الكشف عن أثر العناصر في المعادن باستخدام مطيفافية الانهيار المستحث بالليزر (LIBS)

Detection Of Trace Elements In Metals By LIBS

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الملخص

تتبع العنصر هو عبارة عن عنصر كيميائي يظهر بكميات قليلة في عينة أو بيئة معينة. الكروم، الكوبالت، النحاس، الحديد، المنجنيز، المغنيسيوم، الزنك والعناصر الأخرى التي توجد بكميات صغيرة جدًا كمكونات للكائنات الحية، ضرورية لنموها وتطورها وصحتها وقد تم هذا العمل للكشف عن العناصر باستخدام مطيافية الانهيار المستحث بالليزر (LIBS).

كلمات مفتاحية: التتبع، العناصر، الليزر، التحليل والطيف.

Abstract

Trace Element is a chemical element that presents only in minor amounts in a particular sample or an environment. Chromium, cobalt, copper, iron, manganese, magnesium, zinc, and other elements that occur in very small amounts as constituents of living organisms, are necessary for their growth, development, and health.

This work has been done to detect elements by using laser induced breakdown spectroscopy (LIBS).

Keyword: Trace, Elements, Laser, Spectroscopy& LIBS.

INTRODUCTION

Laser spectroscopy is a main and essential method for realization and breaking down sub atomic, atomic pieces. Mechanical improvements in lasers, spectrometers and identifiers had constructive outcomes on the spectroscopy. Laser sources like pulse lasers, color lasers, and tunable lasers have expanded phantom determination. A semi-traditional way to deal with outflow and retention wonders gives an approach to realize laser spectroscopic methods.

LIBS is a kind of atomic emission spectroscopy which uses a highly energetic laser pulse as the excitation source. The laser is focused to form a plasma that atomizes and excites samples. The principle of LIBS is analyzing any matter in any case of its physical state, whether solid, liquid or gas. As known any element emits light of characteristic frequencies when excited to sufficiently high temperatures, LIBS can detect any element, limited only by the power of the laser as well as the sensitivity and wavelength range of the spectrograph and the detector. If we know the constituents of a material to be analyzed, LIBS also used to evaluate the relative abundance of each constituent element, or to monitor the presence of impurities.

LIBS is a technique that operates by focusing the laser onto a small area at the surface of the sample; when the laser is discharged it ablates a very small amount of material in the range of nano to pico grams. LIBS is an experimental atomic emission spectroscopy (AES) technique that uses a laser to create a plasma source. Since the plasma is created by focused optical radiation, the technique has many benefits, compared to other conventional AES techniques[1]. Technically LIBS is very similar to a number of other laser-based analytical techniques, sharing a lot of the same hardware. These techniques are the vibrational spectroscopic technique of Raman spectroscopy, and the fluorescence spectroscopic technique of laser induced fluorescence (LIF). Actually devices are being manufactured which combine these techniques in a single instrument, allowing the atomic, molecular and structural characterization of a sample as well as giving a deeper insight into physical properties. The LIBS technique is useful for a variety of applications including elemental analysis, detecting airborne biological agents, quantitative analysis of aerosols, etc[2].In LIBS, a pulsed laser with high peak power illuminates a sample. The beam is focused into a small analysis spot. In this spot, material from the sample is ablated, forming a cloud of nanoparticles above a small crater in the sample. Due to the peak energy of the laser beam, absorption and multi photon ionization results in increasing opacity in the gas and aerosol cloud above the sample, even during the short laser pulse. The plasma forms as laser energy is increasingly absorbed in that cloud. The plasma melts the nanoparticles and excites atomic emission. The emission is dispersed onto a detector and we interpret the spectrum that can simultaneously tell us about the presence of multiple elements.

Laser Induced Breakdown Spectroscopy is a direct elemental analysis method which provides rapid results. A tightly focused pulsed laser ablates material at the laser's focal point, and forms an analytical plasma which is the source for elemental analysis.

LIBS is a laser diagnostics, where a laser beam focused onto a material produces transient high density plasma as the laser intensity exceeds the breakdown threshold of the material. First used of LIBS was for the determination of elemental composition of materials in the form of gases, liquids and solids during 1960's.

Research on LIBS has been continued to grow and reached a peak around 1980 and field portable gadgets capable of in situ and real time analysis of samples have been developed in recent years with the availability of reliable, smaller and less costly laser systems along with sensitive optical detectors, like the intensified charge coupled device (ICCD).[3]

In all LIBS experiments the delay time, time interval between the arrival of the laser pulse on the sample and activation of the detector, is to be optimized so as to minimize the background noise because of continuum emission and maximize the emission intensity of the spectral line of interest. In general the background noise is negligible after the delay time of about 0.1µs or less while the intensity of most of the neutral atom spectral lines is maximum in 0.1 to 2.0 µs range have observed that the RSTD is almost constant in 0.1 to 2 µs range while it increases from 5.5% to 14% when the delay time is changed from 2 µs to 4 µs. The increase in RSTD at higher delay times is as result of decrease in signal to noise ratio resulting from the decrease in emission intensity with increase in delay time[4],[5]. Different types of LIBS experimental set up have been used which differ fundamentally in the form of collection optics for the radiation emitted by the plasma plume. In one of the arrangements the emission from plasma is collected in the direction perpendicular to the direction of the incident laser. Additionally, the difficulties of alignment and reduced sensitivity the collected emission exhibits spatial dependence leading to loss of spectral information about emission from the whole plasma plume. These shortcomings are removed in another arrangement where focusing lens itself acts as the collecting lens for the plasma emission. Plasma temperature and electron number density can be estimated from the continuum emission and peak width of atomic and ionic emission lines.

Experimental part

2.1 Sample preparation

The principle of my work is tracing elements in metals, so we bring an alloy and started work to analyse and detect the elements in this alloy.

2.2 LIBS setup

In this experiment we used ND YAG laser 1046 nm , spectrometer with 5 channels, broad band mirror 1046 nm , cooling laser head power supply, delay generator, lenses 10 cm, and computer. First, we bring the alloy and began our experiment by using LIBS. Data analysis software was used to analyse the signals and collect the data. Then we used excel to do calculations and compared the results with NIST Atomic Spectra Database to make sure what are the elements.

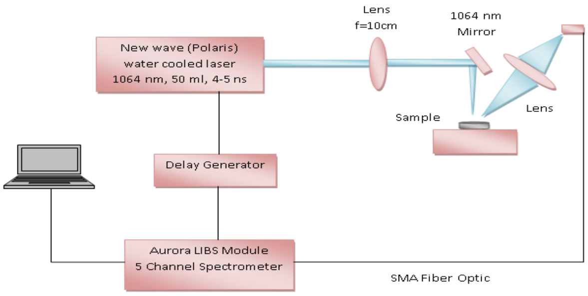

fig (2.1). LIBS experimental setup

Results and Discussion

In this experiment, we used three delay times 0.1, 0.3 and 0.5 µs, also 20, 30 and 40 mJ of power. The alloy was moved in to three locations to get the best data of the alloy, the frequency was 10 hz and 50 shots every time.

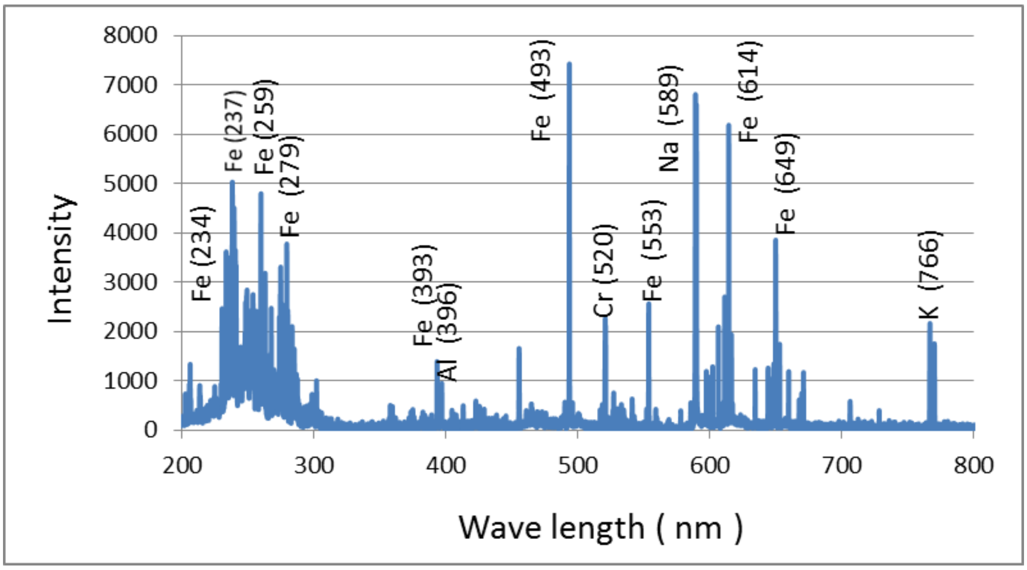

fig (3.1). LIBS spectra for the sample (alloy)

Measurements has been taken with 0,1 µs time delay, and power of 20 mJ, with frequency 10 hz, and 50 shots, then we have moved the alloy in three locations, and we got the following results as shown in the following figures. We found several spectrums of Iron: Fe 234, Fe 237, Fe 259, Fe 279, Fe 393, Fe 493, Fe 553, Fe 614 and Fe 649 in addition to Aluminum (Al396), Chromium (Cr 520), Sodium (Na589), and Potassium (K766). We choose Iron(Fe 259) because it is the highest value of intensity.

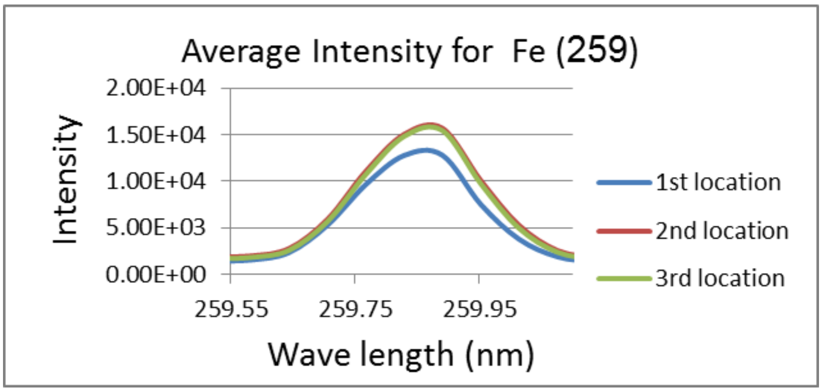

fig (3.2). Average Intensity for Fe (259)

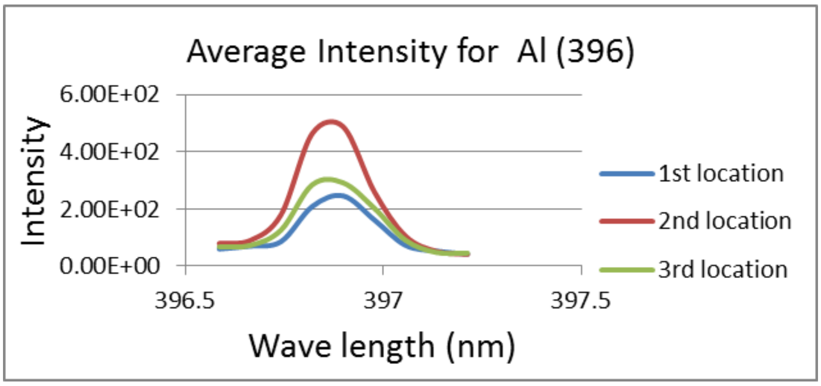

fig (3.3). Average Intensity for Al (396)

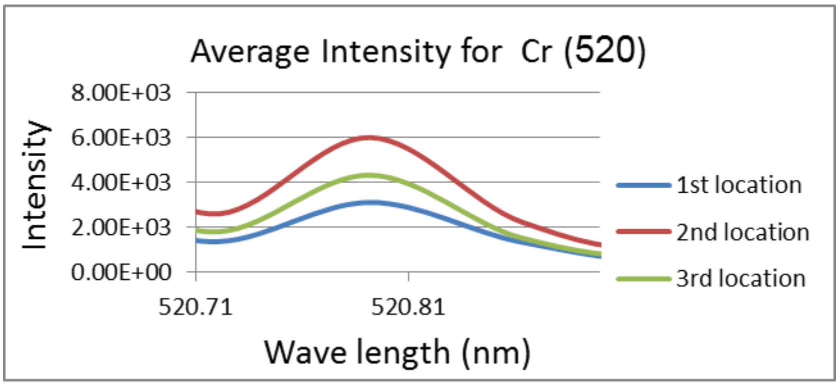

fig (3.4). Average Intensity for Cr (520)

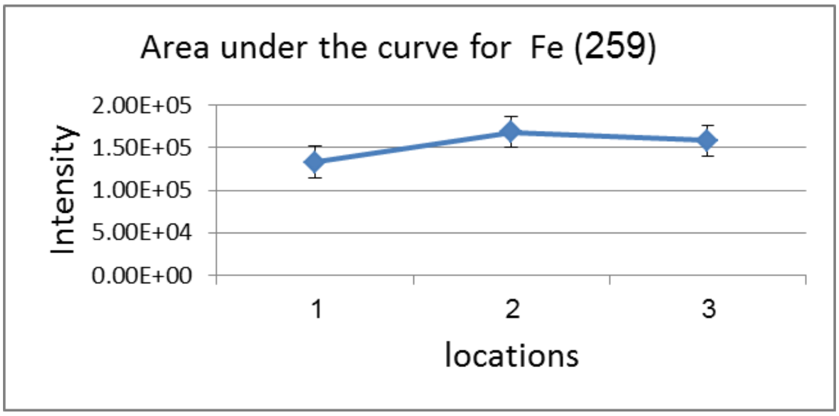

fig (3.5). Area under the curve for Fe (259)

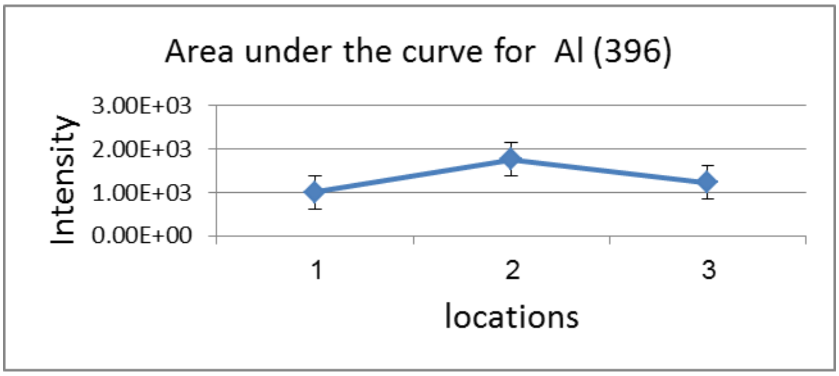

fig (3.6). Area under the curve for Al (396)

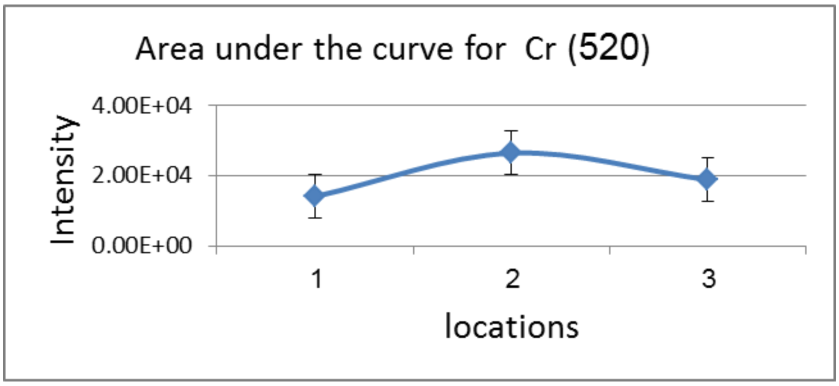

fig (3.7). Area under the curve for Cr (520)

After that we used 0,1 µs time delay, and power of 30 mJ, with frequency 10 hz, and 50 shots, then we have collected the data from the alloy in three locations, and we got the following results as shown in the following figures.

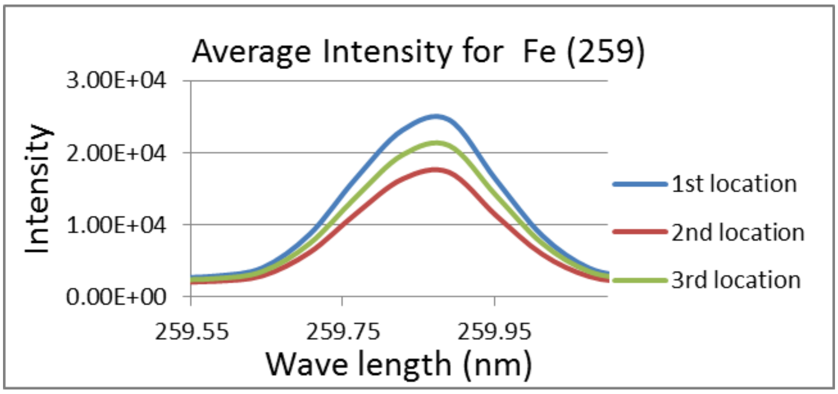

fig (3.8). Average Intensity for Fe (259)

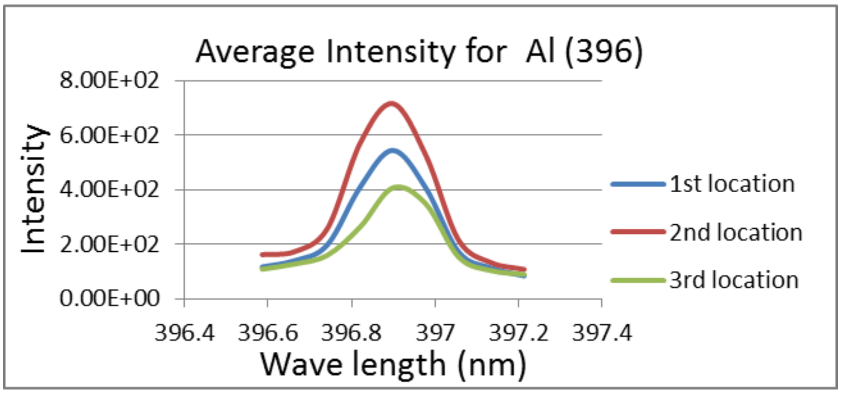

fig (3.9). Average Intensity for Al (396)

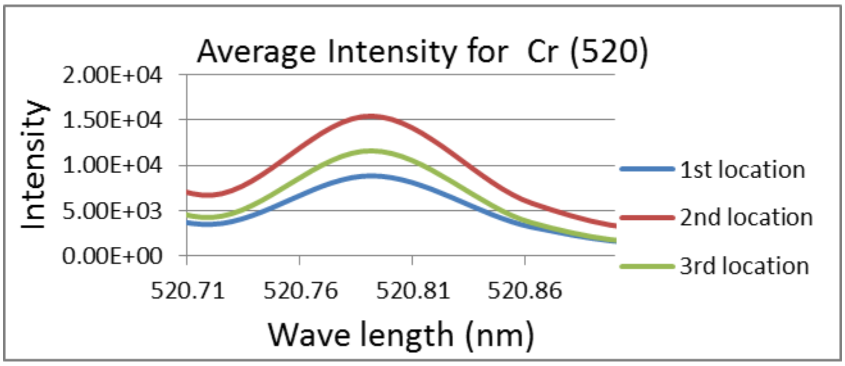

fig (3.10). Average Intensity for Cr (520)

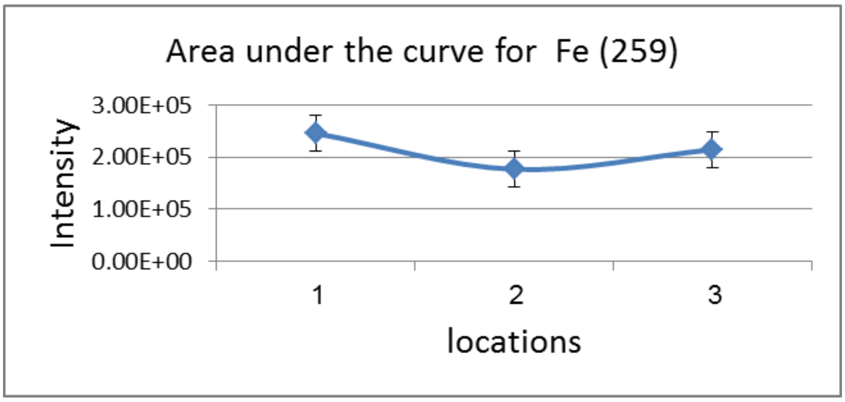

fig (3.11). Area under the curve for Fe (259)

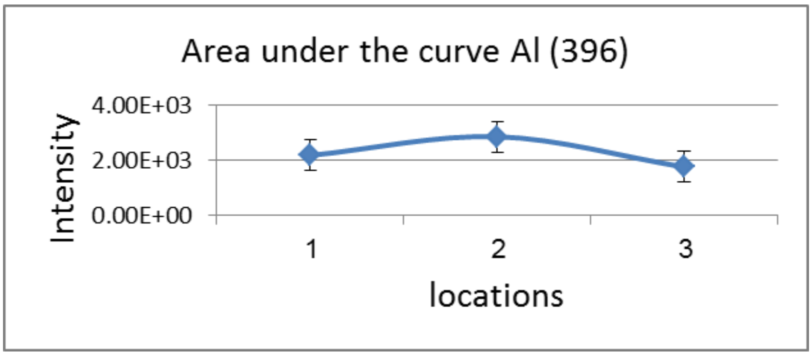

fig (3.12). Area under the curve for Al (396)

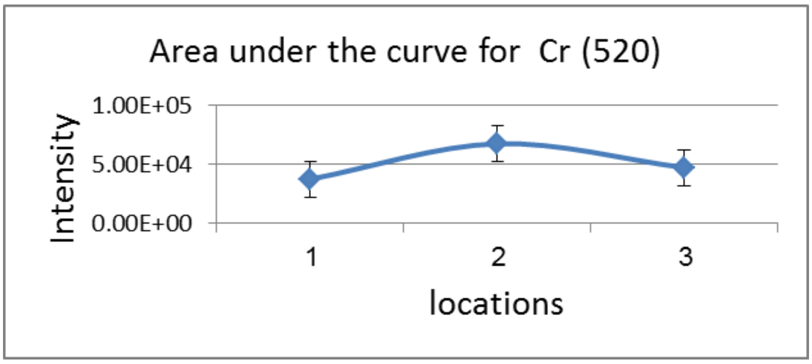

fig (3.13). Area under the curve for Cr (520)

After that we have used 0,1 µs time delay, and power of 40 mJ, with frequency 10 hz, and 50 shots, then we have moved the alloy in three locations, and we got the following results as shown in the following figures.

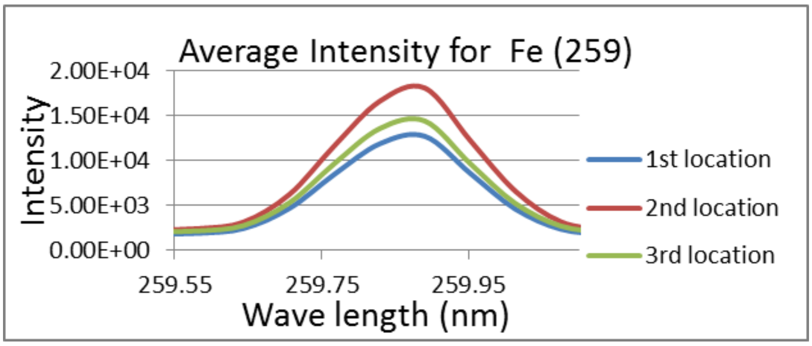

fig (3.14). Average Intensity for Fe (259)

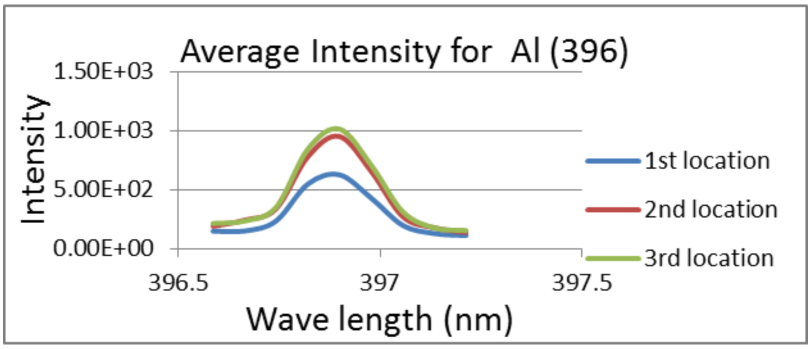

fig (3.15). Average Intensity for Al (396)

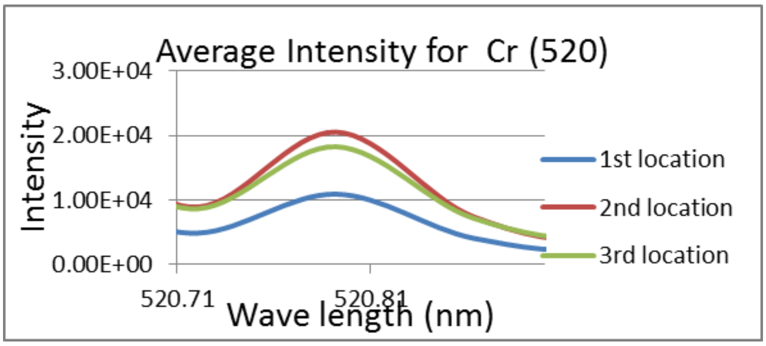

fig (3.16). Average Intensity for Cr (520)

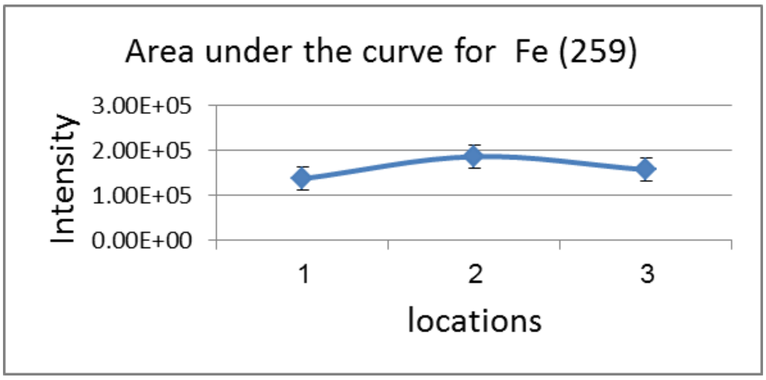

fig (3.17). Area under the curve for Fe (259)

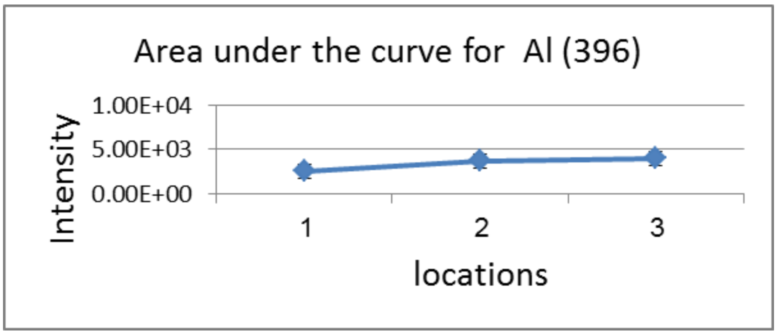

fig (3.18). Area under the curve for Al (396)

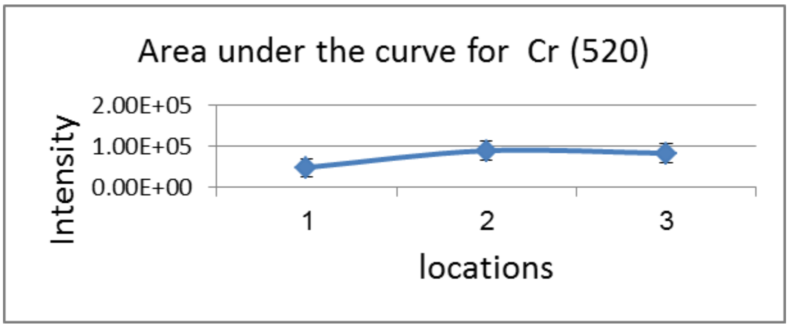

fig (3.19). Area under the curve for Cr (520)

After that we used 0,3 μs time delay, and power of 20 mJ, with frequency 10 hz, and 50 shots, then we have moved the alloy in three locations, and we got the following results as shown in the following figures.

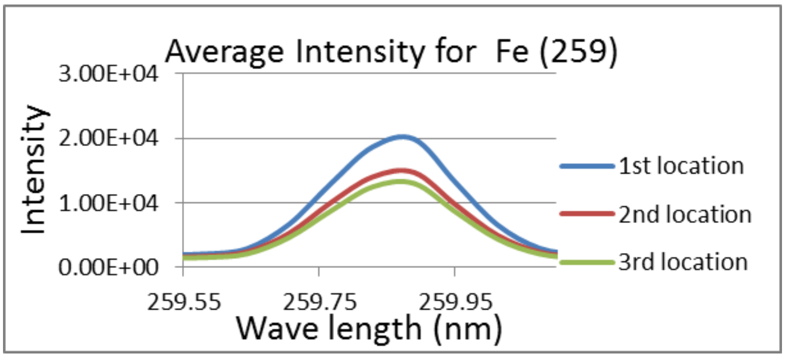

fig (3.20). Average Intensity for Fe (259)

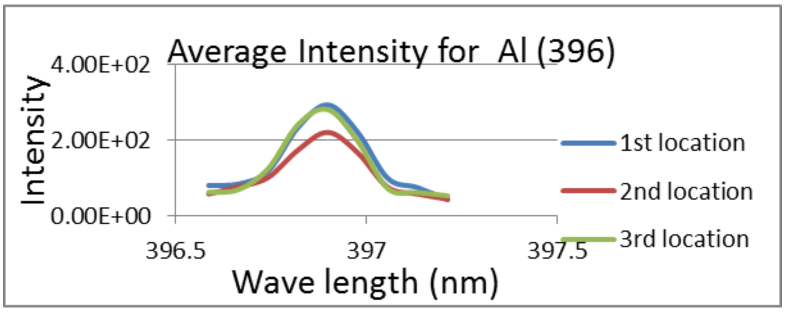

fig (3.21). Average Intensity for Al (396)

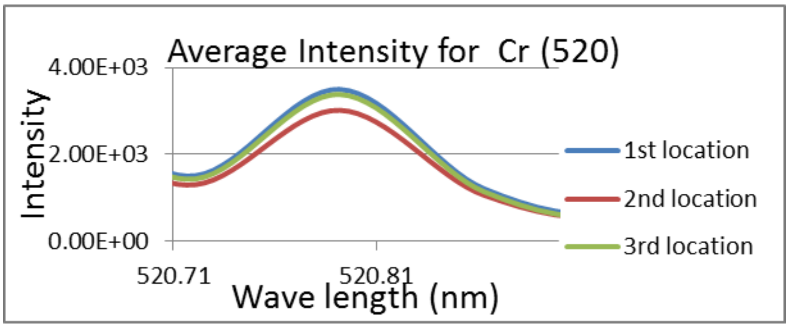

fig (3.22). Average Intensity for Cr (520)

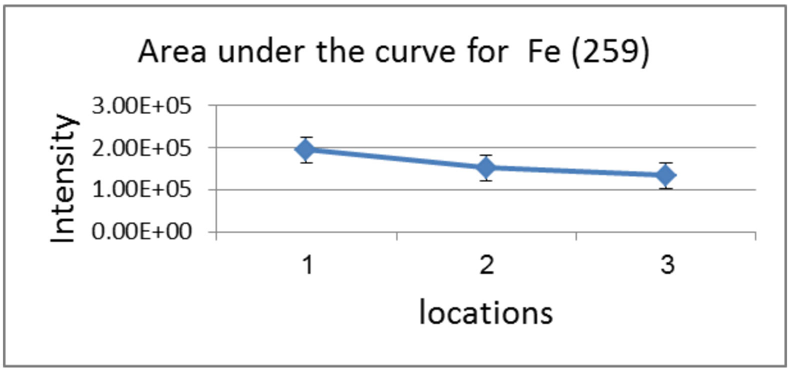

fig (3.23). Area under the curve for Fe (259)

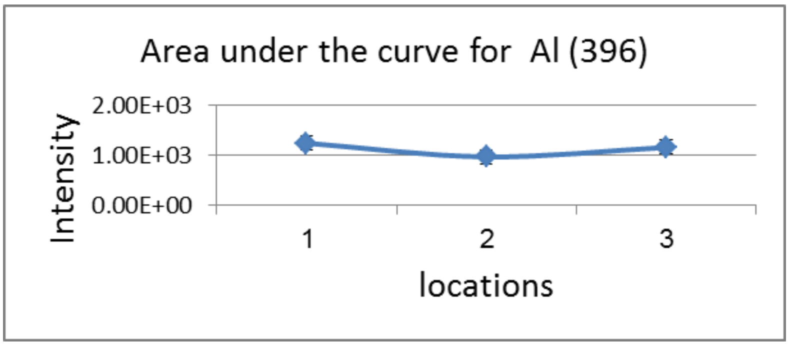

fig (3.24). Area under the curve for Al (396)

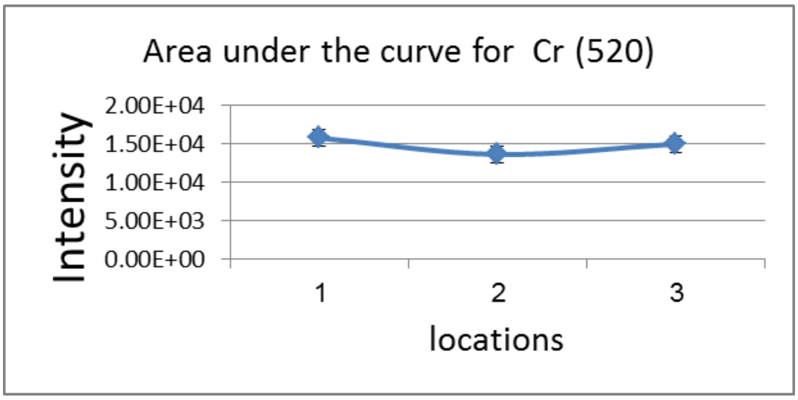

fig (3.25). Area under the curve for Cr (520)

After that we used 0,3 µs time delay, and power of 30 mJ, with frequency 10 hz, and 50 shots, then we have moved the alloy in three locations, and we got the following results as shown in the following figures.

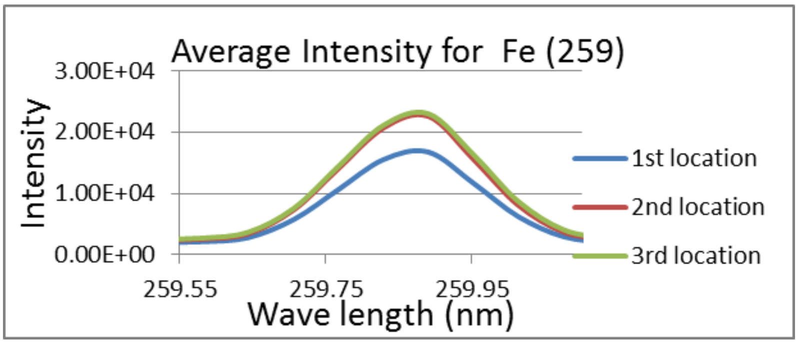

fig (3.26). Average Intensity for Fe (259)

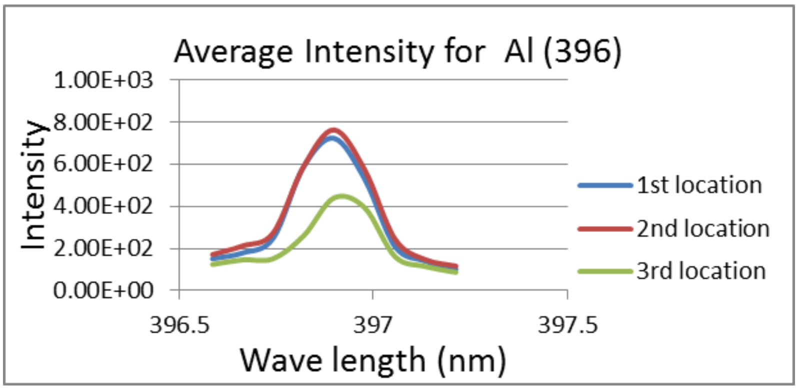

fig (3.27). Average Intensity for Al (396)

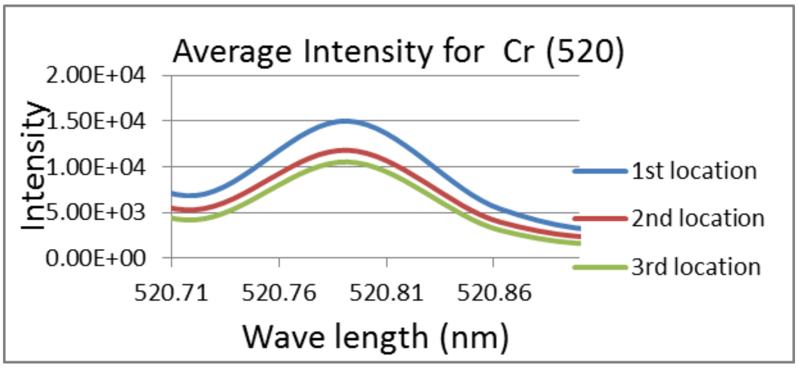

fig (3.28). Average Intensity for Cr (520)

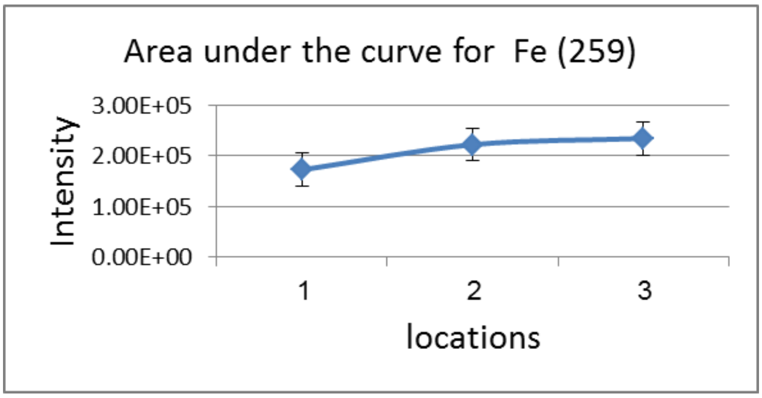

fig (3.29). Area under the curve for Fe (259)

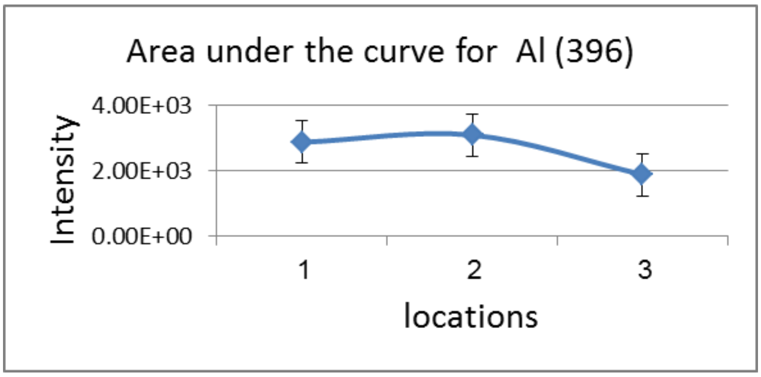

fig (3.30). Area under the curve for Al (396)

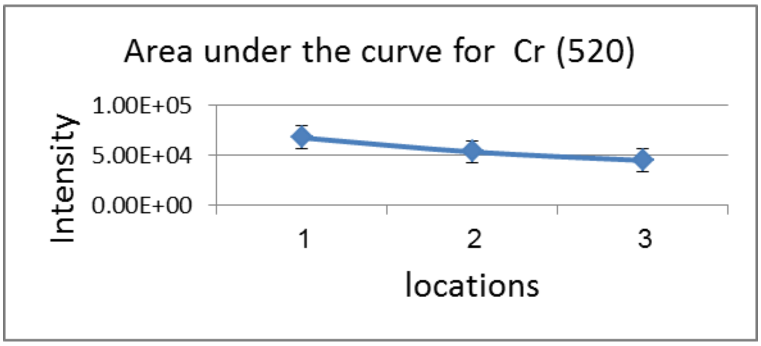

fig (3.31). Area under the curve for Cr (520)

After that we used 0,3 µs time delay, and power of 40 mJ, with frequency 10 hz, and 50 shots, then we have moved the alloy in three locations, and we got the following results as shown in the following figures.

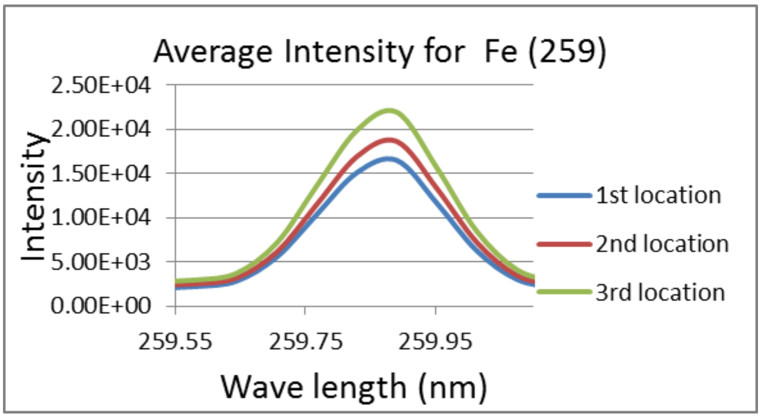

fig (3.32). Average Intensity for Fe (259)

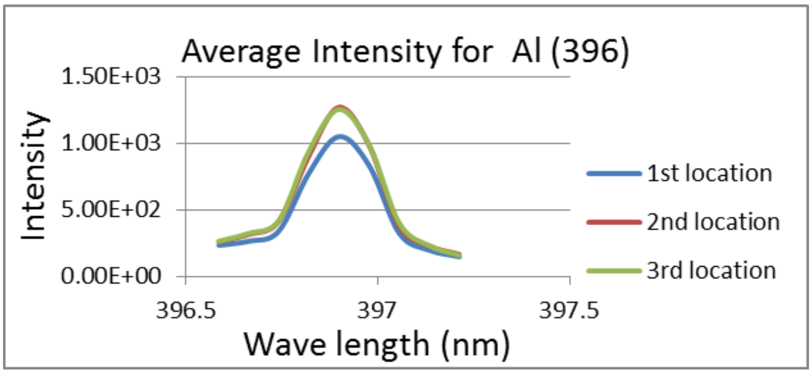

fig (3.33). Average Intensity for Al (396)

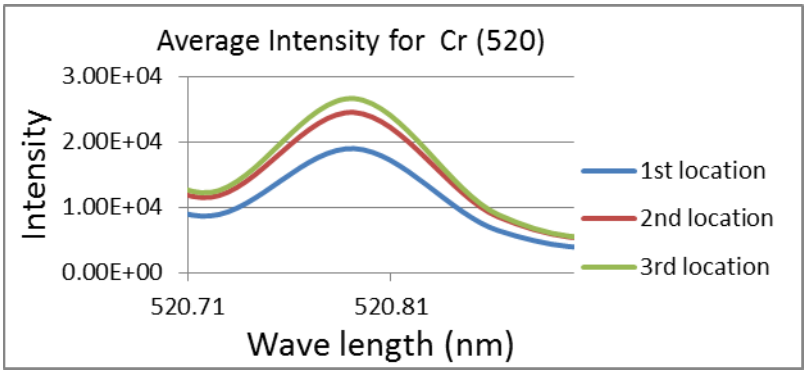

fig (3.34). Average Intensity for Cr (520)

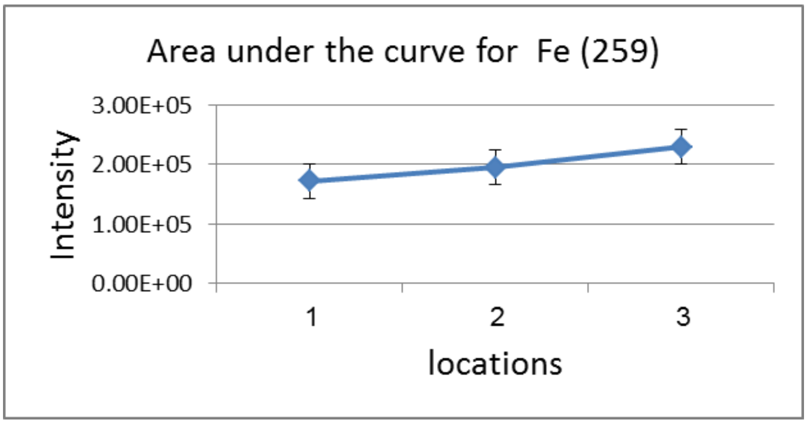

fig (3.35). Area under the curve for Fe (259)

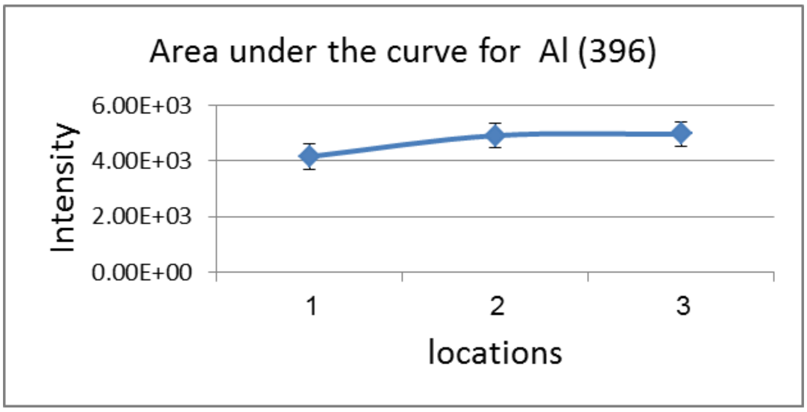

fig (3.36). Area under the curve for Al (396)

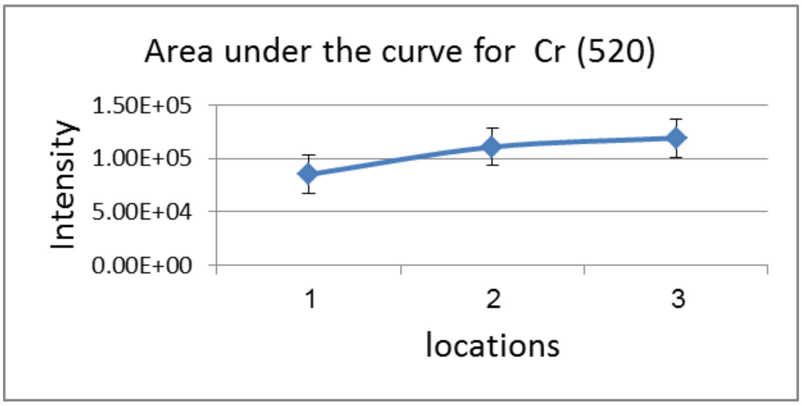

fig (3.37). Area under the curve for Cr (520)

After that we used 0,5 μs time delay, and power of 20 mJ, with frequency 10 hz, and 50 shots, then we have moved the alloy in three locations, and we got the following results as shown in the following figures.

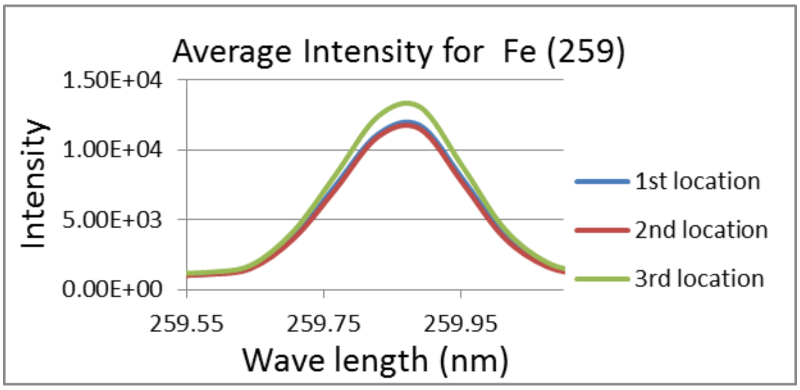

fig (3.38). Average Intensity for Fe (259)

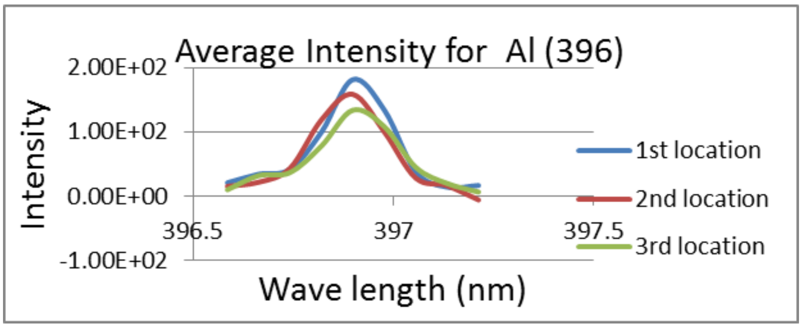

fig (3.39). Average Intensity for Al (396)

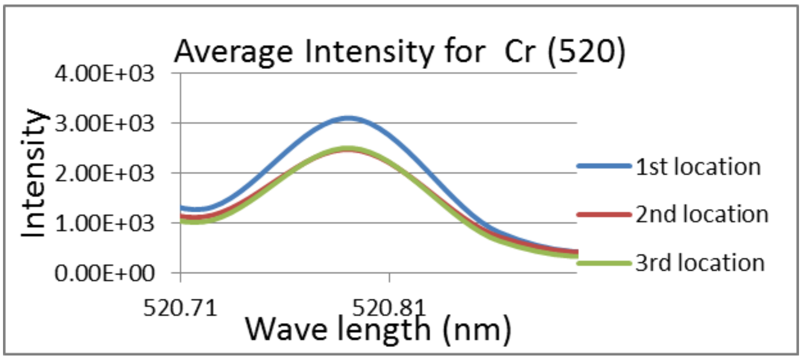

fig (3.40). Average Intensity for Cr (520)

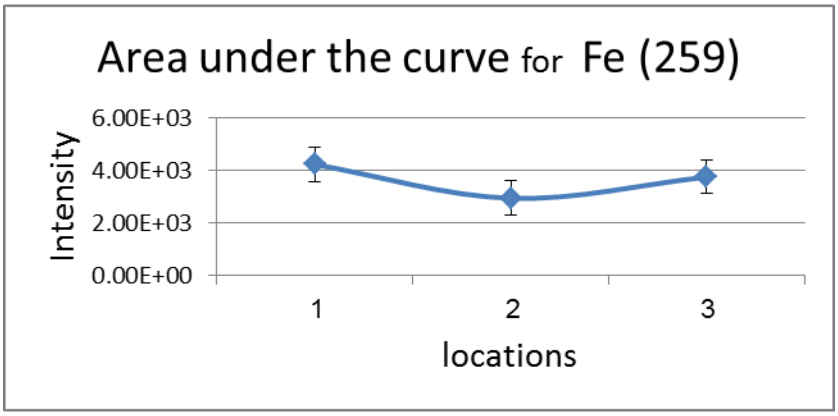

fig (3.41). Area under the curve for Fe (259)

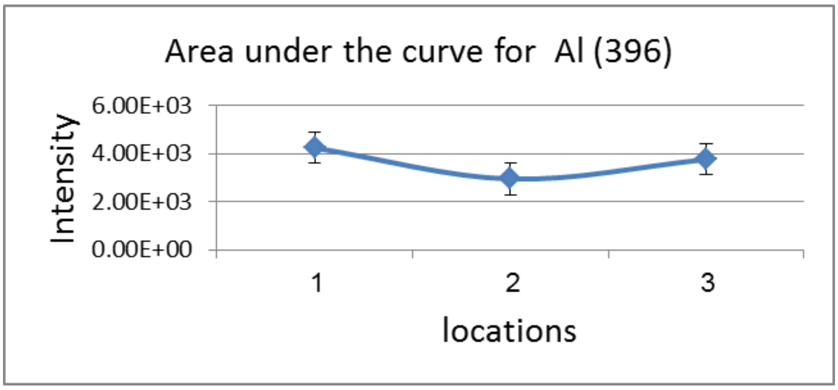

fig (3.42). Area under the curve for Al (396)

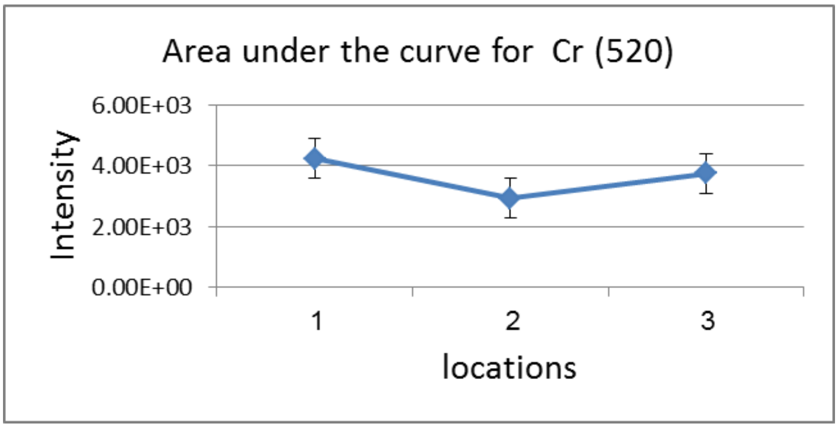

fig (3.43). Area under the curve for Cr (520)

After that we used 0,5 μs time delay, and power of 30 mJ, with frequency 10 hz, and 50 shots, then we have moved the alloy in three locations, and we got the following results as shown in the following figures.

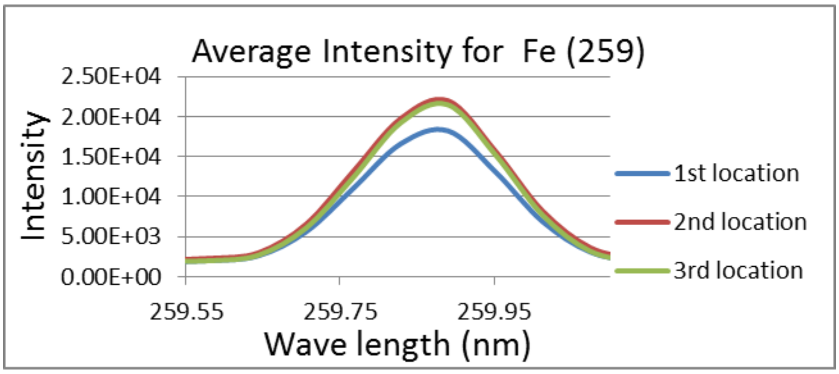

fig (3.44). Average Intensity for Fe (259)

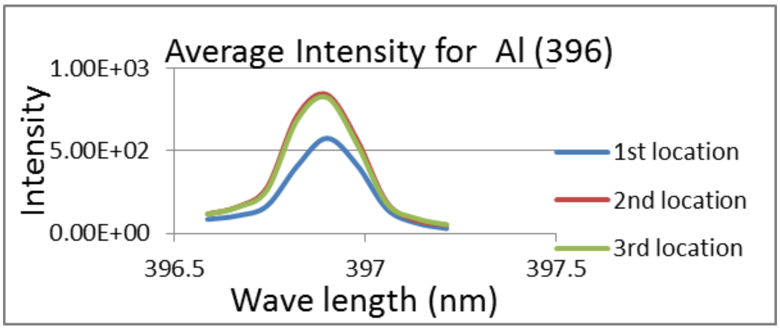

fig (3.45). Average Intensity for Al (396)

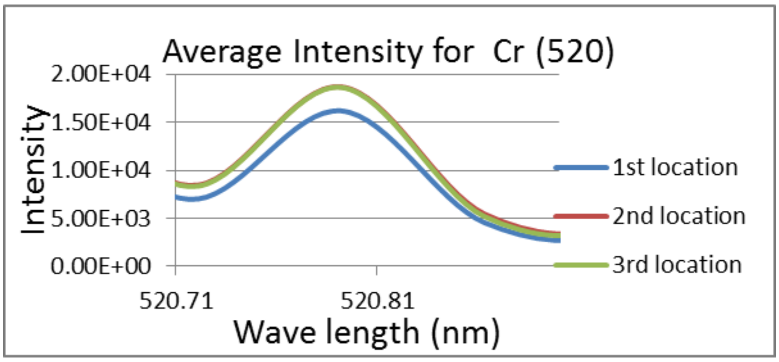

fig (3.46). Average Intensity for Cr (520)

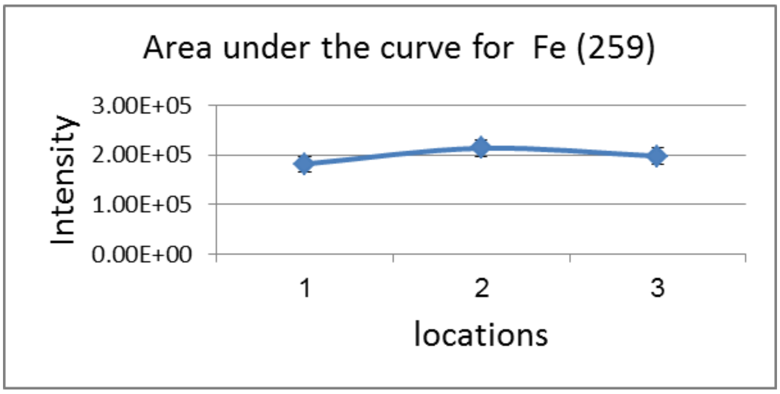

fig (3.47). Area under the curve for Fe (259)

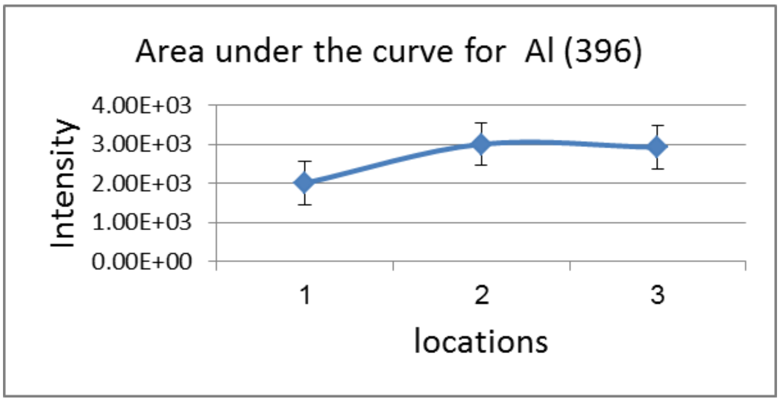

fig (3.48). Area under the curve for Al (396)

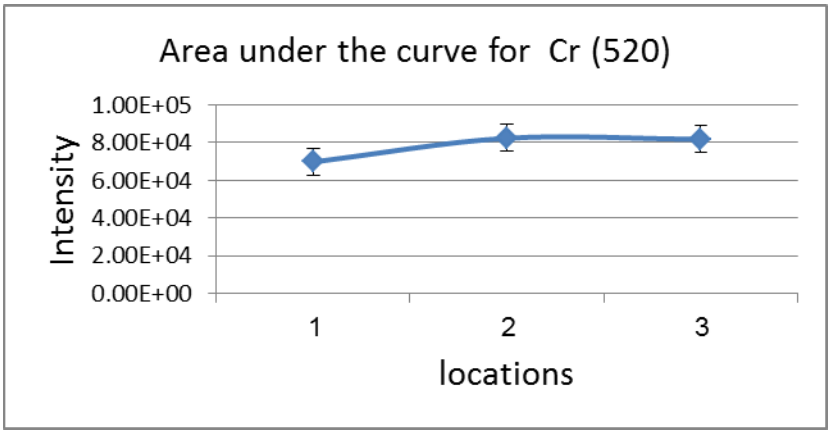

fig (3.49). Area under the curve for Cr (520)

Finally we used 0,5 µs time delay, and power of 40 mJ, with frequency 10 hz, and 50 shots, then we have moved the alloy in three locations, and we got the following results as shown in the following figures.

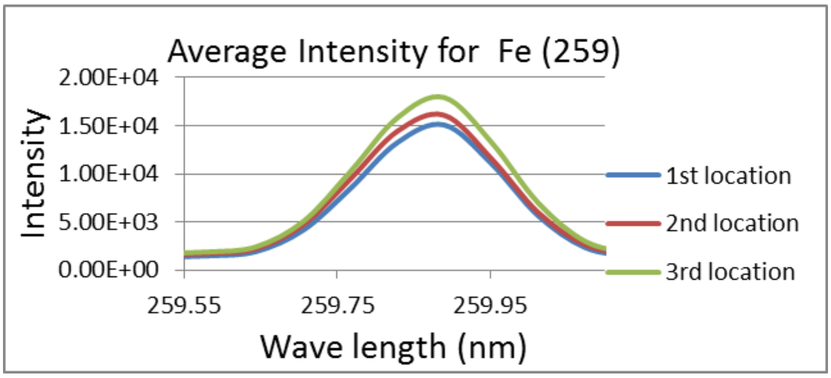

fig (3.50). Average Intensity for Fe (259)

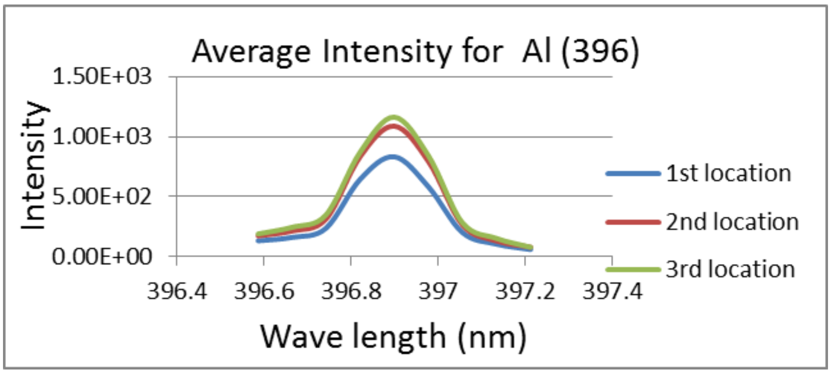

fig (3.51). Average Intensity for Al (396)

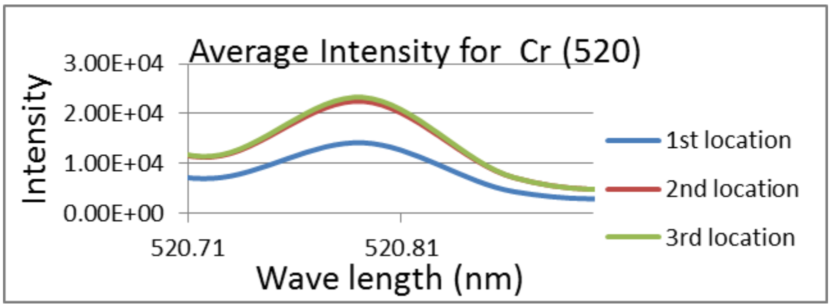

fig (3.52). Average Intensity for Cr (520)

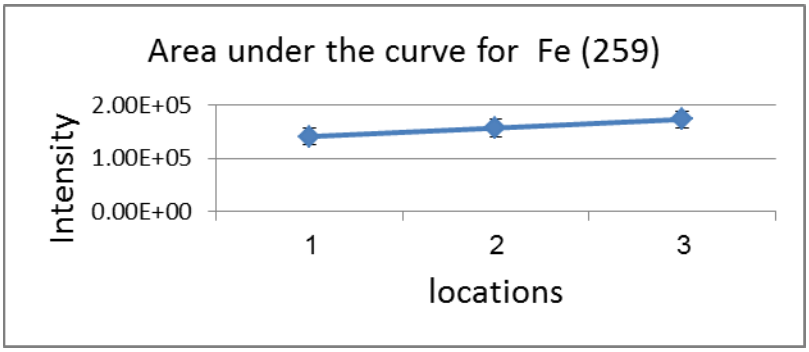

fig (3.53). Area under the curve for Fe (259)

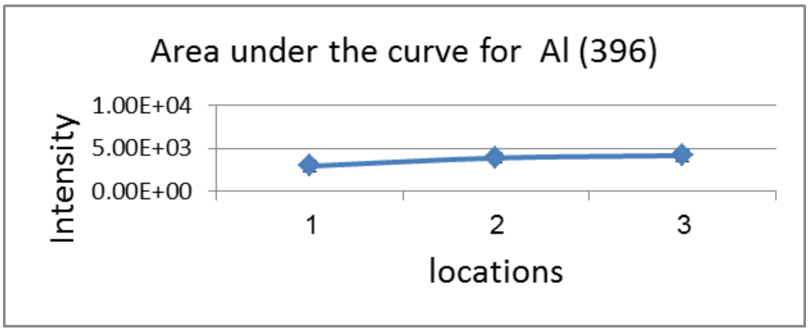

fig (3.54). Area under the curve for Al (396)

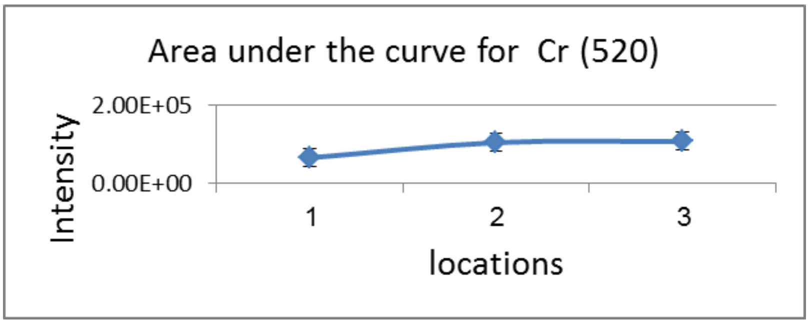

fig (3.55). Area under the curve for Cr (520)

CONCLUSION

LIBS was used in this research for Detection of Trace Elements in Metals. The set up for LIBS was done by analyzing an alloy to do the experiment. After we have done all the steps, we got the results and detect the elements in this alloy. The elements were Iron (Fe) (about 70 % of this alloy), and the other elements were Chromium (Cr), Sodium (Na), Aluminum (Al), and Potassium (K).

We noticed that we got different data when we used three delay times 0.1, 0.3 and 0.5 µs, also 20, 30 and 40 mJ of power. Finally, we have collected data from the alloy in to three locations; the frequency was 10 hz and 50 shots every time. We did all that to see and to get best data and compare the results for each case. We did the calculation by means of average intensity and area under the curve. We found some curves abnormal as result of some elements are not homogeneous. Also we calculated the standard error deviations for area under the curve for all of them. The standard error deviation was different in these curves, it depends on the dispersed of values from the average value or the mean. These calculations were important to analyze the data which we took from data analysis software and calculated by excel to detect the elements.

In this research we found on two elements potassium and sodium which are strange to find in this alloy with iron and aluminum and chromium, we referred that they came by hand touching.

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