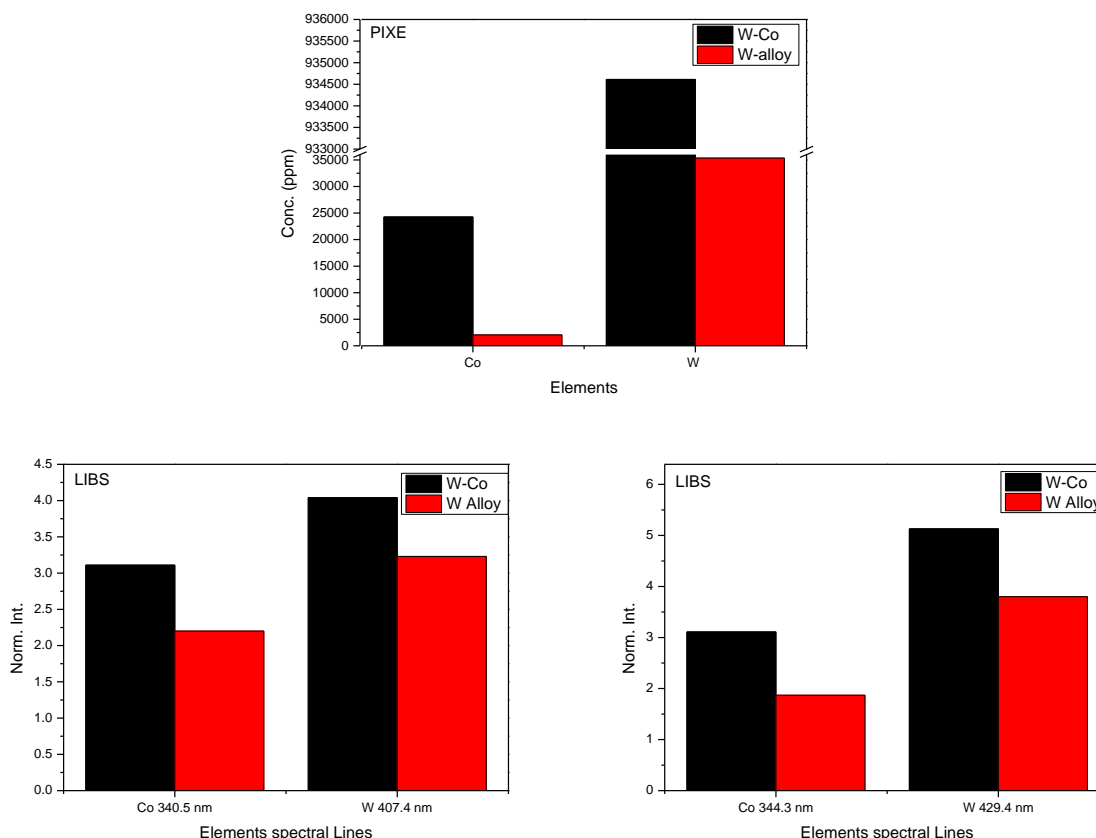


Figure 6: comparison between LIBS results using two line for each element and PIXE results in detecting some of the major elements (Co and W) in W-Co (black) and W alloy samples.

Conclusions:

This work compares between the LIBS technique and PIXE in analyzing two different tungsten alloys. Both techniques are multi-elemental analytical techniques. It was found that both techniques are good in the qualitative analysis of the samples. While for the quantitative analysis, LIBS is better in determining the changes in the concentration of the trace elements. While for major elements, it was found that PIXE is better than LIBS in determining their concentration. This is due to the self absorption that may take place in LIBS that causes the spectral line intensity to be lower that it should be and so can't represent the real concentration of the element in the sample [23].

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