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Application of Laser Induced Breakdown Spectroscopy as an Alternative Method for Identification of Quality of Gold Alloys

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Abstract

In this study a robust and alternative method of gold quality identification is presented. Four different Karats of gold from different origins were used for investigation. Comparison was made between the traditional Quantum Karat meter and Laser Induced Breakdown spectra to compare their quality. The advantage of the new technique over the Karat meter is that the different types of impurities that are found in the gold were clearly identified and their quantities/percentage tabulated. The method is also robust in such a way that it is calibration free. During the experiment, the most resonant atomic line and ionic line of emission of gold were taken at 267.597 nm and at 226.363nm, respectively, in order to reduce the impact of the back ground on the spectral intensities. The experimental result indicated that both atomic and ionic lines of emission were found in very good agreement with Quantum Karat meter and can reliably be applied as an alternative method of quality control or in a place where such equipment is not available. It was found that the ionic to background and atomic to back ground ratios as well as their normalized intensities were in excellent match with the results from the measured quantum Karat meter.

Keywords: *Atomic line, ionic line, resonant lines, Karat meter*

1. Introduction

Different analytical methods have been employed for the quantitative determination of impurities in precious metal alloys. Some of these methods include densitometry, determination of gold content on a touchstone, cupellation, and X-ray fluorescence (XRF) [1]. Now days laser induced breakdown spectroscopic analysis of precious metals and its alloys is emerging as a key analytical tool for its rapid quantitative as well as qualitative information of the sample.

The other advantage of the method is that it does not need internal calibration which is time consuming and difficult for some samples. Calibration free laser induced breakdown spectroscopy (CF-LIBS) has been applied by different researchers in the field even though the application of the method depends on the requirement that the plasma formed during ablation must satisfy the conditions: local thermodynamic equilibrium, optically thin plasma and stoichiometric ablation of the sample [2 - 4]. In addition, these requirements of (CF-LIBS) take too much time to analyze every spectrum so that the contribution from each element in the matrix is correctly assessed. The other limitation of the above techniques is their insufficiency in identifying contributions of impurities in gold alloys in determining hardness [6].

Recently [5, 6] used low energy laser for rapid quantitative determination of base metal in gold alloys using integrated spectra from each element in the alloy. The method is different from the other LIBS techniques in that it introduced the use of the number of elements in photosensitive detector array that depends on the spectral resolution capability of spectrometer used. In the current study, integrated ionic and atomic spectra responses are compared with karat values, unlike other techniques. The purpose of this research is therefore to present an alternative, chemical free and robust method to monitor the quality of precious metals quality such as gold using only spectral analysis of LIBS spectra.

2. Materials and Methods

Pure gold and the gold alloys used in this work were purchased from different places and origin, Ethiopian and India. Pure gold (24 karat) was purchased from (India), 19.5 karat gold was purchased from Ethiopian jewelry shop and 9 karat gold was purchased from jewelry shop in Allahabad, India. XRF was taken at the jewelry shop, India, and the LIBS spectra was taken by Nd:YAG (Continuum Surelite III, USA) at second harmonic (532nm) and 10 HZ pulse repetition rate. The setup of the experiment is shown in Fig.1.

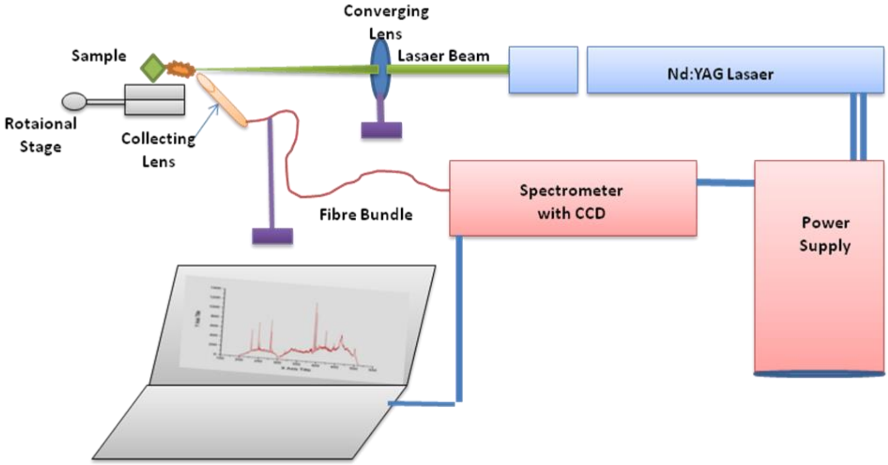

Figure 1. Sketch of the experimental set up LIBS analysis of gold alloy

The X-ray fluorescence (XRF) data was taken from the jewelry shop Using Quantum karat meter (Quantum equipment corporation LTD). Gold samples under investigation were mounted on rotational stage to scan the sample with the pulsed laser in all direction. The converging lens converges the laser beam on to the sample at the required angle and position. Spectra from the sample were collected using a collection lens that feeds to the optical fiber. The spectrometer disperses the laser beam into different wave lengths. The final emission spectra read out was collected and interpreted from a personal computer that has an Ocean Optics software which is important for analysis.

The fundamental equations for analysis of emission spectra depend on calculation of emission intensities. The following mathematical relation was applied to determine total ionic and atomic resonant line spectra to calculated integrated intensities.

$$\sum_{E=Au,Cu,Ag,Cd,Zn} \sum_{i} \sum_{k=a_i{}^E}^{b_j{}^E} \frac{I_k}{N} = C \qquad (1)$$

Where C is the number of elements in the photosensitive cells; I_k is the intensity at wave length λ_k by kth element in the photo detector and N is the normalization constant (the detail has been discussed by [6]). The normalized intensity of the emission from components of the alloy is determined using the formulas:

Applying equations (1) and (2) the total integrated intensity of all spectral lines of the pure gold and each gold alloy was calculated. In calculating the integrated intensities of the samples all the spectral lines of all the elements indicated by the X-Ray fluorescence (XRF) from Table 1 were included. Also the normalization constant in each case was calculated and finally the normalized intensity for all the elements in the samples determined. Calculation of the normalized intensities in terms of (intensity to back ground ratio) for both ionic and atomic lines of gold using their non- resonant lines was done to study relationships between these quantities and karat of gold alloys.

$$I_{Au} = \sum_{i} \sum_{k-a^{Au}{}_i}^{b^{Au}{}_j} \frac{I_k}{N}\ ,\quad I_{Ag} = \sum_{i} \sum_{a^{Ag}{}_i}^{b^{Ag}{}_j} \frac{I_k}{N}\ ,\quad I_{Cu} = \sum_{i} \sum_{a^{Cu}{}_i}^{b^{Cu}{}_j} \frac{I_k}{N},\quad I_{Zn} = \sum_{i} \sum_{a_n}^{b^{Zn}{}_j} \frac{I_k}{N},\quad I_{Cd} = \sum_{i} \sum_{a^{Cd}{}_i}^{b^{Cd}{}_j} \frac{I_k}{N} \qquad (2)$$

3. Results and Discussion

The quantum karat meter's x-ray florescence data indicated the existence of different impurities in the three gold samples while the pure gold did not show any impurity. The elements found as impurity were copper, silver, cadmium and zinc. But, there were no zinc impurity found in the sample from Ethiopia. The elemental data found by the equipment is tabulated in Table 1.

Record of LIBS spectra of each of the above pure gold and gold alloys was taken to check whether additional impurities are found in the alloys. Accordingly, lines of Calcium and Magnesium in all the alloys including the pure gold were recorded. Other impurities like iron and antimony are also found in the gold alloys.

In order to reach at meaningful conclusion intensity versus wave length at non-resonant lines for both atomic and ionic lines, karat values versus normalized intensities were analyzed. The following figures and tables indicate the results found.

Table 1. XRF results from quantum karat meter.

Origin of the gold	Karat	Percentage composition of elements				
		Au	Ag	Cu	Cd	Zn
Indian I	24	99.9	0	0	0	0
Ethiopian	19.5	81.1	7.5	10.4	0.5	0
Indian II	17.2	71.5	11.0	15.5	0.3	1.7
India III	9.2	38.4	9.1	51.1	3.0	0

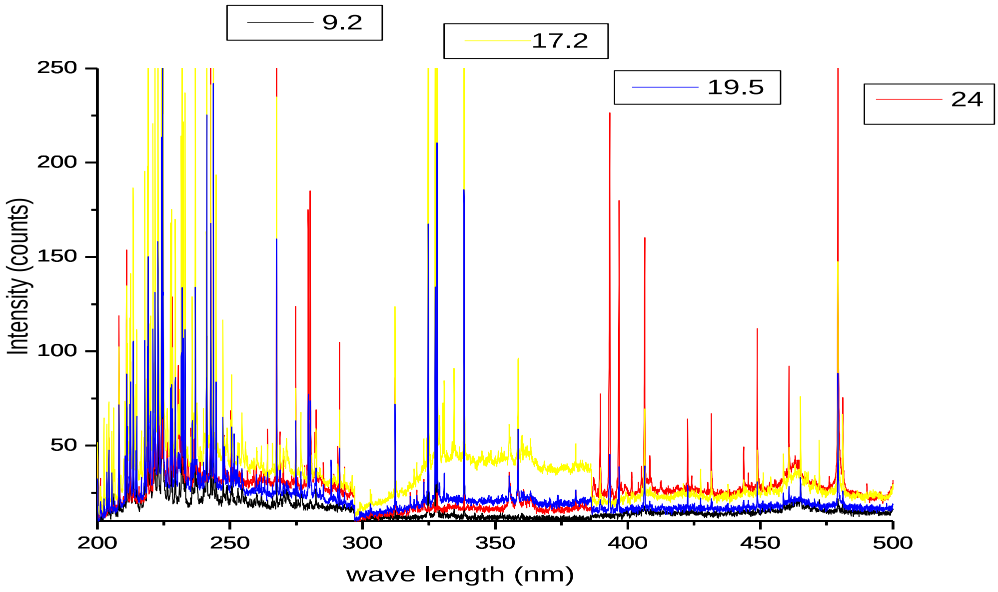

Figure 2. Emission spectra of different gold alloys

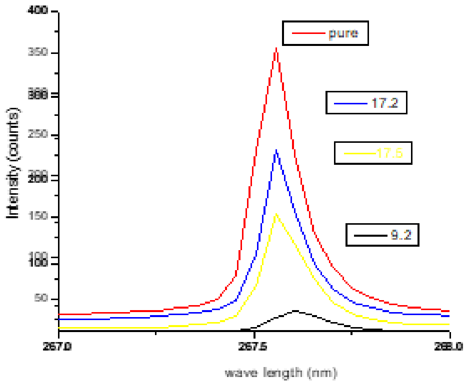

Figure 3. Intensity versus wave length of gold of different karats for atomic line 267.597 nm

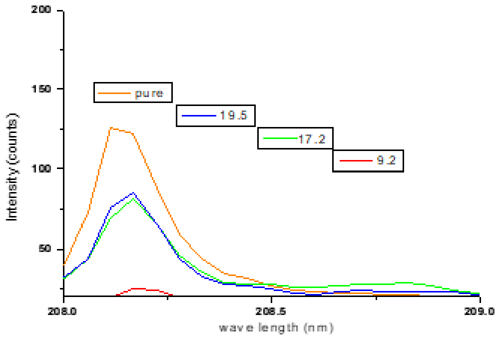

Figure 4. Intensity versus wave length of gold of different karats for ionic line 208.2 nm

Investigation of the integrated spectral intensity of ionic lines to background of gold lines revealed that the purer the gold is, the higher the ratio. The spectral intensity of the gold samples are found in good agreement with the result of the measurement from the karat meter. The gold sample with 9.2 karat, which is the least in the karat range, showed the least integrated intensity. Emission from the samples was investigated non resonant atomic and ionic lines for better resolution. Figure 4 shows the intensity versus emission wavelength at 208.2 nm.

The following tables indicate the normalized intensities, the ionic and the atomic intensities to the integrated background intensity compared to their respective Karat values for each type of gold alloy.

Table 2. Gold Karat versus corresponding ionic intensity to background ratio

Karat	Ionic to background ratio
9.2	1.3
17.2	2.6
19.5	3.0
24	3.7

Table 3. Gold Karat versus corresponding normalized intensity to background ratio

Karat	Normalized intensity (logarithmic)
9.2	1.3
17.2	2.52
19.5	2.68
24	3.31

The ratio of the integrated intensity to the background, as indicated in table 2, was also found in direct proportion with the karat value of the four gold alloys. i.e., the ratio increases with increasing value of karat. This confirms that the method employed well agrees with other measurement techniques like x-ray fluoresce for measuring karat of alloys.

As indicated in table 3 above the logarithm of all emission intensities, when divided to the background were found to increase from 1.3 to 3.31 as the value of the alloy's karat increase from 9.2 to 24. Finally, as the spectral emission lines involve both atomic and ionic lines of emission, the integrated atomic line spectral intensity was used to check whether the method employed yields similar result.

Table 4 shows the result found from the analysis. Similar to the results found in Tables 2 and Table 3 the gold alloys' karat values found from the quantum karat meter showed proportional increase from 6 to 14.26 for atomic line spectral intensity to background ratio as the gold karat values increase from 9.2 to 24 karat. The linear relationship between karat values and corresponding atomic and ionic emission intensities were used as a final proof for the current method. The results of the linear fit for karat versus normalized atomic intensity to back ground ratio and that of karat to normalized ionic intensity (logarithmic) are given in Figures 5 and Figures 6, respectively.

Table 4. Gold Karat versus corresponding atomic line intensity to background

Karat	Atomic line spectral intensity to background ratio
9.2	6
17.2	9.8
19.5	12.03
24	14.26

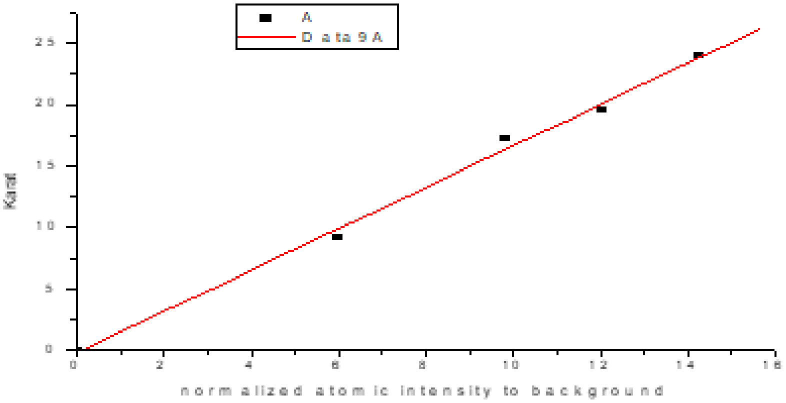

Figure 5. Karat of gold versus normalized atomic intensity

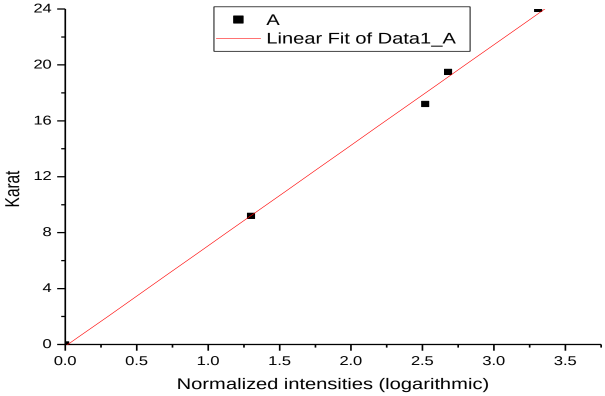

Figure 6. Karat of gold versus normalized ionic intensity

4. Conclusion

The result of the investigation clearly shows that the purity of gold can be asserted from the integrated normalized intensity of all spectra line of gold, as well as from intensity to background ratios of ionic and atomic lines. For the non-resonant atomic emission line at 267.597 nm and ionic emission line at 226.363nm for all the gold samples, it was found that there are direct linear relationships between the karat of gold and the ionic to background and atomic to back ground ratios. The value of the ratios was found to be in direct proportion with the corresponding karat values. It was also notices that gold alloys of different origin could be identified by the type of impurity.in it. The presence of zinc impurity in one type of alloy from India and its absence from that from Ethiopia is good evidence. Therefore one can conclude that the method employed by the researcher could be used as an alternative and also robust method to monitor precious metals quality such as gold.

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