Authentication of gold jewelry based on elemental composition using laser-induced breakdown spectroscopy

D Anggraini, A Khumaeni, B S Hartadi, H Sugito, A Y Wardaya
Department of Physics, Faculty of Science and Mathematics, Diponegoro University
Jl. Prof. Soedarto, SH, Tembalang, Semarang 50275, Indonesia

Corresponding author: khumaeni@fisika.undip.ac.id

Abstract. One method of identifying gold jewelry is laser-induced plasma spectroscopy (LIBS). In the LIBS technique, plasma is produced by the interaction of laser pulses with the material. Plasma formed shows a monochromatic beam of light with a certain wavelength then analyzed using a spectrometer. In this present research, pulse Nd: YAG laser (1064nm) is used to generate plasma. Au spectrum analysis was performed to distinguish 99.9%, 75%, and imitation jewelry. The 99.9% gold jewelry spectrum has similarities to the 75% gold spectrum. However, Au elements in imitation jewelry are not detected. Spectrum data with different treatments according to the repetition rate also conducted to determine the characteristics of the generated plasma.

1. Introduction
Gold is one of the precious metal, which is popular to be used as jewelry. Due to high demand and price, many jewelry imitations appeared, which is similar to real gold jewelry both visually and geometry. It is important to determine its purity because the value of gold depends on its purity. There are various levels of gold on the market such as 24 carats, 22 carats, 18 carats, 14 carats, 12 carats and 10 carats [1,2]. Therefore is necessary high-tech gold jewelry identification for accurate results. In analyzing jewelry, it must use the ideal method that is quantitative, accurate, reliable, but above all non-destructive.

Several gold jewelry identification methods have been carried out such as Atomic Absorption Spectrometry (AAS) which have high-sensitivity. However, the method has disadvantages such as using expensive solvents, digestion, reactive contamination, use of harmful reagents, etc. [3,4]. Proton induced X-ray emission spectrometry (PIXE) can also be used for jewelry identification but is dangerous for the human body [5]. One method for elemental analysis is laser-induced plasma spectroscopy (LIBS). In the LIBS technique, a plasma is produced by the interaction of laser pulses with the material. Plasma formed shows a monochromatic beam of light with a certain wavelength then analyzed using a spectrometer. The LIBS method is used because it can produce results fast and easy, at a low cost, and is suitable for the analysis of solid, liquid, gas, aerosol and other elements [6]. Also, the advantage of the LIBS method is that it can be measured directly without preparation so that it is possible to measure on-site and to obtain online results [7]. In this present study, the authentication of gold as jewelry was made by using the LIBS technique. The samples used were gold jewelry at a pure concentration of 99%, 75%, and imitation of gold jewelry.
2. Method

Identification of authenticity jewelry was carried out on gold jewelry samples with purity levels of 99%, 75%, and imitation jewelry. The experimental treatment for this sample is the same, using 1 atm pressure, 45 mL, and 20 Hz repetition rate. In the next session, variations in the repetition rate of laser pulses were also carried out in this study. The frequency of laser shots is 10 Hz, 15 Hz, and 20 Hz. Environmental Pressure adjusted to Atm pressure.

The experimental set up used in this work is shown in Figure 1. The laser used is a type of Nd-YAG laser with a 1064 nm wavelength. The laser beam is focused on the surface of the sample with the help of a convex lens with a 30 mm focus length. When the laser hits a sample, a plasma is formed which carries optical information in the sample, the information then captured by fiber-optic and brought to OMA to analyzed. Finally, a spectrum graph on the computer was produced. The obtained spectra revealed the basic characteristics of the sample composition. Measurement of the wavelength of each spectrum peak intensity refers to the spectral database from National Institute Standard and Technology (NIST) [8].

![Figure 1. The experimental setup used in this work](image)

3. Results and discussion

In the analysis of jewelry identification data, each sample was given the same experimental treatment, which was shot with a laser at Atm pressure, 45 mL, and 20 Hz repetition rate. The spectrum characteristics present the content of elements with varying intensities. The higher the intensity of the spectrum the greater the concentration of atoms in the sample.

![Figure 2. The emission spectrum of elements obtained from 99% gold](image)
Figure 2 shows a graph of the emission spectrum in a gold plate sample of 99%. The spectrum data shows that all appeared wavelengths are Au wavelengths. This shows that the sample has a high level of purity. Au wavelengths appeared are Au I 268 nm, Au I 274.8 nm, Au I 287.2 nm, Au I 312.2 nm, Au I 389.7 nm, Au I 406.5 nm, Au I 479.2 nm, Au I 448.8 nm, and Au I 583.73 nm.

Figure 3. The emission spectrum of elements obtained from 75% gold jewelry is shown in Fig. 3. Wavelengths that appear include Au I 268 nm, Au I 274.8 nm, Au I 287.2 nm, Au I 312.2 nm, Cu I 324.7 nm, Cu I 327.9 nm, Cu I 338.5 nm, Ni I 408.5 nm, Au I 479.2 nm, and Cu I 514.2 nm. From the data obtained in this method, other elements besides Au were detected, in the spectrum graph detected elements of Cu I and Ni I. This result indicated that 75% gold jewelry is composed of a combination of gold, copper, and nickel elements.

Figure 4 shows the spectrum graphic of the imitation jewelry sample. It can be found that the appeared wavelength is mostly Cu and Fe. The following wavelength is Fe I 272.2 nm, Fe I 424.7 nm, Cu I 514.4 nm, Cu I 521.1 nm, Cu I 521.1 nm, Cu I 285.8 nm, and Cu I 327.9 nm, while the detected Ce wave is Ce I 482.2 nm. Au element wavelength was not detected. That indicates the imitation jewelry sample was not produced by the Au component.
The determination of the authenticity of the Au sample is done by calculating the intensity of the Au I ratio at wavelengths of 268 nm and 274.8 nm. These two wavelengths were chosen because they are the dominant wavelength. The intensity ratio formed from Au I 99.9%, Au I 75%, and imitation jewelry are 1,517, 1.33, and 0. The intensity ratio at Au I 99.9% is greater than Au I 75%. This shows that the higher the value of the intensity ratio the greater the content of the elements in the sample.

Figure 5 shows a graph of the spectrum captured by OMA at different rates of pulse repetition. The pulse repetition rate is the number of pulses fired per second. The shooting frequencies used were 10 Hz, 15 Hz, and 20 Hz. The difference can be seen from the intensity graph that is formed. On the graph, the 20 Hz pulse repetition rate produces a higher intensity than at the 10 Hz and 15 Hz repetition rates. The intensities in figure 5 are shown in this following Table 1.

From Table 1, can be stated that the 20 Hz repetition rate is the highest ratio intensity than the 15 Hz or 10 Hz repetition rate. In the qualitative sector, the Table shows that the higher the repetition rate used,
the intensity peak becomes more clear. So, the analysis of appeared wavelength is easier to do. For the quantitative side, the higher repetition rate makes the increment of the ratio intensity. It can be assumed that the excitation and de-excitation process occurred more intensively than generated background intensity. In the common, increment of repetition rate cause many particles ablated from the material. More material ablated, more excitation de-excitation incident can happen and create any amount of intensity increment of the sample wavelength.

Table 1. Ratio Intensity with repetition rate variation

| Wavelength (nm) | Ratio Intensity (Peak/Background) |
|----------------|----------------------------------|
| 20 Hz          | 15 Hz                            | 10 Hz                        |
| 268.0          | 2.509472                         | 1.718497                     | 2.054463                     |
| 282.6          | 2.087353                         | 1.562918                     | 1.746209                     |
| 294.0          | 1.715968                         | 1.457095                     | 1.544684                     |
| 312.2          | 0.823742                         | 1.571796                     | 1.633785                     |
| 406.5          | 2.308714                         | 1.674908                     | 1.443027                     |
| 449.8          | 1.381072                         | 1.341652                     | 1.125884                     |
| 479.2          | 2.756019                         | 2.15915                      | 1.561289                     |
| 583.7          | 1.554842                         | 1.769673                     | 1.330467                     |

A comparative study was then made by using the standard spectroscopy technique of XRF. Table 2 is elements obtained from the 75% gold jewelry using the XRF technique. It can be seen that the elements contained in the 75% gold jewelry sample include Au, Cu, and Ni. Those elements are the same as the elements identified by using the LIBS technique present in this study. Therefore, the LIBS technique is powerful for distinguishing the pure gold metal from its imitation.

Table 2. Elements obtained from the 75% gold jewelry using XRF technique

| No. | Component | Result | Unit | Det. limit | El. line | Intensity | w/o normal |
|-----|-----------|--------|------|------------|----------|-----------|-------------|
| 1   | Si        | 5.24   | mass%| 0.02039    | Si-KA    | 0.4978    | 0.9464     |
| 2   | Cl        | 0.343  | mass%| 0.01947    | Cl-KA    | 0.0919    | 0.0619     |
| 3   | K         | 0.727  | mass%| 0.04490    | K-KA     | 0.1021    | 0.1314     |
| 4   | Ca        | 0.449  | mass%| 0.03017    | Ca-KA    | 0.1150    | 0.0810     |
| 5   | Fe        | 0.851  | mass%| 0.01491    | Fe-KA    | 0.2588    | 0.1556     |
| 6   | Ni        | 0.179  | mass%| 0.01107    | Ni-KA    | 0.0930    | 0.0324     |
| 7   | Cu        | 20.2   | mass%| 0.01303    | Cu-KA    | 12.3458   | 6.3699     |
| 8   | Zn        | 1.72   | mass%| 0.01592    | Zn-KA    | 1.5337    | 0.3107     |
| 9   | Ag        | 3.35   | mass%| 0.05475    | Ag-KA    | 0.0608    | 0.6050     |
| 10  | Au        | 67.0   | mass%| 0.05812    | Au-LA    | 17.0821   | 12.0953    |

4. Conclusion
The identification of elements in gold jewelry has been made by using the LIBS technique. The sample used was the gold-containing various concentration of 99%, 75%, and imitation of gold jewelry. The result shows that in 99% gold, only emission lines of Au are identified, while for 75% gold, additional elements are detected including Cu and Ni. For imitation of gold jewelry, completely no Au lines are identified and only Fe and Cu lines are detected. A comparative study was also made using the XRF technique. The results certified that elements identified from the 75% gold jewelry using LIBS present in this study are the same with the elements obtained by the XRF technique, namely the 75% gold jewelry contained Au, Cu, and Ni.
Acknowledgment
This study was financially supported by PNBP Undip under the project of research for the international publication scheme 2019.

References
[1] Corti C W 1999 Gold Bulletin 32 (1) p 39-47
[2] Ning Y 2005 Gold Bulletin 38 (1) p 3-8
[3] Kryazhov A, Panova S, Kolpakova N, Pshenichkin A 2014 Procedia Chemistry 10 437 – 440
[4] Anais R S, Amaral C D B, Fialho L L, Schiavo D, Nobrega J A 2014 Anal. 6 4516–4520
[5] Demortier, G 1984 Gold Bull 17
[6] Kearton B and Mattley Y 2008 Nature Photonics vol 2 pp 537–540
[7] Wiggenhauser H, Schaurich D, Welsch G 1998 NDT & E Int 31 307–313
[8] NIST Atomic Spectra Database (National Institute of Standards and Technology) http://physics.nist.gov/PhysRefData/ASD/lines_form.html (accessed August 2019)
[9] Flavio O L, Quienly G, Paulo H M Kiyataka, Dario S, Jr, José, Agnelli A M, Francisco J K 2012 Applied Surface Science 258 3598–3603
[10] Golik S S, Ilyin A A, Babiy M Y, Biryukova Y S, Agapova T M, Mayor A Y, Bukin O A and Kulchin Y N 2015 Technical Physics Letters 41 11 1044–1046