Rapid detection of the authenticity of silver jewelry by laser induced shockwave plasma spectroscopy using Nd:YAG laser 1064 nm

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Abstract. Identification of the authenticity of silver jewelry has been carried out by using laser induced shockwaves plasma spectroscopy (LISPS) method. In this study, a plasma was generated by laser firing Nd:YAG (1064 nm, 40 mJ, 7 Hz) at a pressure of 1.5 torr to the target surface. The study was made to distinguish 99.9% silver samples, 92.5% silver jewelry, and imitation jewelry. The emission spectrum obtained from the 99.9% silver sample shows similarities with the 92.5% silver jewelry. However, imitation jewelry does not show the resemblance and undetectable elements of Ag. The detection limit of Ag was 2.74%. In 92.5% silver jewelry, the other detected elements are Fe and Cu, while in the imitation jewelry, the other detected elements are Fe, Cu, and Zn with varying wavelengths. For comparison, imitation jewelry was also analyzed by using X-Ray Diffraction (XRD) method. The result of the XRD method shows that the imitation jewelry is identical to Cu-Zn crystal structure.

1. Introduction

Silver is one type of metal used as jewelry and decorative items [1]. Silver jewelry has a more affordable price compared to gold jewelry. Pure silver that has a soft texture should be combined with other metals for the jewelry industry. Commercial silver jewelry generally has a grade of 92.5% with the remaining 7.5% being copper or other elements having a support characteristic as a mixture [2]. However, nowadays there has been developed imitation jewelry that is very similar to the original silver jewelry both visually and geometry. Technological advances in the manufacture of costume jewelry make it difficult to distinguish from original silver jewelry. Therefore, there is an effort to identify jewelry, especially silver jewelry based on technology to get more accurate results.

Various methods have been used in the identification of jewelry such as neutron activation analysis (NAA) [3], atomic absorption spectrometry (AAS) [4], Raman spectra, photoluminescence spectra, UV-Vis-NIR reflectance spectra, and Laser Ablation-Inductively Coupled Plasma- Mass Spectrometry (LA-ICP-MS) [5]. However, the method requires special treatment, which can damage the jewelry.

Identification of silver jewelry can be done by utilizing the Laser Induced Breakdown Spectroscopy (LIBS) method. This method is able to analyze all kinds of elements without special treatment to the samples [6, 7] so that the material analysis becomes faster. In this study, the high-energy laser is focused on the target surface for the plasma generation process. The laser shot will only
excite the atoms on a small portion of the sample surface [8] so that it does not cause damage. The light spectrum of the resulting plasma carries the atomic information of the material [9].

The LIBS method becomes a spectrochemical technique, which is capable of being used for the analysis of solid, liquid, gas, and aerosol elements. The researches proved this method is appropriate for environmental analysis [10], industry, biological and chemical agents, security, food technology [11,12], cultural heritage [13], artwork [14], and even space exploration. The rapid development of both the working principle and its application encourages scientists to learn and utilize in other fields. Judging from the principle of work and the composition of a simple device can reduce costs and improve operations. This is related to rapid response and high sensitivity [15].

Laser interaction with the target surface will result in temperature rise and ablation. The target will absorb the energy of the laser beam so that the atoms at the ground state level will make a transition to a higher energy level, which is then called excitation process. This process will produce the plasma emissions that match the given experimental conditions. [16]

The utilization of LIBS method for jewelry and alloy analyses has been done by other researchers [17]. The results of the experiment stated that LIBS method is able to identify gold jewelry and its alloys both qualitatively and quantitatively. As the study of LIBS methods for sample identification, Laser Induced Shockwave Plasma Spectroscopy (LISPS) is present as an expansion of the LIBS method at low pressure [18]. The plasma intensity produced in the LIBS method will continue to decrease due to the appearance of holes on the sample surface. At low pressure, the formed laser plasma consists of two different areas [19]. First is the primary plasma formed in a small area of the target surface. Other areas (secondary plasma) develop and surround around the primary plasma, with low background intensity. The magnitude of the secondary plasma radius depends on the amount of laser energy and also the gas pressure around it [20].

In this research, it will be examined the ability of LISPS method to distinguish original silver jewelry and imitation jewelry. The sample authenticity test by laser plasma method has been used in the original and false tax holographic test on the liquor bottle [21]. Silver (Ag) element tests have been performed on historic objects using LIBS method [22]. However, this study has deficiencies in the spectral data of Ag. This research is important because of the increasing circulation of imitation jewelry in the market. There are 3 types of samples used in this study, namely 99.9% pure silver, 92.5% silver jewelry, and unknown elemental imitation jewelry. Imitation jewelry is also identified using X-Ray Diffraction (XRD) method to compare with experimental data using LISPS method.

2. Research Method
The equipment used in this study is shown in Fig. 1. A pulse Nd: YAG laser as an energy source produced a laser beam that is fired into the mirror to reflect to the lens as the focus of a laser beam. The laser was then absorbed by the sample and a luminous plasma was produced just above the sample. The resulting laser plasma was detected by using optical fiber connected to the Optical Multichannel Analyzer (OMA). All samples were subjected to the same experimental treatment, ie raised at low pressure of 1.5 Torr, 40 mJ laser energy and 10 Hz repetition rate.
First, sample preparation was made. Preparation was done by cleaning the surface of the sample using 70% alcohol. This treatment is to remove impurities found on the surface of the sample before being inserted in the chamber. The determination of an element in the sample can be known through the spectrum graph data. Data from each of the detected wavelength intensities are adjusted with reference data of the Atomic Spectra Database Line Form from NIST (National Institute of Standard and Technology) Physical Measurement Laboratory and Wavelength Tables Massachusetts Institute of Technology (MIT). Imitation jewellery was then carried out in advanced analysis using XRD method as a comparison.

![Figure 1. Composition LISPS Method](image)

**Figure 1.** Composition LISPS Method

3. Result and Discussion
Plasma formed from the mechanism of generation with the shooting of laser light has a unique characteristic. Laser interaction with the target will cause an increase in temperature on the surface. This will cause the ablation of the target surface. The target will absorb the energy of the laser beam so that the atoms at the ground state level will make transition to a higher energy level. The accumulated
energy will become vapor and cause the atomic bonding material to be disconnected. The ionized and excited gas from the material constituents emits specific elements of wavelength with the color and size of the various laser plasmas corresponding to their transition energy levels.

3.1 Visual Analysis of Jewelry Identification

Figure 3 shows that the resulting plasma has various colors and sizes. The color difference is caused by the emission characteristics of each element. Figure 3(a) and 3(b) are green color because the wavelengths of Ag elements that have the dominant intensity appear in the wavelength range 500 nm – 560 nm. While in Fig. 3(c), the dominant wavelength appears is the range of values for the blue color to forage that is 435 nm - 560 nm. The LISPS method able to distinguish between the original samples of silver jewelry and imitation jewelry using a visible characteristics.

![Laser plasma obtained from (a) the silver 99.9%, (b) the jewelry 92.5%, (c) imitation jewelry.](image)

Plasma formed in this condition has clear regional differences between primary plasma and secondary plasma. The first area is the primary plasma which produces a continuous emission spectrum with a short time on the target surface. The second area is a secondary plasma that emits a discrete spectrum containing atomic information of materials with sharp intensity and low background signals. This secondary plasma is the result of the expansion of the primary plasma. Plasma expands moving at high speeds pushing and pressing the surrounding gas.

3.2 Spectroscopy Analysis of Jewelry Identification

The spectrum characteristics that present the element content have varying intensities. Each element has a different energy level with each other. The magnitude of the spectrum intensity of the spectroscopic method is influenced by three factors, namely transition probability, population at every level, and sample concentration [23]. The high spectrum intensity of a particular atom in the sample hence the atomic concentration is large in the sample.
Figure 4. The emission spectra of silver 99.9%

Figure 5. The emission spectra of silver jewelry 92.5%
Figure 6. The emission spectra of imitation jewelry

On the spectrum it is confirmed that the LISPS method is able to detect Ag elements and distinguish original silver jewelry and imitation jewelry. From the data obtained LISPS method is also able to detect other elements contained in the sample. The resulting wavelength of spectrum data for imitation jewelry is identical with iron (Fe), copper (Cu) and zinc (Zn) elements.

Based on the spectra in Fig. 6, 92.5% silver jewelry contains Ag, Cu, and Fe elements, while imitation jewelry contains Fe, Cu and Zn elements. The Fe and Zn elements have metallic gray characteristics, while the Cu elements have characteristics of forged and corrosion resistant. So the two elements are suitable to be a material alloy as a jewel. The color characteristics of Fe and Zn have similarities with Ag element, which makes it difficult to distinguish silver jewelry and imitation jewelry.

| Sample        | Wavelength (nm) | Relative Intensity |
|---------------|-----------------|--------------------|
| Pure silver   |                 |                    |
| 99,9%         | Ag I 328,06     | 4665               |
|               | Ag I 338,28     | 6139               |
|               | Ag I 405,54     | 2012               |
|               | Ag I 421,09     | 2383               |
|               | Ag I 520,90     | 2529               |
|               | Ag I 546,54     | 3706               |
| Silver jewelry|                 |                    |
| 92,5%         | Ag I 328,06     | 3113               |
|               | Ag I 338,28     | 3385               |
|               | Fe I 369,74     | 1725               |
|               | Cu I 380,52     | 1529               |
|               | Ag I 405,54     | 1335               |
|               | Ag I 421,09     | 1501               |
|               | Ag I 520,90     | 1609               |
|               | Ag I 546,54     | 2085               |
The 92.5% silver jewelry spectrum have similarities with pure silver spectrum of 99.9%. While on imitation jewelry did not show the resemblance of spectrum with 92.5% silver jewelry sample and 99.9% pure silver.

### Imitation jewelry

| Element  | Wavelength (nm) | Intensity |
|----------|-----------------|-----------|
| Cu I     | 324.75          | 5575      |
| Cu I     | 327.39          | 5953      |
| Fe I     | 340.43          | 2830      |
| Fe I     | 346.58          | 3647      |
| Cu I     | 360.92          | 4218      |
| Zn I     | 468.01          | 2858      |
| Zn I     | 481.05          | 3977      |
| Fe I     | 508.33          | 4470      |
| Cu I     | 521.82          | 2751      |
| Fe I     | 537.14          | 2240      |

3.3 Measurement of limit detection

Validation of analytical methods as quality monitoring on which an important procedure is performed. The detection limit is an analytical amount explaining the value or the smallest concentration of a detected sample. The detection limit can be determined by calculating the relative intensity value on the sample spectrum. Measurement of limit detection aims to determine the percentage of concentration of Ag elements that can be detected. The measurement result was obtained by detection limit value 2.74% at Ag (I) 338.28.

To ensure that the imitation jewelry sample did not contain Ag, the study was continued using the XRD method as a comparison. Figure 8 shows the emission spectrum of the detection result using the XRD method. The data obtained results that the imitation jewelry has compatibility with Cu-Zn crystals. XRD method validation result does not detect Ag element.
Figure 8. The emission spectra of various sample taken by using XRD (X-Ray Diffraction)

The resulting diffraction pattern corresponds to Crystallography Open Database (COD) no. 4307128 based on Entry # 96-430-7129 on Match crystallographic applications. In the data base, it is known that the material is Cu-Zn [24]. Compared with XRD method, LISPS method obtained more accurate results because it is also able to detect the element of Fe in imitation jewelry.

4. Conclusion
Research shows that LISPS method is able to detect Ag elements and distinguish original silver jewelry from imitation jewelry. The resulting wavelength of spectrum data is identical with silver (Ag), iron (Fe), copper (Cu) and zinc (Zn) elements. The result of the measurement obtained by the detection limit value of Ag (I) 338.28 is 2.74%. The LISPS method is the right method for the use in the jewelry industry, because it has high sensitivity, fast, and no damage, so this technique is promising for identification of jewelry or items, which has a high price. The XRD method has also ensured the absence of the existence of Ag in imitation jewelry.

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