Classification of alloys using laser induced breakdown spectroscopy with principle component analysis

Aneez Syuhada Mangsor¹, Zuhaib Haider Rizvi¹, Kashif Chaudhary¹,², Muhammad Safwan Aziz¹,²

¹Physics Department, Universiti Teknologi Malaysia, Johor Bahru, Malaysia.
²Laser Centre, Ibnu Sina Institute for Scientific and Industrial Research (ISI-SIR), Universiti Teknologi Malaysia (UTM), Johor Bahru, 81300, Malaysia.

Corresponding author: safwanaziz@utm.my

Abstract. The study of atomic spectroscopy has contributed to a wide range of scientific applications. In principle, laser induced breakdown spectroscopy (LIBS) method has been used to analyse various types of matter regardless of its physical state, either it is solid, liquid or gas because all elements emit light of characteristic frequencies when it is excited to sufficiently high energy. The aim of this work was to analyse the signature spectrums of each element contained in three different types of samples. Metal alloys of Aluminium, Titanium and Brass with the purities of 75%, 80%, 85%, 90% and 95% were used as the manipulated variable and their LIBS spectra were recorded. The characteristic emission lines of main elements were identified from the spectra as well as its corresponding contents. Principal component analysis (PCA) was carried out using the data from LIBS spectra. Three obvious clusters were observed in 3-dimensional PCA plot which corresponding to the different group of alloys. Findings from this study showed that LIBS technology with the help of principle component analysis could conduct the variety discrimination of alloys demonstrating the capability of LIBS-PCA method in field of spectro-analysis. Thus, LIBS-PCA method is believed to be an effective method for classifying alloys with different percentage of purifications, which was high-cost and time-consuming before.

1. Introduction
Laser Induced Breakdown Spectroscopy (LIBS), also known as laser induced plasma spectroscopy (LIPS), is an elemental analysis technique applicable for both qualitative and quantitative analysis of samples with unknown composition [1]. LIBS technique for the determination of elemental composition of materials in the form of solids, liquids and gases was first discovered on 1960’s [2]. Researches in LIBS have reaching its peak on 1970 and continued to grow during the past decades due to the factor of it is a method in which numerous application have been realised. For instance, number of papers published on LIBS in the year 2005 was about 350 and in 2007, the number of papers related to fundamentals and applications of LIBS reached the number of 600 [3]. The development on LIBS during these recent years had narrowed down the gap performance of LIBS compared to the other well-known approaches used for the analytical atomic spectrometry of the samples [4]. The examples of the conventional methods are inductively coupled plasma-atomic emission spectrometry (ICP-AES), electro thermal atomization-atomic absorption spectrometry (ETA-AAS), and inductively
coupled plasma-mass spectrometry (ICP-MS). It is said that LIBS is a more effective and up-to-date technique suitable for faster processing of data compared to the conventional methods. LIBS had been recognized as an attractive and promising technique to be used for the fast and whole chemical analyzation due to its “put & play” technique suitable for a wide range of applications [5].

Principle Component Analysis (PCA), also known as Karhunen-Loeve expansion is a technique where it is considered as a classical feature extraction and data representation. By using this technique, the variation can be emphasized and the strong patterns of the dataset can be visualized. PCA make it possible to represent the pattern of the similarity of the observations and it will be viewed in points on a map [6]. Multivariate analyses have been already applied for the classification purposes of LIBS samples [7] such as the classifications of samples using partial least squares discriminant analysis (PLS-DA) [8] and soft independent modeling of class analogy (SIMCA) [9]. However, few studies on variety classification of alloys using LIBS couple with principle component analysis (PCA) have been reported.

This research aimed to analysis the spectral lines of the target samples and to distinguish between metallic alloys using LIBS-PCA technique. In this study, the pattern of the spectrum lines of each target samples will be observed. Nd:YAG laser pulse (1064 nm, 740 mj, 6ns) will be used to produce plasma on different types of alloys which are Aluminium, Titanium and Brass with the metallic purities of 75%, 80%, 85%, 90% and 95%. This research is designed to contribute to the existing knowledge on spectral analysis of laser induced plasma spectroscopy. This research aimed to explore the characteristics of various spectral lines associated with atomic and ionic transitions of different types of alloys that are susceptible to variations in plasma conditions. It will help in the understanding of the dynamics of spectral line emissions from laser induced plasma and selection of lines to determine plasma parameters. The choice of metal alloys purities in this experiment is important to get the knowledge of the composition of the elements in the targeted sample based on different purities. This method is remarkably useful for the industries in the interest of removing the foreign or contaminating substances to get the optimum production of the output required.

2. Experimental

![Figure 1. Schematic of LIBS experimental setup](image-url)
Figure 1 shows the schematic diagram of LIBS experimental setup to generate laser induces plasma of alloy samples and capture the optical emissions using optical spectrometer. The experiments were conducted in air. Firstly, the focusing lens is cleaned using the propanol. This step is to make sure the lens is clean and free from dust. The apparatus setup is prepared as in figure 3.2.1. Nd:YAG laser (1064nm, 6ns), operating at fundamental harmonic is directed at 90\(^\circ\) on alloy sample surface using plano-convex lens with focal length (10 cm). The lens position is optimized and readjusted to attain the best focusing. The target sample is placed on translation stage to expose the fresh position of target material and avoid crater. The environmental air is kept ambient. Radiations emitted from plasma are collected via collecting lens attached in front of a 600\(\mu\)m core diameter attached to Ocean Optics MayaPro spectrometer. Optical emission spectra rom plasma is collected in the direction parallel to the target surface.

For each and every alloy samples, the samples undergo at least five laser shot before the real shot. This step is to ensure dust and any contamination on the surface of the samples is totally penetrated. Only the elements contained inside the samples themselves are taken into account in the LIBS spectra. Each sample of the three alloys of different purity is exposed at one specific distinct spot on the surface to five laser shots. For each laser shot an emission spectrum from the plasma is recorded on the computer. Origin software was used to analyzed the spectra of laser induced plasma spectroscopy. Dataset with many variables will tend to measure the same driving principle governing the system. In the experiment, there are five different purities of 75%, 80%, 85%, 90% and 95% of three different alloys of Al, Brass and Cu. Even though the purities are different, the major element of each samples shows the overlapping content. This concept makes it relevant to apply the principle component analysis to group the dataset according to the family.

3. Result and discussion

Identification of lines is done by matching the spectral lines and relative intensities with the NIST atomic spectral database (https://www.nist.gov/pml/atomic-spectra-database) and data published in literature. The wavelength range for all LIBS spectra are starting at 200 nm in the ultraviolet (UV) and extending into the near-infrared (NIR) to 700 nm. Based on the graphs of all spectra, the high intensity spectral lines can be observed in the range in between 250nm and 600nm. The major peaks with high intensity value represent the major element contained in the samples. Several obvious peaks are observed that give indication of the presence of Aluminium, Brass and Copper even though the samples come from different purities.

![Figure 2. Optical emission of sample 1 Aluminium alloy](image-url)
For Aluminium, the wavelengths of the four major peaks from five samples value are quite close to the value of Al II provided by the NIST which are 280.1178nm and 308.8516 nm. Figure 2 give an example of the optical emission of LIBS spectra of sample 1 of Aluminium with several obvious peaks around the wavelengths at 279.47nm, 308.91nm, 393.94nm and 395.93nm. For Brass, the wavelengths of the five major peaks from five samples value are quite close to the value of Cu I provided by the NIST which is 521.8202nm. It is proven that the major peak gives meaning that the Cu is among the major element contained in the Brass samples. For Copper, the wavelengths of the three major peaks from five samples value are quite close to the value of Cu I provided by the NIST which is 521.8202nm.

![Principle Component Scatter Plot in two dimensional](image)

**Figure 3.** Principle Component Scatter Plot in two dimensional

75 samples in which 25 samples comes from each types of alloys are transformed into principle component (PCs). The principle component scatter plot was executed to display the variation among the three types of alloy samples. The 2 PCs explained the variations of the spectra as well as their scores. For one spectrum will produce one point on the score plot. Apparent clustering can be noticed from the figure 3 where there is an obvious difference between three groups of alloy samples. Al, Brass and Cu from different purifications are grouping into their family of major element. This is a proof that is relevant to show the effectiveness of PCA technique in discriminate group differences into their constituent major elements.
Figure 4. Principle Component Scatter Plot in three dimensional

PCA had compressed the variance of the LIBS spectra into three PCs showing the score plot of the three PCs in three dimensional view. It can be seen points of LIBS spectra were clustered in three group. It draws a clear boundary between the different types of samples.

4. Conclusion

Based on the LIBS spectra, the wavelengths of the major peaks have been identified. The wavelengths of the peak with high intensities are then being compared to the NIST data spectral database to identify the elements contained within the samples. PCA analysis then being carried out to the LIBS spectra. Three obvious clusters were observed and the clusters were analysed. Results demonstrated that LIBS-PCA is a combined technique applicable in distinguishing the samples according to the different variables contained within the studied samples. LIBS-PCA is a relevant technique to be used to identify the composition of the elements without consuming too much money and time.

References
[1] R J Lasheras, C Bello-Galvez, E M Roriguez-Celis and J Anzano 2011 Discrimination of organic solid materials by LIBS using methods of correlation and normalized coordinates. Journal of hazardous materials 192(2) 704-713
[2] E R Runge, R W Minck and F R Bryan 1964 Spectrochim. Acta. 20B 73323.
[3] Noll R 2006 Terms and notations for laser-induced breakdown spectroscopy. Analytical and bioanalytical chemistry 385(2) 214-218
[4] J D Winefordner, I B Gornushkin, T Correll, E Gibb, B W Smith and N Omenetto 2004 Comparing several atomic spectrometric methods to the super stars: special emphasis on laser induced breakdown spectrometry, LIBS, a future super star. Journal of Analytical Atomic Spectrometry 19(9) 1061–1083
[5] B Kearton and Y Mattley 2008 Laser-induced breakdown spectroscopy: sparking new applications. Nature Photonics 2(9) 537–540
[6] Jolliffe I T 2002 Principal Component Analysis. New York: Springer
[7] Martin M Z, Labbé N, Rials T G and Wullschleger S D 2005 Analysis of preservative-treated wood by multivariate analysis of laser-induced breakdown spectroscopy spectra. Spectrochim. Acta B 60 1179–1185
Zhang T, et. al. 201 Quantitative and classification analysis of slag samples by Laser-induced breakdown spectroscopy (LIBS) coupled with support vector machine (SVM) and partial least square (PLS) methods. *J. Anal. Atom. Spectrom* **30** 368–374

Sirven J B, et. Al. 2007 Feasibility study of rock identification at the surface of Mars by remote laser-induced breakdown spectroscopy and three chemometric methods. *J. Anal. At. Spectrom* **22** 1471–1480